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Radiation Curing Conference

Proceedings

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The scope of RadTech Asia'95 Conference ranging from Chemistry, to Application, to Measurement and Equipment, and to Material Modification. A large number of presentations including overviews, invited lectures and oral or poster contributions has been arranged in the conference. This has lead to considerable reduction in time for presentation and discussion. For rapidly advancing subjects, this special issue will devote to critical surveys of specialist topics and to increase need for personal contacts and discussions remains.

The total presentations in the Conference is eighty-six papers, including 5 overviews, 11 invited lectures and 69 oral or poster contributions. Each paper is marked with abbreviation classification number for author's reference, which is same as in the Preliminary Program delivered to participants in August, 1995. The invited lectures marked with asterisks is also same as in the Preliminary Program. The manuscripts of some papers have not been submitted before the time of publishing, those papers with their numbers were excluded in this proceedings.

The organizers appreciate and acknowledge the great supports and cooperation from all the authors.

The organizers would like to beg further cooperation of all authors and participants to gain the final success of this conference.

Chen Wenxiu
Executive Editor
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AUTHOR INDEX
Leaders and delegates, Ladies and Gentleman,

After intense preparation for more than one year, the 5th RadTech Asia '95 Conference is opened today in Guilin, one of the most beautiful cities of China. On behalf of the Organization Committee and as the chairman of this conference, I would like to extend our warmest welcome to all of our friends from America, Europe and Asia, as well as to our Chinese colleagues, the invited leaders and reporters from the press.

Four years ago, I suggested to Japanese Professor Y. Tabata that the Association of RadTech China was willing to host a conference of RadTech Asia. In 1993, the 4th RadTech Asia '93 Conference accepted the offer from China. With the help of Professor Tabata and many other friends and with the support of the Chinese government, our dream has finally come true.

In the modern world, radiation technology has been developed to be used in industry; it is playing a greater and greater role in many aspects of the society and economy. Recently there have been two major developments in radiation technology. First is the emergence of new radiation methods, in which γ-ray, electron beam, and heavy ion radiation technology have shown strong competitive and promising applications in such fields as electronics, metallurgy, chemical engineering and biological engineering. Second is the widespread applications, where in radiation technology has entered into many traditional industries and has become a primary process in production lines. It plays a unique role in the technical reform, products by making possible a new generation while at same time reducing energy consumption and protecting the environment.

The 5th RadTech Asia '95 Conference has a special meaning for China. China has a population of 1.2 billion and its economy is growing very rapidly. The Chinese government has stressed that its strategic policy of economic development is based on science and technology. Economic development can be promoted by modifying the industrial structure, rationlizing the industrial structure and transforming production model into market products. Under these circumstances, many industries are in an urgent need of the radiation technology and its products. The Chinese people will need more and more new consumer goods. It is believed that radiation curing technology and radiation processing products have an extensive market in China both at present and in the future. The present radiation technology industry in China is growing at an annual rate of 30%. China has a cadre of excellent scientists in the field of radiation technology. They have explored many new applications. It is our sincere hope that this conference provides the opportunities to exchange the latest research results, to study the prospects of radiation curing technology for industrial applications and to strengthen international cooperation. It is also our hope that this conference may be a good chance to “Let China know the world and make China known to the world.”

We welcome you to Guilin, a famous resort city of China, famous for her beautiful mountains and waters. Friends from all over the world may take this occasion to enjoy the picturesque scenery of China. Guilin is also a developing city in China. It will be a great opportunity for you to learn of the past, the present and the future of China.

It is my hope that this conference will be a great success in increasing friendship, strengthening cooperation, and promoting the development of radiation curing technology in Asia.

Thank you.

Zhao Wenyan
Chairman of Organizing Committee
Conference of RadTech Asia '95
ABSTRACT
The use of UV/EB curable technology continues to grow in North America at a rate of 12-13%. The annual volume of the materials used now exceeds 42,000 metric tons. The growth rate for the balance of the decade is expected to continue at about 13%. The majority of materials are used in the field of graphic arts; but there are new and rapidly growing uses in wood finishing, plastics, and specialty applications.

In 1991 this writer chaired a study conducted by members of RadTech International North America to assess the markets for UV and EB curable products. The study involved a representative cross section of end users and suppliers of equipment, raw materials, and services. This current update has utilized a modified "Delphi" technique with the input of over 30 industry participants who have shared their expertise and experience during four rounds of questions. After each round participants have compared their impressions with those of others and then had the opportunity of adjusting their own estimates or "holding fast." The result is a consensus of opinion which fairly represents the reality of the industry's current status and a reasonable projection of the growth and opportunities ahead.

Growth
The growth of UV/EB curing has been slightly more rapid than was projected in the 1991 study. Average growth in the last five years has been 12% per year and the total North American market now uses over 42,000 metric tons of UV and EB curable products. By comparison, this represents over 2% of the industrial coatings market (solids basis) and is about 40% the size of the powder coatings tonnage in North America. Continued growth is anticipated at a rate of about 13% for each of the next five years as the motivators for the use of these highly productive, environmentally friendly products will continue to gain importance.

Graphic Arts
Clear overprint coatings for paper and paper board comprise the largest market for UV and EB curable products. As a group, materials used in graphic arts and converting industries comprise about one half of the total volume. The more mature overprint coatings have captured a significant share of the market for high gloss finishing of point of purchase signage, folding cartons, magazines and pocket book covers. Nevertheless, new application techniques (flexo) and the growth of standard techniques results in expansion of about 7% per year.

The growth of UV/EB curable inks has been strong, particularly in the area of flexography where a number of wide web machines have joined the thousands of
narrow web presses which have used UV curable inks and overprint coatings for over a decade. Well established screen and off-set printing, using UV curable inks, continues to grow from a larger base, but at a lower rate.

**Metal Packaging**

Rigid metal packaging (metal decorating or can coating) was a field of major effort for UV inks and coatings in the mid-1970's. As the manufacturing methods for beer and beverage containers moved from three piece cans, made from pre-decorated flat sheets to pre-formed aluminum two piece cans, UV coatings were largely dropped in favor of thermally cured products. One exception was the Adolf Coors Brewing Company which has about 5% of the U.S. beer market. For environmental reasons they built two piece lines which have used both UV cured inks and coatings at speeds in excess of 1,200 cans per minute. At the same time several manufacturers of composite cans (aluminum foil/paperboard side walls with aluminum ends) have installed lines for UV curing the can ends. Three piece aerosol cans are still decorated with UV cured inks and coatings when outstanding product and solvent resistance is required.

The rigid packaging market has remained relatively stable over the last decade. However, several panelists believe that significant growth will occur in the next decade as environmental and productivity requirements increase. Growth will be further enhanced with the development of cationic cured epoxies which provide improved (good) adhesion to and protection of metal substrates. Should products be developed which have government (Food & Drug Administration) approval for direct food contact the growth can be phenomenal. Because the UV curing mechanism leaves some uncured bonds (residual unsaturation), the probability of wide spread usage is improbable in the next decade.

**Electronic/Opto-Electronics**

Photoresist materials and optical fiber coatings are two examples of applications where "special properties" were responsible for the adoption of photo curable materials. In the early stages of development optical fibers were coated with two component, heat curable silicones. Top line speeds were about 2 m/sec. using ovens as hot as 600°C. With UV curable coatings line speeds have been increased to 10-20 m/sec. using "ovens" of about the same size and length. Photoresists make possible the manufacture of integrated circuits using positive or negative photoresists to transfer circuit patterns which are later etched and plated, forming very thin and small circuits in a stepped manner. The process is vital to the manufacturing process and the technology has become so complex and specialized that this use of radiation curing is generally not considered to be part of the UV/EB curable market.

**Water Reducible Products**

Water reducible, UV/EB curable formulations have been developed for a number of markets. Water dilution of a compatible resin system provides:

Lower viscosities
Application of thinner films
Improved flow and leveling
Lower applied costs
Reduction/elimination of monomers and solvents

This technology is being directed towards numerous applications including flexo and gravure inks, clear coatings for wood furniture and dipping or sprayable coatings for plastics. The use of water as a viscosity reducer can minimize or eliminate the use of lower molecular weight diluents which tend to be skin irritants. Some work has indicated that small amounts (1%) of water can reduce the viscosity of oligomers substantially and the uses of larger amounts of water can be used as a formulation tool to vary gloss and to reduce web temperatures in critical applications.

Disadvantages include the time/energy required to remove any water added as well as the effects of water on the drying/curing system and the substrate to which it is applied. If cured before the water is fully evaporated film properties will be changed.

Motivators for Use of UV/EB
UV and EB curing applications are still referred to as niches of specialty businesses. There are still very few markets using over 1,000 tons of product per year (Appendix 1C). Nevertheless, the advantages of UV curing (Appendix 1H) lead many users into successful and often extremely profitable applications. Although the cost per kg of these products is usually higher than that of the conventional products they replace, the overall applied cost per unit is almost always lower and new products are often made possible as UV/EB curable products provide properties not otherwise achievable with conventional materials. Much has been said about the "Green Advantages" of UV/EB curing. While it is true that they emit very little volatile organic content (V.O.C.) to the atmosphere, and are energy efficient, the motivators driving their increased use are more often related to lower unit costs (which include faster production rates, rapid curing at near ambient temperatures and less space).

Impediments to Growth
Much has been made of the impediments or barriers to the use of UV and EB curable materials. Obviously these have been overcome or eliminated by the thousands of successful users of the technology. Still, the limitations (Appendix 1.1) must be studied and considered by the prospective user and eliminated before a successful switch in technology can be made.

Costs
When evaluated on a cost per liter (or Kg) basis, UV/EB curable raw materials and formulated products are almost always more expensive than their conventionally cured counterparts. This cost premium is caused by several factors.

- Materials are generally purchased without solvent, i.e., high solids.
- Lower volumes (specialty products). Little economy of scale.
- Manufacture of monomers and oligomers is a relatively complex, multistage batch process.
• Less competitive intensity.
• Newer technologies, not fully depreciated.
• Higher R&D cost component per unit sold.

The panel believes that the cost differences will moderate, but will continue to remain higher than most alternative technologies. However, applied costs of UV/EB curable products are already competitive for many applications.

The Future
The following charts indicate the uses for UV/EB curable materials. Even more important are the projections for growth (Appendix 1-D,E,F,) in both existing and new segments of business and the changes expected in equipment and chemistry. The prospective user of UV/EB curing will benefit from the knowledge of how this technology has benefited so many others and how it is expected to be of help to others.

A. North American Growth rate for all uses of UV/EB Curing.

<table>
<thead>
<tr>
<th>Growth Rate for North America</th>
<th>Average Growth Rate</th>
<th>Range of Panelists Input</th>
</tr>
</thead>
<tbody>
<tr>
<td>Last 5 yrs. (1990-94)</td>
<td>12%</td>
<td>11-15%</td>
</tr>
<tr>
<td>Next 5 yrs (1995-99)</td>
<td>14%</td>
<td>12-17%</td>
</tr>
</tbody>
</table>

B. Growth by country.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>U.S.A. 12%</td>
<td>10-20%</td>
<td>88%</td>
<td>80-94%</td>
</tr>
<tr>
<td>Canada 9%</td>
<td>6-15%</td>
<td>9%</td>
<td>5-16%</td>
</tr>
<tr>
<td>Mexico 11%</td>
<td>4-35%</td>
<td>3%</td>
<td>2-8%</td>
</tr>
</tbody>
</table>

C. Major Areas of Largest Current Use - Total North American Market -

<table>
<thead>
<tr>
<th>Estimated Use of Formulated Products - Metric Tons/Per Year</th>
<th>Estimated Selling Price ($/lb.) to User</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Clear overprint coatings - Paper &amp; Paperboard 12,000</td>
<td>$2.50-3.40 -</td>
</tr>
<tr>
<td>2. Photopolymer Printing Plates 5,000</td>
<td>8.00 ?</td>
</tr>
<tr>
<td>3. Clear Floor Coatings (wood and vinyl) 5,000</td>
<td>4.50-5.50</td>
</tr>
<tr>
<td>4. Lithographic Inks 3,500</td>
<td>6.00-10.00</td>
</tr>
<tr>
<td>5. Screen Print Inks 3,000</td>
<td>7.00-15.00</td>
</tr>
<tr>
<td>6. Electronics (including opto-electronics) 3,000</td>
<td>Wide Variation</td>
</tr>
<tr>
<td>7. Photo Resists (As supplied at low N.V.) 2,000</td>
<td>20-160</td>
</tr>
<tr>
<td>-------------------------------------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>1. Medical Devices</td>
<td>45</td>
</tr>
<tr>
<td>2. Electronics Packaging</td>
<td>35</td>
</tr>
<tr>
<td>3. Flexo Inks - Wide Web</td>
<td>35</td>
</tr>
<tr>
<td>4. Silicone Release Coatings</td>
<td>20</td>
</tr>
<tr>
<td>5. Metal Coatings</td>
<td>20</td>
</tr>
<tr>
<td>6. Flexo Inks - Narrow Web</td>
<td>20</td>
</tr>
<tr>
<td>7. Wood Coatings - Flat Line</td>
<td>15</td>
</tr>
<tr>
<td>8. Laminating Adhesives</td>
<td>15</td>
</tr>
<tr>
<td>9. Optical Fiber Coatings</td>
<td>15</td>
</tr>
<tr>
<td>10. Automotive Applications - Miscellaneous</td>
<td>15</td>
</tr>
<tr>
<td>11. Specialty Coated Papers</td>
<td>10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>New/Emerging Opportunities for UV/EB Applications (Areas to Watch)</th>
<th>% Probability of Wide-spread Commercialization Within 5 Years</th>
<th>Possible Tonnage By 1999</th>
<th>Range of Panelists</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Photoinitiators to make possible opaque pigmented systems.</td>
<td>80%</td>
<td>750 Tons</td>
<td>200-1200 Tons</td>
</tr>
<tr>
<td>2. Two piece can coatings</td>
<td>65</td>
<td>1,000</td>
<td>800-1200</td>
</tr>
<tr>
<td>3. Water reducible (low viscosity) UV/EB curable systems.</td>
<td>50</td>
<td>200</td>
<td>50-500</td>
</tr>
</tbody>
</table>
### F.

<table>
<thead>
<tr>
<th>New Advances in Equipment for Curing with UV/EB (Listed in order of importance)</th>
<th>Probability of Significant Commercial Success by 1999</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Effective intensity measurement and monitoring</td>
<td>75%</td>
</tr>
<tr>
<td>2. Continuous energy feedback controls</td>
<td>90</td>
</tr>
<tr>
<td>3. Improved heat management</td>
<td>75</td>
</tr>
<tr>
<td>4. High Intensity/Concentrated Light Sources</td>
<td>70</td>
</tr>
<tr>
<td>5. Increased lamp life</td>
<td>60</td>
</tr>
<tr>
<td>6. Improved spectrum control</td>
<td>50</td>
</tr>
<tr>
<td>7. Higher Efficiency Ballasts and Controls</td>
<td>65</td>
</tr>
<tr>
<td>8. Expanded spectrum frequency range</td>
<td>50</td>
</tr>
<tr>
<td>9. More efficient 3-dimensional curing</td>
<td>50</td>
</tr>
</tbody>
</table>

### G.

<table>
<thead>
<tr>
<th>Industry Usage of Various Chemistries</th>
<th>Percent of Total Used</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Acrylates</td>
<td>83%</td>
</tr>
<tr>
<td>2. Polyesters (Unsaturated)</td>
<td>9</td>
</tr>
<tr>
<td>3. Epoxies - Cationically Cured</td>
<td>5</td>
</tr>
<tr>
<td>4. Others</td>
<td>3</td>
</tr>
<tr>
<td>Total</td>
<td>100%</td>
</tr>
</tbody>
</table>

### H.

**Major reasons** (motivators) that UV/EB is being adopted in favor of conventionally cured materials.

(Ranked in order of importance.)

1. **Reduced cost/unit. Net economic advantage.**
   - V.O.C. reduction - Improved air quality.
   - Faster production rates.

2. Properties not otherwise achieved with conventional materials.
3. Low temperature cure. Generally at not more than 25°C above ambient temperature.

4. Energy reduction

5. Space Savings

6. Also mentioned
   Higher gloss
   Lower waste and rejects
   Quick product changes
   Easier to use/control
   Production reliability/uniform quality.

I. Major reasons (impediments) to the growth of UV/EB curing, i.e., the replacement of conventionally cured products.

Ranked in order of importance
1. Most important reason
11. Least important reason

1. Materials - too costly
2. Equipment - too costly
3. Difficult to cure pigmented products
4. Limited to Line-of-sight cure
5. Too complicated
6. Hard to apply at 100% "solids" (high viscosity)
7. Toxicity - Skin irritation
8. Inadequate adhesion
9. Gloss/appearance properties limited
10. Chemistry is too limited
    Needed properties are not available.
11. Other concerns mentioned.

   Poor exterior durability.
   Adhesion, flexibility and formability are limited for many fast curing, highly cross-linked products

J. Distribution of UV/EB usage.

Estimate of the % of the market (~42,000 metric tons) cured by UV or by EB.

<table>
<thead>
<tr>
<th>SSL Volume</th>
<th>90%</th>
</tr>
</thead>
<tbody>
<tr>
<td>EB Volume</td>
<td>10%</td>
</tr>
<tr>
<td>Total</td>
<td>100%</td>
</tr>
</tbody>
</table>

K. Self Manufacture (formulation) by users -

Estimate of the % of the total market (~42,000 Tons) which is formulated (in house) by the user, as contrasted to that which is purchased ready to use from a formulator.

<table>
<thead>
<tr>
<th>Self Formulated Products</th>
<th>12%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purchased as a formulated product</td>
<td>88%</td>
</tr>
<tr>
<td>Total</td>
<td>100%</td>
</tr>
</tbody>
</table>
Introduction

What has happened in the European radiation curing market in the last four years?

Since no review paper was prepared for the ’93 conference we must go back to excellent reviews on European activities presented in ’91(Edinburgh/1) and ’92(Boston/2) for reference. The professional service office of RadTech Europe volunteered to answer this question by telephone interviews, reviewing conference papers and other publications from a still to secretive industry, to prepare this European state of the art. The result will be incomplete, and we hope for a lot of criticism and « reactive » information from people who know better and more, to be used for future dissemination.

Positive and negative influences

A recession period which has started in 1991 in the UK, has touched most European countries and markets in the following years; it still continues in Spain and Portugal and in the Eastern bloc the partial change to private enterprise has brought many radiation curing activities close to a stop. Since ’94 the situation improves in most countries, very often on the back of thousands of layed-off workers and managers. The German reunion brought a straw-fire of activities and investments to the building, equipment and furniture industries, but now a slow-down or back to normal is observed much earlier than expected. A large UV-equipment supplier was able to announce proudly: «1994 was our best wood year ever». The chemical suppliers in general look back on reasonable growth of 8 to 12% in 1994. For this year they expect similar figures; they could be higher, but their growth is smoothened by several factors:

a) since several months there is a lack of acrylic acid, glycols and other raw materials

b) since Spring 94 prices for most raw materials have moved from « depressive » to explosive, and this in short intervals. Despite a compression of margins, oligomers, monomers and additives have reached price levels which make potential users hesitate if they shall take the radcure road.

c) new producers and importers (Asia) try to gain part of the European market, mainly in the field of overprint varnishes, where the discrepancy: raw material - market prices hurts and often is accompanied by poor quality, with a risk of bringing discredit to UV-curing.

News about new installations for AA and epoxies, ready towards the end of this year, about good equipment sales for UV and EB, hopes about a return to acceptable prices and margins, allow most of us to look for better results with growth forecasts between 10 and 15% for the next year as in the USA. Almost in opposition to this not yet proven optimism we have received a report with critical thoughts from Scheid(3) about our industry, written after a visit to DRUPA 1995.
He observes a rising number of suppliers and sales to new markets and for new applications. But even the largest fields (wood and graphic arts) are considered to be only niche applications - because « they cover less than 5% of all possible curing techniques ». Due to competition and volume, prices and margins will come down - allowing an even stronger growth of the radcure market, because it becomes more favourable compared to traditional methods. « if pressure on prices and margins becomes more important than technology, we are getting into a mature market ». This is most visible for overprint varnishes and unsaturated polyesters for wood coatings. We agree to be in a bad situation, if for OPVs safe quality levels are no longer affordable. To replace unsaturated styrene/polester coatings, regulations and gain in surface quality will help to pass slowly to more expensive acrylate coatings, even in low cost countries.

Many new applications have been developed during the recession period, investments were postponed, but many are introduced now and will allow a healthy growth in the late nineties. The cited reporter admits this fact, but believes that « identifying new application areas will become more difficult ... and will have its limitations. »

We are more optimistic, because:

- regulations about VOC reduction will push users to use more radiation curing both in the wood coating and printing industries;
- « now even small furniture manufacturers buy their own UVC line » (ref. IST)
- « many wide web flexo printers will in the coming years replace solvent by UV inks »
- « the competitive water-based inks and varnishes make deinking and recycling of paper and board very difficult because of mud formation » (ref. Voith-Sulzer)

It can be imagined that these two « niches » will grow to more than 10% of potential applications in the coming years, which means doubling above too low figures!

-research efforts and expenditures will rise with a growing market and competition. More and safer raw materials become available, hybrid curing methods will increase the chances of feasibility.

The number of research institutes, universities cooperating with industry has resulted in a surprising spectrum of useful products and applications; the most active participated at our recent conference. France alone has at least five such laboratories (4). It is estimated that about 200 professors and searchers are active to prepare future radiation curable chemicals (see Proceedings Academic Day 95, ref 5).

-improved and new equipment on one side, new chemical systems, additives and formulations on the other, are of great assistance to the accelerated introduction of new applications and investments. It is not the task of this paper to give details, but let's at least mention the tendency to cooler and more powerful UV lamps/systems, the simplification and cost reduction for certain EB accelerators, the success of cationically UV curable silicones, additives for improved abrasion resistance, non-irritant diluants for wood coatings and flexo inks, and several more breakthroughs have been presented during RadTech Europe 95.

Another positive influence comes from the growing number of available pilot lines and laboratory equipment for the curing of samples or for pre-industrial trials. Equipment suppliers, especially for EBC have their own or access to industrial size and speed lines, often one finds combinations of curing equipment at coating suppliers' plants. Many chemical suppliers can test and demonstrate both curing techniques, in special cases make comparisons to thermal curing, and larger companies have pilot lines for preparing, coating and curing of panels, printing and lamination of sheets, coating of flexible substrates.
Several pilot lines for coating and EB/UV curing are accessible in Europe; their availability helps to create new products, to make fine-adjustments of coatings and to help preparing investors' decisions. (A list of the major lines can be supplied on request to the author).

Application fields

We could analyse and separate them into UV and EB applications, or describe the activities of the major user countries. A better way seems to look at the substrate, product or special function families and compare them to alternative methods where they bother. We hope to be able one day to present a detailed review and forecast of applications like our American colleague Lawson(6).

Graphic Arts

An exciting field with many realized and potential applications. For sheets and narrow-web letterpress and offset, easy installation of standard UV curing equipment by the press supplier or even the user eliminate hesitation and problems. For label printing, screen printing up to sheet-size and direct-mail web printing, UV curing is practically state of the art: gloss, adhesion, abrasion resistance are improved. OPV on heat-set inks is more difficult with UV, adhesion may be difficult on certain colours, and there is competition by water-based varnishes which look more economical to press suppliers and users.

Sheet and web-offset

There is a different tendency in web-offset printing with EBC between the USA and Europe. The US packaging industry still seems to favour EB, maybe for higher safety or longer runs. In Europe there is a preference for sheet offset with UVC -because of smaller jobs? and the biggest customer of EB lines, Tetrapak, no longer seems to request EB inks to print safe PE-coated board for liquid food packaging. Apparently UV ink suppliers have obtained a declaration of « harmlessness » for their products from official laboratories, allowing them to print secondary food packaging on less expensive UVC web-offset presses. Anyway there is probably some hesitation in the market about the printing and curing technique to be installed in the future: water-based-, UVC- or cationic flexo, UVC-offset ? - all promising better print quality and reduction/elimination of solvent emissions.

Flexo printing

Serious development work is going on for at least four years. The USA talked earlier about this idea, seminars were organized and inks were offered. At a closer look they were paste inks, what we would call dry-offset, only printable on narrow web label equipment with stiff cylinders. Wide web printers wanted to try and test all the promises made including solvent-free working. But the offered ink-samples had too high viscosity, not enough coverage and adhesion on films, and there was no high-speed press/ UV combination available for testing and development. Since it was very difficult to find reactive low-viscosity, low-odor diluents after the withdrawal of NVP, water was considered as an alternative. Press builders started to offer stiffer printing stations, allowing to work with flexo-inks with somewhat higher viscosities. For many as a surprise, Bolte, a European pioneer presented extensive development results in late 1992 and at the following RadTech '93 conference(7). A Windmöller-Hölscher press with a central four colour cylinder was the key development tool. Four UV lamps curing on the central cylinder introduced too much heat, resulting in deformations. Many other details had and still have to be solved. Other users, suppliers, institutes are engaged in this project with an enormous potential; let's only cite a study group with a pilot line at PIRA International in the UK, directed by Mr Chamberlain present in Maastricht as chair of the printing session.
Screen printing

is making constant progress with UVC on label presses and sheets up to poster size. Many screen inks are now water based; I have no information about a possible need of evaporating part of the water by an IR ramp.

Intaglio printing

Already in 1993 it was reported that the Printing Works of the Danish National Bank were printing banknotes on both sides with EB curable intaglio inks. To strengthen development efforts and the possibility of security printing pilot runs DeLaRue-Giori in Lausanne installed an EB pilot line. The British and Americans despite as many years of R&D are apparently still not using EBC. The French and Italians may use some UV, but mainly for the much « flatter » offset inks. In Australia several UV processes, including varnishing and holographic inserts are used for the production of the polymer film based new $ bills. This chapter is certainly incomplete due to extreme secrecy in the security printing business.

Finishing of paper and board

Base-coat for metallization

About 10 years ago, 3 pioneers installed EB lines for the curing of base-coating for vacuum-metallization of label paper and gift wrap: Illochroma in Belgium, Vacumet in Australia and Hallmark in the USA (also for selective transfer-metallization). Since then it was relatively quiet, some investors choose water- or solvent based varnishing systems. They knew that their products would not have a mirror-like finish and that they might emit vapour in the vacuum metallizer. Very recently a UK converter, experienced in EB paper decoration, decided to install a new lowest voltage (125kV) multi-cathode accelerator with a very high dose delivery, on a 1,6m wide Kroenert coater (8). UV curing in this field is not known - there might be a risk of fogging (oxidation of the metal layer) due to uncured components.

Siliconization

Since about 15 years several techniques attempt to be the favourite in the paper and film siliconization market: solvent- and water-based, solvent-free, UV radical, UV cationic and EB curable. Only recently it has become relatively quiet about the three traditional curing processes. Only few users in Europe accepted the advantages of EB with the lowest heat-load on thermoplastic films, without paper dryout and need for rehumidification, but nobody liked the need for inerting of the one source silicone-acrylate. One label-paper producer opted many years ago for a high-speed UV radical curing system with inerting. Converting machine builders favoured for years equipment which required huge ovens, rather than buying EB or UV equipment from third parties. In the meantime they have understood that radcure could create a new family of equipment and now they help to promote EB or UV siliconisation with cost-intensive industrial demonstration plants. With the introduction of UV cationic curable silicones by GE and Rhone-Poulenc, with a smaller investment and without the need for inerting, most of a rising number of investments go into this direction (Italy, Switzerland and probably in other countries). One converting machine builder reports that three out of four lines will use radiation curing, and that 95/96 seem to be excellent years. Most are wide-web, high performance equipments.

Wood decor paper

One of the earliest EB applications in Germany and the USA, slowed down for years, certain obsolete and slow lines were even stopped. WKP with their multi-machine investment
may have saturated the market for a certain time, perhaps there has been a period when paper coated chipboard panels were disliked because of cases of formaldehyde emissions due to the glue. Now we observe a revival: new decors are offered, e.g. parquet patterns, coating weight is no longer a minimum, but may go up to 100g/m² and use a highly abrasion resistant formulation and EB curing. It will be laminated to MDF panels for the production of parquet, apparently strong enough to walk on. Why not? PVC flooring is UV coated since years with satisfactory results, and here we have thicker EB coating layers. A second company in Germany decided recently also to buy a high performance EB line.

In Belgium a producer has opted for UV curing of thinner layers on porous decor paper. The odour of the samples reminds uncured components, cheap raw materials or photoinitiators; this seems to confirm that UV can not cure monomers penetrated into the paper. Do they count on a thermal post-cure in the lamination press?

Wood and Building Materials

A field with a large consumption, many realized and potential applications, a lot of contradictory figures and an excellent review paper presented in the wood coating session. In 1987 the W-European consumption of wood-coatings was estimated to more than 350kT, with Italy and Spain consuming together about 50%. For 1994 another source (RCL 3/1995) only finds about 180kT, with 20%, including unsaturated polyesters, used for UV and EB curing. Chemical and equipment suppliers observe a steady growth in both fields.

Italy as biggest consumer is proud to work at the highest average solid content (>56%) in Europe, compared to the UK situated at only ~24% of solids. This is possible by practically eliminating the use of NC based and acid curing systems. UV curing will rise from 13% of all wood coating systems in Italy (1990) to 18%(1998) and 20-22% in 2003. PUR systems which still use 65% of VOC are expected to decrease and be replaced by water based and others. The use of EB curables can for the moment be neglected, because the only, but biggest installation ASTRID(2.6 m wide), is only working one shift and still working on development of better and more regular results. Their aims and samples shown last Fall look very impressive - at least for a layman.

In Scandinavia, acid curing was the preferred method, with the risk of free formaldehyde formation; therefore UV and some EB curing find a lively interest. Today radiation curing represents here about 10%. The double-sided EB equipment for profiles and mouldings at Bjelkes runs now during two shifts and creates interest in other countries. Several producers of picture frames have replaced spraying and thermal curing by vacuum coating followed by UVC.

Different types of parquet obtain abrasion resistant UV or EB coatings either with sealer or on printed paper, and/or a mat finish layer. Matting is obtained either with additives in the top layer, or by dual-cure or by temporary lamination with a mat-finish film, which at the same time reduces the need of inerting. Detailed cost calculation for a combined UV/EB parquet production were presented by Holl(12). Even if other companies and countries may use different costs or product design, a useful outline is available for completion and comparison to own figures.

Thanks to development work on UV-absorbers and the selection of acrylates with improved weathering behaviour we find a growing number of building products for outdoor application (panels, paper laminates) cured by EB processors.

Other wood, chipboard and MDF board panels and doors are produced in several countries with EBC or combined with UV, mainly for the sealing layer and matting effects.

Even if most informations come from Germany, Italy, Scandinavia, a growing activity can be observed in other countries and on other building materials from cork to plastic and metallic substrates. We refer the readers to the special sessions treating a selection of these applications.
A selection of other applications

Automotive, Glass

It seems that most UV applications in the car industry have been developed in the USA. Fusion UV Systems seem to be the most active promoter of techniques they have realized at home(13). Now we see them also appearing in Europe, very slowly and at isolated suppliers’ plants. At two French RadTech seminars Renault France has presented studies for head-light lens protection (polycarbonate « organic glass ») and for decorative hub caps. They have reached satisfactory results, but they leave it to their suppliers if they want to fine-tune these processes and offer car parts using UVC. Apparently there is also at least one line for screen printing the black ceramic coating on the windshield to protect the sealer. UV only brings this highly pigmented ink to a non-sticky state for handling, the real curing (vitrification) takes place in the glass lamination or tempering ovens!

Let’s stay a moment with glass: flat or bent glass can be laminated by a layer of 1-3 mm of a special adhesive and 7-20 minutes of curing by UVA; depending on the formulation it becomes safety glass (hard) or acoustic glass (soft), which can reduce the noise level typically by 36 dBA. Most European countries have several small to medium production sites. An alternative process developed at Battelle and Galvolux (CH), is the lamination of printed films between two layers of glass and quicker curing by UVC to create decorative glass panels, eg. with a marble look. We ignore if UV mirror backings are produced in Europe.

Glass fibre sheets and composites become an important field of product improvement by radiation technologies. It has been reported that borders of glass-fibre sheets can be sealed by a narrow band of UV curable varnish. Glass-fibre composites are used for large space vehicle parts. Aérospatiale (15) started development work in 1979 to replace oven curing at 100-150°C with risks of deformation and cycle times up to 100 h by high energy EB/XR (10 MeV, 20 kW) curing near room temperature and a reduced cycle time of 8 hours. Fibers, resins and formulation had to be adapted for good adhesion and performance at elevated temperature. Since 1991 the unique Unipolis process is in operation in the South of France.

Based on a Japanese paper, Matra and Sciaiky/GMM (16) have built a UV surface treatment equipment which after a dose of 7 J/cm² before coating (!) improves considerably the adhesion of primers on SMC (fibre composites) and polypropylene parts, used eg. for the Renault Espace vehicle.

Everybody knows that a special type of glass-fibres: the optical fibres are coated, protected and assembled to cables with UV curable coatings at very high speeds, by a growing number of users (and suppliers).

Plastics (3d)

Primers, inks, protective and functional varnishes are deposited on a wide range of sport equipment (skis, raquets, fishing rods, golf balls) and cured with UV. The protection and screen printing of CD (compact disks) is another growing application, preparing its introduction also in Russia. The cosmetic and beverage industries give gloss, information and protection on (metallized) plastic capsules and covers by applying UV varnishes.

Metals

Several labs attempt since years to develop acceptable formulations for coil coating with UV or EB curing. Even if adhesion is found with good substrate preparation and priming, the problems may arise when the steel panels are mechanically shaped; the known coatings can better withstand traction than compression.
The above development activity may be slowed or stopped, because the recent idea to combine new types of powder coatings with UV or EB crosslinking, may bring desired results more easily. Considered for a long time a physical impossibility, lower fusion point formulations will be given storage stability. The applications may one day be possible for wood and plastic substrates, including three-dimensional objects. The coating will be applied by tribo-spraying, flow obtained by IR heat, and the «hardening» will be completed by a UV treatment. Many publications can be found, recently also in RadTech publications (16/ Proceedings 93 and 95 and RadCureLetter 3/1995).

A simple UV coating for non-degreased steel pipes/tubes is now also used in Europe, to give them temporary corrosion protection. The coating withstands a 300h salt-spray test, which is considered quite a performance.

It is known and has been treated in more detail, that cationic curing systems give better adhesion on metal (mainly Al) and polymer surfaces. Their limited shrinkage and slower curing rate, often followed by a (thermal) postcure are an evident explanation. This curing method has a promising future.

Conclusion

Time and space allotted are exceeded, the enumeration and short description of many more realized or potential applications of radiation curing must come to a halt. Please find additional information in the Proceedings, the RadCureLetter and during meetings with suppliers and other members of the growing RadTech family.

Acknowledgments

The author wishes to thank the following companies and individuals who have contributed to this paper with written information or have answered questions by telephone interviews: Akcros Chemicals (Bate, Hutchinson), BASF (Bankowsky), Ciba (Scheidt), Cray Valley (Zwanenburg), Eltosch (Klamann), ESI (Stronkhorst), Lamberti (Gianinetto), Polymer Physik (Holl), Polytype (Zimmermann), UCB Radcure (Pernell, Philips, Nuijten), and Union Carbide (Keaveny).

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ABSTRACT

Radiation curing in Japan is still showing a growth of 8-10 percent a year, although the deepest recession since years. Environmental issues, productivity improvement, energy saving as well as technological changes keep Radiation curing moving forward despite all economic turbulences.

The information on the main direction of research and development of radiation curing technologies, some features and industrial applications, and some trends of the future development are presented.

INTRODUCTION

This overview discusses the latest developments in UV and EB curing technologies and applications in Japan. The increasing attention to environmental pollution problems, requirements of health and safety legislation, problems relating to the use of volatile organic solvents (VOCs) typically found in coatings, inks and adhesives, continues to influence the trend towards a more extensive utilisation of water borne and higher solids products. Under such a situation technological changes are promising to solve the issues of productivity, improvement, energy and space saving, and minimization of VOCs.

The market had continued to grow at an average rate of more than ten percent until 1991, and is anticipated to grow at a rate of eight to ten percent since 1993. It should be noted that the major market segments are changed. Up to 1991, wood coatings, automotive parts coatings, plastic coatings such as reflective coatings for lamp reflectors, graphic arts with overprint varnishes, and printing inks and plates had higher growth rates. Since then, electronics with UV or EB curing applications such as photoresists for printing plate, printed circuit boards, and integrated circuits, liquid crystal display (LCD), and coating for compact disks (CD) or magnetic optical disks (MD) have higher growth rates [1-3].

For the latest five years (1991-1995) the average annual growth for UV and EB curing has been about 8%. This rate is expected to continue for the coming years, although growth rates should slow thereafter as saturation of the more obvious opportunities take place.

In this paper, the current status of Radcure in Japan with an emphasis on the recent results are presented.
THE MARKET

Table 1 shows the consumption of raw materials for monomers, oligomers, and photoinitiators in Japan. The annual growth rates for the consumption in 1993 and 1994 increased compared with their fall down in 1992, but again the rate is estimated to fall in 1995. The growth has resulted in the progressive decrease in the prices of basic chemicals so that certain radiation cured products can be relatively cheap, particularly for UV/EB printing inks and varnishes.

In terms of market segments, printing inks and overprint varnishes are the major, building materials and photoresists are the other major users. The remainder comprises various other applications such as electronics, electrical and functional plastic coatings.

UV / EB CURING TECHNOLOGY

This review covers developments in UV/EB curing technology in Japan [4]

UV CURING

Progress in certain UV/EB processes has been relatively strong and has been fuelled predominantly by environmental consideration. In UV/EB curing, new and improved materials and equipment are becoming commercially available. These include monomers of higher level of purity and consistent quality, lower viscosity oligomers, various polymers, copolymers and monomer-oligomer blends, and efficient wavelength specific photoinitiators. Attempt to lower the toxicities such as skin irritation of acrylate monomers are proposed by Osaka Organic Chemical Ind.. Skin irritation has been reduced by using poly-ethoxylated or poly-propoxylated monomers which have been purified of residual impurities. Efficient UV lamps featuring up to 320 watt/cm has been developed by Iwasaki Electric Co.

Raw material manufacturers are promoting to develop non-acrylate type monomers such as vinyl ethers, water-reducible oligomers, polyester acrylates, polymerization initiators for cationic system, water soluble or water reducible initiators. The demand for raw materials for radiation curing indicate that reactive diluents and resins are the most important group, unsaturated polyesters diluted in styrene or acrylates and acrylic resins diluted in acrylic monomers or oligomers are the common used raw materials. New UV/EB curable resin formulation will provide low viscosity oligomers not needing monomers as reactive diluents. Epoxides, urethanes, and vinyl ethers are still a small but growing part of the market.

WATER BORNE MATERIALS

There is an increasing demand for UV/EB formulations without monomers from the viewpoints of minimization of VOCs, health and safety. Water reducible oligomers offer one approach to water borne formulations. Several ways to use water are a primary means of reducing oligomer
viscosities. A number of new water reducible oligomers are put on the market. Water borne system is expected to grow much in the future.

CATONIC POLYMERIZATION
The practical application of cationic polymerization is one of the recent topics. Benzyl sulfonium salts as latent initiators which initiate cationic polymerization by UV or heating over a given temperature are proposed, and photoinitiators for cationic polymerization including these latent initiators have been developed. The well-known monomers and oligomers applied in the cationic polymerization are epoxides and vinyl ethers, the latter monomers are profoundly interesting. They are still a small but growing part of the market. Cationic systems are under development in various chemical companies.

EB PROCESSING
The conventional application of EB processing, crosslinking of electric wire insulation, polyethylene foam, and of automobile tire components have been the most important part of industrial EB application in Japan. A wide range of electron beam machines are put on the market by three EBM supplier, Iwasaki Electric Co., Nisshin-High Voltage Co., and Sumitomo Heavy Ind.. They are continuing to develop and improve EB equipment to meet the requirements of the applications, for instance, the wide EB machine equipped with a coater-laminator, WIP unit with a coater, and a more compact EBM which is less than half in height compared with foregoing units are developed and supplied. Table 2 shows total number of EB processing systems installed in Japan.

RADCURE APPLICATIONS
The following article describes the market segments where UV/EB curable materials widely used in Japan [1-3]. It is needless to say that these materials have been adopted for commercial use.

PRINTING INKS AND OVERPRINT VARNISHES
The market of UV curable lithographic inks is continuing to expand. Lithography is the major printing process in the UV curing printing processes. Printings are carried on paper, plastic and metal substrates. Especially, in the printing on business forms, securities, cosmetic boxes, food cartons, telephone cards, disposable cups and bottles, containers, labels and seals. UV curable overprint varnishes is active because of its fast curing feature at ambient temperature. It is expected to grow much, due to tighter legal restrictions regarding VOCs. High printing quality and printing performance are the key-success-factors. In accordance of the movement towards VOCs, UV curable flexo printing ink is expected to grow much in the field of flexible packagings and plastic film printings in near future. As for the area of gravure printing, UV curable varnishes
are also continuing a steady growth. UV screen printing is used in the fields of electronics such as the production of printed circuit boards, and graphic arts.

COATINGS FOR BUILDING MATERIALS
The major market segments are floor material coatings, especially for wood and PVC floor, and rust preventive coatings for steel pipes. Unsaturated polyesters diluted in styrene and urethane acrylates diluted in acrylates are the most used raw materials for floor materials. Water reducible urethanes are used in the segments to avoid environmental problems. The vacuum coating system for three dimensional parts has been introduced as an environment friendly process, and is becoming popular in the segment. Silk screen process has been applied for interior decorative panels where they have produced good quality and competitive results.

Rust preventive UV coatings for steel pipes are superior in curing feature, adhesion, and rust prevention to conventional coatings.

PRINTING PLATES
There are several processes currently used in printing which involves the use of UV curing, i.e. letterpress, flexography, gravure, screen printing, and lithography. The processes in which photopolymer plates are used to carry ink and transfer it to paper, plastic, and metal substrates. In terms of consumption of raw materials, letterpress and flexographic plates are the major. Photopolymer composition for flexographic plates differ from letterpress plate in that less crosslinking. Recently, water processible flexographic plates which meet the environmental requirements has been commercialized by Nippon Paint Co..

PIGMENTED COLOR COATINGS
The coatings and printing ink market are working to develop thicker coatings. To achieve this and still have acceptable hiding properties, a higher level of pigmentation is required. Photoinitiators with strong absorption at longer wavelengths toward 440nm allow the curing of heavily pigmented coatings. The photoinitiator developments render new opportunities in more highly pigmented thick coatings. The white pigmented UV curable coating market, particularly in food metal can coatings will not explode, because the move to replace the existing system with water borne system or steel laminates is under way.

COATINGS FOR PLASTICS
The market for plastic coatings are applied in plastic containers for packagings, protective coatings of electronic devices, magnetic optical diskes, vehicles, and building materials. An excellent anti-electrostatic coating system with use of high molecular weight anti-electrostatic agents for magnetic disk has been developed. The good weather stability in combination with suitable hardness and anti-fogging activity has also applied protective coatings for automotive head lamp lenses and optical
PHOTORESISTS

1. ELECTRODEPOSITION PHOETOETCHING RESIST FOR PRINTED CIRCUIT BOARDS

Electrodeposition photoetching resists are developed which give finer patterns by photographic process at reasonable expense and more reliability than dry film resists. Electrodeposition coating is a well-known technology in automotive coatings. Principle of the coating is consisted of migration of negatively or positively charged colloidal particles by electrophoresis and following coagulation on the copper plated surface of circuit boards.

2. RESISTS FOR PREPARING COLOR FILTER FOR LCD

At the moment few processes, that is, dyeing, pigment dispersed, printing, and electrodeposition are available. In terms of technology, electrodeposition process is promising. The direct electrodeposition process to unpatterned ITO (Indium Tin Oxide) on a glass substrate in order to shorten the color filter fabrication process has been developed. By this process, the fine patterned color filter uniformly across the large area of substrate is obtainable. The major market of LCD are notebook type computers, TV game machine, and car navigation systems.

3. RESISTS FOR MICROLITHOGRAPHY

As for the materials, with increasing integration density of circuits, the requirements for fine resolution is growing rapidly. The share of i-line resists is increasing that of g-line resists which have been predominant to dates. The required ultimate resolution is finer than 0.25μm, and a resolution of 0.35μm is required at production lines. Small amounts of EB resists are in commercial use.

Computer industry in Japan is good shape in these days, the very rapid growth of LSI production has been achieved.

RADIATION CURABLE ADHESIVES

Radiation curable adhesives are predominately used for precise adherence of microparts, for instance, mounting of devices on printed circuit boards, adhesion of segments of optical lenses and prisms, fixing of glass plates and pins in LCDs, adhesion of needles of disposable syringes. Both UV and EB have been used to cure wide varieties of application as above mentioned, but the commercialization of these has been slow. Thermal, anaerobic, humidity or multi-component curable formulations are studied for the applications under less or unexposable conditions. Radiation curable adhesion have been elusive, however, they would have a great potential to grow up in near future.

EB CURABLE SILICONE RELEASE COATINGS

The acrylic groups incorporated silicone resins are coated on the substrates such as paper or plastic film. The resin layer of thickness of 1μm or less was cured in a short time by low energy EB accelerator (2~3 Mrad). With the introduction of acrylic groups the release properties

...
OPTICAL FIBER COATINGS
Coatings for the silica optical fibers for telecommunication has grown. According to official data provided by Government, the optical fiber cable cores produced amounted to 2,800,000 km in 1993. Installations were dominated by trunk lines until 1990 and by distribution lines until 1993. The consumption for installing subscribers' lines have been increasing and seems to be the predominant market. Optical fiber coatings are composed of two layers: flexible one which directly contacting the silica fiber and overlaying hard one, and overcoated diameter is 250 µm. These coatings are requested to meet various performance to fill a somewhat delicate role to transfer signals.

STEREO LITHOGRAPHY
New liquid UV curable resins which adhere well to one another, moreover, improved toughness, curing speed and reduced distortion are developed to build the desired three-dimensional objects of complex shape. It can build three-dimensional models directly from CAD/CAM data and is far efficient than conventional carving processes. At the moment, two systems, one using radically curable acrylates, the other using cationically curable vinyl ethers are available.

MISCELLANEOUS COATINGS
The remaining UV coatings for glass and inorganic materials, coatings for metals and papers, and dental materials are widely used and will continue to grow.

RELATIVE MERITS OF UV AND EB CURING
There are instances for which only one of the two technologies is applicable. In graphic arts segments, it is neccesary to have several radiation sources in line. For reasons of cost and space, this is hardly feasible for EB, therefore, is a typical domain for UV curing. Another example is the screen printing of printed boards, which, for practical reasons, will remain a typical UV application. Pigmented materials are no problem for EB curing, whereas they require special pigments or adjustment of the wavelength in applying UV curing. For certain users, the photoinitiators required for UV curing may be a problem, for instance, medical or food applications, fragments formed from the photoinitiator upon irradiation may be not acceptable for physiological reasons or because of their odor. These may be overcome by using oligomeric or polymeric photoinitiators.

Little is reported about qualitative differences of products cured by UV and EB. That is, due to the fact that an exact comparison is difficult and only possible if all the parameters affecting UV curing are taken
into consideration.
* Characteristics and amount of photoinitiator,
* Wavelength emission and energy output of UV source,
* Atmosphere (with or without inert gas), and
* IR emission of UV source
  (e.g. undesired warm up of the lacquered items)
For the EB cured products, the dependence of the radiation dose must be taken into account.
There are significant differences between UV and EB, with regards to positive and negative effects of irradiation as discussed above. The decisive factor influencing the decision will most frequently be the size of manufacturing operation, investment to be justified, and the quality of products cured by UV or EB.

**CONCLUSION**

As already mentioned, recent trend suggests that development of materials having improved physical and chemical properties, as well as technological changes are dispensable for further growth of Radcure. Water based systems are providing strong competition in many market segments.

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- T.Sasaki Japan Atomic Energy Research Institute
- M.Takayama Toyo Ink Manufacturing Co., Ltd.
- M.Tsunoka University of Osaka Prefecture

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TABLE 1 CONSUMPTION HISTORY OF RAW MATERIALS IN JAPAN

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<tr>
<th></th>
<th>'91</th>
<th>'92</th>
<th>'93</th>
<th>'94</th>
<th>'95</th>
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<tr>
<td>MONOMERS</td>
<td>VOL.,T</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td>4,500</td>
<td>4,700</td>
<td>5,080</td>
<td>5,490</td>
<td>5,840</td>
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<tr>
<td></td>
<td>% AGR</td>
<td>-</td>
<td>4.4</td>
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<tr>
<td></td>
<td>B Yen</td>
<td>4.5</td>
<td>4.5</td>
<td>4.68</td>
<td>4.87</td>
</tr>
<tr>
<td></td>
<td>% AGR</td>
<td>-</td>
<td>4.0</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>OLIGOMERS</td>
<td>VOL.,T</td>
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<td>7,900</td>
<td>8,530</td>
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<td></td>
<td>% AGR</td>
<td>-</td>
<td>5.3</td>
<td>8.0</td>
<td>10.8</td>
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<tr>
<td></td>
<td>B Yen</td>
<td>7.5</td>
<td>7.65</td>
<td>8.26</td>
<td>8.84</td>
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<td>% AGR</td>
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<td>8.0</td>
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<tr>
<td>INITIATORS</td>
<td>VOL.,T</td>
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<td>665</td>
<td>731</td>
<td>805</td>
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<td>% AGR</td>
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<td>9.9</td>
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<td></td>
<td>B Yen</td>
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<td>3.49</td>
<td>3.77</td>
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<tr>
<td></td>
<td>% AGR</td>
<td>-</td>
<td>5.1</td>
<td>7.1</td>
<td>8.0</td>
</tr>
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</table>

★ Cost/price information is unobtainable at present.
* AGR: annual growth rate, B Yen: billion JY

TABLE 2 TOTAL NUMBER OF EB PROCESSING SYSTEM

(AS OF APRIL 1, 1995)

<table>
<thead>
<tr>
<th></th>
<th>200kV ~300kV</th>
<th>350kV ~1200kV</th>
<th>1500kV ~5000kV</th>
<th>TOTAL</th>
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<tbody>
<tr>
<td>RESEARCH AND DEVELOPMENT</td>
<td>49</td>
<td>6</td>
<td>5</td>
<td>60</td>
</tr>
<tr>
<td>WIRE &amp; CABLE</td>
<td>1</td>
<td>50</td>
<td>5</td>
<td>56</td>
</tr>
<tr>
<td>POLYETHYLENE FOAM</td>
<td>-</td>
<td>15</td>
<td>1</td>
<td>16</td>
</tr>
<tr>
<td>HEAT-SHRINKABLE SHEET &amp; TUBE</td>
<td>3</td>
<td>3</td>
<td>4</td>
<td>10</td>
</tr>
<tr>
<td>CURING &amp; CONVERTING</td>
<td>14</td>
<td>2</td>
<td>-</td>
<td>16</td>
</tr>
<tr>
<td>AUTOMOBILE TIRE</td>
<td>4</td>
<td>22</td>
<td>-</td>
<td>26</td>
</tr>
<tr>
<td>STERILIZATION</td>
<td>-</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>FLUE GAS TREATMENT</td>
<td>-</td>
<td>5</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>OTHERS</td>
<td>5</td>
<td>10</td>
<td>4</td>
<td>19</td>
</tr>
<tr>
<td>TOTAL</td>
<td>76</td>
<td>114</td>
<td>20</td>
<td>210</td>
</tr>
</tbody>
</table>

* Including "under construction"
CURRENT STATUS OF RADIATION PROCESSING (INCLUDING RADIATION CURING) IN RUSSIA

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ABSTRACT

The paper is a brief review of current status of radiation processing in Russia. The main attention is paid to the most developing areas of radiation processing in the region: radiation sterilization of medical products, radiation curing, environmental applications, and manufacture of electron accelerators.

INTRODUCTION

In Russia, in spite of very poor economic situation, radiation processing is developed at a comparatively high rate. As earlier [1], the main directions of the development are: 1) radiation modification of materials (mainly polymers), 2) radiation polymerization and copolymerization (including curing of coatings and graft-polymerization), 3) radiation degradation of polymeric materials, 4) radiation sterilization, 5) radiation treatment of food, 6) environmental applications, 7) radiation-chemical syntheses on the basis of chain reactions, 8) technological dosimetry, and 9) radiation engineering (manufacture of electron accelerators, construction of radiation plants etc.). The most developing areas are radiation sterilization of medical products, radiation curing of coatings, environmental applications of radiation processing, and manufacture of electron accelerators.

The present paper is a brief review of current status of radiation processing in Russia. It is compiled on the basis of the information reported in a number of books (see, e.g., [2,3]), various reviews (see, e.g., [1,4-7]) and numerous articles. The main attention is paid to the most developing areas mentioned above.

ELECTRON ACCELERATORS

At present new developments in the field of radiation processing in Russia are based predominantly on electron accelerators. The machines of low and middle energies are used for radiation curing, radiation treatment of flue gases, radiation cross-linking of polyolefin insulation etc. The accelerators of "Avrora", "Elektron", ELV, ILU and EOL types were and are utilized for these purposes. Their parameters were given earlier [1]. They are manufactured and supplied by Efremov Scientific Research Institute of Electrophysical Equipment in S.-Petersburgh (the accelerators of "Avrora" and "Elektron" types), Institute of Nuclear Physics of Siberian Division of Russian Academy of Sciences in Novosibirsk and Vladimir Il'ich Electromechanical Factory in Moscow (the accelerators of ELV and ILU types), and Radiotechnical Institute in Moscow (the accelerators of EOL type). The electron beams generated by these accelerators have a power up to 90-100 kW; they are magnetically
scanned (the width of the beams reaches 2 m). It is necessary to mention that there are projects to construct the accelerators with a beam power up several megawatts (for the electron-beam purification of flue gases from SO₂ and NO₃).

One of the recent modifications of the "Elektron" type machines is "Elektron-16" accelerator [8]. The machine is self-shielded; it is proposed for radiation treatment of thin-layer materials and gaseous media. Its parameters are shown in Table 1.

A number of low-energy electron accelerators with extended cathodes have been developed recently. Among them are TUR-M accelerator [9], "Astra-II" [10], "Tapir", "Kenguru", and "Finval" accelerators [11]. Their parameters are shown in Table 1. At present some of them are functioning as parts of pilot and commercial plants for electron-beam treatment of materials (see, e.g., [11,12]).

Table 1. Parameters of Russian low-energy electron accelerators

<table>
<thead>
<tr>
<th>Trade mark</th>
<th>Manufacturer</th>
<th>Energy, keV</th>
<th>Maximum beam power, kW</th>
<th>Maximum beam width, m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elektron-16</td>
<td>Efremov Institute of Electro-physical Equipment</td>
<td>250-300</td>
<td>30</td>
<td>2.0</td>
</tr>
<tr>
<td>EOL-400</td>
<td>Radiotechnical Institute</td>
<td>400</td>
<td>14</td>
<td>2.0</td>
</tr>
<tr>
<td>TUR-M</td>
<td>Scientific Technical Centre &quot;Energiya&quot; (S.-Petersburgh)</td>
<td>150-280</td>
<td>10</td>
<td>1.8</td>
</tr>
<tr>
<td>Astra-II</td>
<td>Scientific Production Association &quot;Astrofizika&quot; (Moscow)</td>
<td>200-300</td>
<td>25</td>
<td>0.6a</td>
</tr>
<tr>
<td>Tapir</td>
<td>Scientific Technical Company &quot;Tekra&quot; (S.-Petersburgh)</td>
<td>300</td>
<td>30</td>
<td>2.1</td>
</tr>
<tr>
<td>Kenguru</td>
<td>The same</td>
<td>250</td>
<td>5</td>
<td>0.36</td>
</tr>
<tr>
<td>Finvalb</td>
<td>The same</td>
<td>300</td>
<td>150</td>
<td>6.0</td>
</tr>
</tbody>
</table>

a The successive arrangement of modules with such parameters allows to form production lines of any widths.
b It is a project which foresees a construction of the machine with several windows; shown is for 6 windows.

It is noteworthy that at present in Russia there is a considerable enlargement of using linear electron accelerators (energy 6-10 MeV, power 5-15 kW) in radiation processing. The main area of the application is radiation sterilization of medical products. Manufacturers of these machines are Efremov Scientific Research Institute of Electrophysical Equipment, Research and Production Company "Torii" (Moscow), and Radiotechnical Institute.
RADIATION CURING

Radiation curing, i.e. curing under the action of ionizing radiation (predominantly electron beams), is one of the most important areas of radiation processing in Russia. The respective researches and developments are being carried out in the following directions: 1). the development of the formulations of monomer-oligomer blends for their curing on different surfaces; 2). the study on kinetics of radiation-induced thin-layer polymerization of such blends; 3). the investigation of curing technology; 4). the design and construction of respective plants including radiation sources; 5). the transfer of developed processes to a commercial scale. They are being conducted in state institutions (in the first, second, third, and fourth (partly) directions) and private (and semi-private) companies (in the third, fourth and fifth directions).

As a rule, the electron beams used in radiation curing have an energy to 0.5-0.7 MeV. However, the electron accelerators of ELV type with an energy of 1.2-1.5 MeV are utilized for radiation curing of coatings on artificial leather. In this case curing is accomplished by cross-linking of elastomeric material of the leather.

Electron-beam curing in Russia was realized on pilot and commercial scales. The respective information is presented in Table 2. It includes also the information from other countries of the CIS.

Table 2. Products with electron-beam cured coatings

<table>
<thead>
<tr>
<th>Product</th>
<th>Location of the plant</th>
<th>Maximum output</th>
</tr>
</thead>
<tbody>
<tr>
<td>Artificial leather for footwear production</td>
<td>Kirov (Russia)(^a)</td>
<td>1.3 t/h</td>
</tr>
<tr>
<td>Asbestos-cement panels covered with decorative paper (as construction materials)</td>
<td>Near Moscow</td>
<td>200,000 m(^2)/year</td>
</tr>
<tr>
<td>Ceramic facing tiles with decorative coatings (as construction materials)</td>
<td>Dnepropetrovsk (Ukraine)</td>
<td>5 m(^2)/min (project)</td>
</tr>
<tr>
<td>Furniture wood panels</td>
<td>Kiev(^b) and Moscow</td>
<td>950,000 m(^2)/year (Moscow)</td>
</tr>
<tr>
<td>Gypsum panels with decorative coatings (as construction materials)</td>
<td>Near Moscow</td>
<td>-</td>
</tr>
<tr>
<td>Prepregs for production of copper-clad glass fibre laminates</td>
<td>Moscow</td>
<td>-</td>
</tr>
<tr>
<td>Pressure-sensitive adhesives on the basis of polymeric films</td>
<td>Moscow</td>
<td>-</td>
</tr>
<tr>
<td>Three-layer laminated composite consisting of poly(ethylene terephthalate) film and aramid paper (as electrical insulating materials)</td>
<td>Moscow</td>
<td>-</td>
</tr>
<tr>
<td>Wood panels for cabinets of color TV sets(^b)</td>
<td>L'vov and Simferopol(^b)  (Ukraine), Samara (Russia)</td>
<td>11 m(^2)/min (L'vov)</td>
</tr>
</tbody>
</table>

\(^a\) There is a project to construct the analogous facility in Tver' (Russia).

\(^b\) At present the plants are not operating.
Among the recent works it is necessary to mention the process of production of gypsum panels with radiation-cured decorative coatings developed by Joint-Stock Company "Dialog-ELOM" (Russia). The dual-cure method is proposed for curing. The electron-beam source is the accelerator of ELV type (energy 0.4-0.7 MeV, power 25 kW); several mercury ultraviolet lamps are intended for additional drying (to exclude the negative effect of air).

RADIATION STERILIZATION

In Russia the last ten-year period is characterized by a fast increase in the productivity of disposable medical products (mainly syringes). For instance, there is an intention to manufacture in 1995 6 billion disposable syringes, 190 million containers for blood storage, and 320 million devices for blood transfusion [13]. This situation gave rise to the simultaneous intense development of radiation sterilization of such products.

At present $^{60}\text{Co}$ gamma-ray sources and linear electron accelerators (energy 5-10 MeV, power 3-15 kW) are used for radiation sterilization of disposable medical products in Russia. Table 3 gives some information on commercial radiation sterilizers in this country.

Table 3. Commercial radiation sterilizers in Russia

<table>
<thead>
<tr>
<th>Location of sterilizer</th>
<th>Radiation source</th>
<th>Activity or power</th>
</tr>
</thead>
<tbody>
<tr>
<td>S.-Petersburgh'</td>
<td>$^{60}\text{Co}$</td>
<td>0.93 MCi</td>
</tr>
<tr>
<td>Near Moscow</td>
<td>$^{60}\text{Co}$</td>
<td>0.12 MCi</td>
</tr>
<tr>
<td>Near Kaluga (Russia)</td>
<td>$^{60}\text{Co}$</td>
<td>0.67 MCi</td>
</tr>
<tr>
<td>Kazan' (Russia)</td>
<td>$^{60}\text{Co}$</td>
<td>0.17 MCi</td>
</tr>
<tr>
<td>Tyumen' (Russia)</td>
<td>$^{60}\text{Co}$</td>
<td>0.47 MCi</td>
</tr>
<tr>
<td>Dimitrovgrad (Russia)$^{a}$</td>
<td>$^{60}\text{Co}$</td>
<td>1.5 MCi</td>
</tr>
<tr>
<td>Kurgan (Russia)$^{b}$</td>
<td>2 linear electron accelerators LUE-8-5B (energy 8 MeV)</td>
<td>2x10 kW</td>
</tr>
<tr>
<td>Kostroma (Russia)$^{a}$</td>
<td>Linear electron accelerator UELV-10-10 (energy 10 MeV)</td>
<td>10 kW</td>
</tr>
<tr>
<td>Moscow$^{a}$</td>
<td>Linear electron accelerator (energy 10 MeV)</td>
<td>10 kW</td>
</tr>
<tr>
<td>Near S.-Petersburgh$^{a}$</td>
<td>2 linear electron accelerators LUE-8-15C (energy 8 MeV)</td>
<td>2x15 kW</td>
</tr>
</tbody>
</table>

$^{a}$ Under construction.

$^{b}$ At present the modernization of sterilizer is being conducted. Two linear electron accelerators of LUE-8-15C (energy 8 MeV, power 15 kW) will be in operation (annual output 1400 t for each machine) [13].
Besides commercial plants, the facilities on the basis of linear electron accelerators located in research institutes are used for radiation sterilization. Among such institutes are Institute of Biophysics of Ministry of Health of Russian Federation, Institute of Physical Chemistry of Russian Academy of Sciences, Russian Scientific Centre "Kurchatov Institute", Obninsk branch of Russian Scientific Centre "Karpov Institute" and so on.

Total amount of radiation sterilizers operating in Russia (including located in research institutes) is about 30 [14]. Total activity of $^{60}\text{Co}$ gamma-ray sources in sterilizers is about 3.5 MCi (it corresponds to power of about 52 kW). Total power of electron accelerators used for radiation sterilization is approximately 50-60 kW. Speaking by other words, at present in Russia the ratio of $^{60}\text{Co}$ gamma-radiation and electron-beam powers is equal to about 1. It is necessary to note that the worldwide ratio is more than 10 (see, e.g., [3]).

The doses used in Russia for radiation sterilization of medical products are 15-25 kGy; in some cases the dose is 15 kGy [13-15].

ENVIRONMENTAL APPLICATIONS

Presently, the main directions for researches and developments in the field of environmental applications of radiation technology in Russia are: 1) radiation treatment of natural and polluted drinking water, 2) radiation purification of industrial liquid wastes, and 3) radiation purification of flue gases.

As in other regions, it was established that the useful methods for purification of industrial liquid wastes are combined ones (e.g., radiation-flotation, radiation-ozonation, radiation-biological etc.). The combined electron-beam and biological method of purification of industrial wastewater from nekal (it is a non-biodegradable hard surfactant which is a mixture of isomeric isobutylnapthalene sulfonates) was realized on a commercial scale at the Voronezh synthetic rubber plant in Russia (see, e.g., [16,17]). Two purification lines each equipped with an electron accelerator (energy 0.7-1.0 MeV, power 50 kW) function successfully during long time. The foamed wastewater (density of 0.02-0.03 g/cm$^3$) is irradiated to a dose of 2-3 kGy (at a nekal concentration of about 100-150 mg/dm$^3$). The tertiary biological purification is carried out after irradiation. On more precise data, the output of the plant is about 12,000 m$^3$ a day (at beam power 65-70 kW, dose 3 kGy and fraction of beam energy utilized 0.6-0.7). If the saturation of wastewater with ozone is used, the output is somewhat higher.

The combined methods were proposed also for the purification of wastewater of aniline-dye factories (dilution of industrial wastewater with municipal wastes + electron-beam irradiation + tertiary biological treatment), of highly-coloured drinking water (electron-beam irradiation + sedimentation + filtration), of wastewater polluted with nitrogen-containing organic compounds (ozonation + electron beam irradiation) etc. For example, recently the study on electron-beam treatment of water from Segezha River (Karelia) was performed [18]. This water is highly-coloured by natural organics and finely-dispersed particles. As it was obtained, electron-beam irradiation to dose of several kilograys leads to the decolouration of the water required by the respective Russian State Standard. The dose is less if the saturation of water with ozone-air mixture is used.

Several projects for the construction of commercial facilities on the basis of electron accelerators (their total power is ~ 0.9 MW) were developed [6,19-21]. The largest of them was proposed for the radiation treatment of municipal wastewater from one of the towns near S.-Petersburgh. The planned output of the plant was 110,000 m$^3$/day [21]. However, their practical realization is restricted by poor economic situation in Russia. In addition, it is necessary to note the design and construction of the special facility on the basis of $^{60}\text{Co}$ gamma-radiation source (its trade name is Gammatok-100) for the treatment of polluted water and hospital wastes (output is 65 m$^3$/day) [22].

As in some other countries, in Russia the significant attention is paid to the electron-beam purification of flue gases from SO$_2$ and NO$_X$ (see, e.g., [6,7]). At present in Novosibirsk the pilot plant with an electron accelerator (energy 0.5-0.7 MeV, power 50 kW) is in operation for radiation
purification of tin smeltery flue gases from SO\textsubscript{2} with the production of sulfuric acid of a medium concentration [19,23]. There are developed projects to construct several pilot plants with electron accelerators for the purification of flue gases from SO\textsubscript{2} and NO\textsubscript{X} (at a metallurgical works in Lipetsk, at a gas works in Orenburg, at one of the boilers in Moscow etc.). However, these projects are still not realized.

OTHER APPLICATIONS

Among the other areas of radiation processing it should be described briefly the status of radiation cross-linking of polymeric materials. It is well-known that radiation cross-linking of polymeric materials is one of the most important practical applications of ionizing radiation. This phenomenon is used for the production of durable polyolefin wire and cable insulation and heat-shrinkable films and tubes. Total amount of electron accelerators utilized for the manufacture of radiation cross-linked polyolefin insulation is about 20 (power is approximately 400 kW). About 10 electron accelerators are used for the production of heat-shrinkable polyolefin films and tubes. The recent achievement is the construction of two technological lines with electron accelerators for the manufacture of heat-shrinkable anticorrosion strips (total output is 1600 t a year) in Syzran (Russia) [24]. However, at present the production of radiation cross-linked insulation and heat-shrinkable materials was reduced dramatically because of the poor economic situation in the region.

REFERENCES


Present Status of Radiation Curing in China

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19 Zhongguancun Road, Beijing 100080, China

At the beginning of 1970's, research on radiation curing basic theory as well as other forward topics was initially undertaken by several institutes, universities and companies in China. Pilot production began in the middle of 1980's. In this period, among those fruitful research findings and pilot products were the PS plate developed by the Institute of Chemistry and the Institute of Photographic Chemistry of Academia Sinica, pilot EB curing line at the Shanghai Science and Technology University, EB curing membrane developed by the Wuxi Chemical Engineering Institute and some photosensitizers synthesized by the Beijing Normal University. The total annual consumption of radiation curing coating, ink and adhesive is estimated to be not more than 700 to 800 tons with an average annual increase rate of 10% during 1980's.

In the later period of the 1980's, significant progress was made on radiation curing technology in China, especially in terms of application. The main current application areas are presented in Table 1. Total annual consumption of monomers used for radiation curing is estimated approximately to be 1,500 tons/year with an average annual growth rate of about 20%.

<table>
<thead>
<tr>
<th>Sector</th>
<th>Item</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronic</td>
<td>EB curing membrane, solder mask</td>
<td>PCB (TV, facsimile machine, printed</td>
</tr>
<tr>
<td></td>
<td></td>
<td>circuit board), screen printing</td>
</tr>
<tr>
<td>Graphic Arts</td>
<td>photosensitive plates, UV overprint coatings, liquid resin board</td>
<td>printing plates, magazine covers, packing, offset, screen printing</td>
</tr>
<tr>
<td>Wood</td>
<td>UV curable varnish UV, UV curable primer furniture</td>
<td>furniture, wood board, decoration</td>
</tr>
<tr>
<td>Raw Materials</td>
<td>acrylic acid / functional monomer, photosensitizer</td>
<td>UV/EB inks, coatings</td>
</tr>
</tbody>
</table>

Application of radiation curing technology has been developed rapidly in the 1990's on account of the rapid growth of Chinese economy, and the involvement of foreign investment and introduction of foreign advanced technologies. It was estimated that the consumption of solder mask used in electronics exceeded 500 tons in 1994. The consumption of UV curable coatings and inks was over 3,800 tons in the same year. Furthermore, radiation curing technology has been also employed to improve old processes in some areas such as fiber optics telecommunication, adhesive, automobile and glass industry.
In China, the development of radiation curing technologies is characterized as:

1. Increasing Market for Radcure Products

In China, total consumption of radiation coatings and inks was increased from 1,500 tons in 1990 to 4,000 tons in 1994. The increasing rate was approximate 35% annually. Major areas of the largest current use and corresponding growth potential of each kind of radcure products in China are presented in Table 2.

Table 2  Radcure Products Market in China (excluding Taiwan)

<table>
<thead>
<tr>
<th>Area</th>
<th>1994 (ton)</th>
<th>1997-98 (ton)</th>
<th>Increase Rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Industrial Coating</td>
<td>1,800-2,000</td>
<td>3,500</td>
<td>21-28</td>
</tr>
<tr>
<td>wood flooring</td>
<td>300-320</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>decoration board</td>
<td>400-450</td>
<td>600-700</td>
<td></td>
</tr>
<tr>
<td>furniture</td>
<td>150-180</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>plastic board</td>
<td>100</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>can coating</td>
<td>-</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td>plastic flooring</td>
<td>10-30</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>metal component</td>
<td>170</td>
<td>300-350</td>
<td></td>
</tr>
<tr>
<td>electronics coating</td>
<td>250-300</td>
<td>550-600</td>
<td></td>
</tr>
<tr>
<td>overprint coating</td>
<td>300</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td>others</td>
<td>150</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>Printing Ink</td>
<td>900-1,000</td>
<td>2,200</td>
<td>33-44</td>
</tr>
<tr>
<td>overprint varnish</td>
<td>800</td>
<td>1900</td>
<td></td>
</tr>
<tr>
<td>higher speed printing</td>
<td>10</td>
<td>&gt;100</td>
<td></td>
</tr>
<tr>
<td>specialized printing</td>
<td>30</td>
<td>&lt;100</td>
<td></td>
</tr>
<tr>
<td>packaging</td>
<td>-</td>
<td>&gt;100</td>
<td></td>
</tr>
<tr>
<td>Electronics</td>
<td>580-600</td>
<td>850</td>
<td>11-15</td>
</tr>
<tr>
<td>solder mask</td>
<td>450</td>
<td>550</td>
<td></td>
</tr>
<tr>
<td>photoresists</td>
<td>40</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>LCD</td>
<td>40</td>
<td>50-70</td>
<td></td>
</tr>
<tr>
<td>label inks</td>
<td>50</td>
<td>50-70</td>
<td></td>
</tr>
<tr>
<td>dry film</td>
<td>100</td>
<td>600</td>
<td>120-167</td>
</tr>
<tr>
<td>Automotive Coating</td>
<td>100</td>
<td>350-400</td>
<td></td>
</tr>
<tr>
<td>parts and components</td>
<td>0</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>body</td>
<td>0</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>safety glass</td>
<td>70-80</td>
<td>300</td>
<td>8-11</td>
</tr>
<tr>
<td>Adhesive</td>
<td>20</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Information Transfer</td>
<td>50</td>
<td>23-30</td>
<td></td>
</tr>
<tr>
<td>optical fiber coating</td>
<td>210</td>
<td>400</td>
<td></td>
</tr>
<tr>
<td>CD/LD</td>
<td>40</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Printing</td>
<td>170</td>
<td>260</td>
<td>6-8</td>
</tr>
<tr>
<td>liquid photosensitizing</td>
<td>0</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>solid photosensitizing</td>
<td>200</td>
<td>250</td>
<td></td>
</tr>
<tr>
<td>Textile/Dying</td>
<td>3,800-4,000</td>
<td>8,200</td>
<td>23-37</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2. Rapid Development in Industrial Production of Raw Materials

Chemical sectors manufacturing important raw materials utilized in radiation curing inks and coatings such as acrylic acid, acrylate, methacrylic acid and methacrylate as well as epoxy resin have advanced at a significant pace in the past five years. Acrylic acid and acrylate were only produced by Beijing Eastern Chemicals Works in 1980s. In the 1990s, however, other key chemicals producers in China, such as the Shanghai Gaoqiao Petroleum Works and the Jilin Chemicals Industry Co., began to manufacture raw materials for radiation curing. The main products and capacities of some producers of the raw materials are listed in Table 3.

Table 3 Manufacture of Raw Materials in China

<table>
<thead>
<tr>
<th>Producer</th>
<th>Products</th>
<th>Annual Capacity (10,000 t/y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beijing Eastern Chemicals Works</td>
<td>acrylic acid, acrylate/methacrylate, functional monomer (EO-TMPTA, TMPTA, TEGDA, HPPA, NPTA)</td>
<td>5</td>
</tr>
<tr>
<td>Jilian Chemicals Industry Co.</td>
<td>acrylic acid, acrylate/methacrylate</td>
<td>5</td>
</tr>
<tr>
<td>Shanghai Gaoqiao Petroleum Works</td>
<td>acrylic acid, acrylate/methacrylate</td>
<td>3</td>
</tr>
<tr>
<td>Shanghai Resin Plant</td>
<td>epoxies</td>
<td>5</td>
</tr>
<tr>
<td>Wuxi Resin Plant</td>
<td>epoxies</td>
<td>3</td>
</tr>
<tr>
<td>Yueyang Petroleum Co.</td>
<td>epoxies</td>
<td>5</td>
</tr>
<tr>
<td>Baling Petroleum Co.</td>
<td>epoxies</td>
<td>3</td>
</tr>
<tr>
<td>Dalian No.2 Organic Chemicals Works</td>
<td>functional monomer</td>
<td>0.05</td>
</tr>
<tr>
<td>Huaxin Industrial Development Co. Ltd.</td>
<td>functional monomer</td>
<td>0.05</td>
</tr>
</tbody>
</table>

3. The basic researches are adjusted to meet the marketing requirements

The laboratory findings and achievement are incorporated rapidly into industrial products. Much closer relationship has been established between research institutes and enterprises to develop jointly new products such as photoresists, photocurable inks and coatings, etc. Main research units on radiation curing technologies are shown in Table 4.

4. The Chinese government is paying more and more attention to radiation technology

Radiation technology is one of the first selected six projects included in the "High-Tech Industrialization Project Implemented by Production, University and Research Institute Sector". This project is organized and put into practice jointly by the State Economic Committee, the State Education Committee and Chinese Academy of Sciences. Financial and policy support is offered to the implementation units such as the Radiat. Tech. Inc., Chinese
Academy of Sciences. A Radiation Technology mission composed of five members and organized by the State Economic Committee visited the USA for a month in the last November. The mission visited RadTech North America and had an interview with the Chairman, Camille Kallendort, and the General Secretary Christine Dionne. It is a rewarding visit.

Table 4 Main Research Institutes on Radiation Curing in China

<table>
<thead>
<tr>
<th>Unit</th>
<th>Location</th>
<th>Item</th>
</tr>
</thead>
<tbody>
<tr>
<td>Institute of Photographic Chemistry, Chinese Academy of Sciences</td>
<td>Beijing</td>
<td>UV curing inks and coatings</td>
</tr>
<tr>
<td>Beijing Normal University</td>
<td>Beijing</td>
<td></td>
</tr>
<tr>
<td>Shanghai University of Science and Technology</td>
<td>Shanghai</td>
<td></td>
</tr>
<tr>
<td>University of Science and Technology of China</td>
<td>Hefei</td>
<td></td>
</tr>
<tr>
<td>Beijing University of Chemical Technology</td>
<td>Beijing</td>
<td></td>
</tr>
<tr>
<td>Wuxi Chemical Research and Design Institute</td>
<td>Wuxi</td>
<td></td>
</tr>
<tr>
<td>Institute of Photographic Chemistry, Chinese Academy of Sciences</td>
<td>Beijing</td>
<td>Photoresists</td>
</tr>
<tr>
<td>Tsinghua University</td>
<td>Beijing</td>
<td></td>
</tr>
<tr>
<td>University Beijing Normal University</td>
<td>Beijing</td>
<td></td>
</tr>
<tr>
<td>Wuxi Chemical Research and Design Institute</td>
<td>Wuxi</td>
<td></td>
</tr>
<tr>
<td>Suzhou University</td>
<td>Suzhou</td>
<td></td>
</tr>
<tr>
<td>Shanghai Jiaotong University</td>
<td>Shanghai</td>
<td></td>
</tr>
<tr>
<td>Beijing Chemical Reagent Institute</td>
<td>Beijing</td>
<td></td>
</tr>
<tr>
<td>Institute of Photographic Chemistry, Chinese Academy of Sciences</td>
<td>Beijing</td>
<td>Photopolymer Printing</td>
</tr>
<tr>
<td>Peking University</td>
<td>Beijing</td>
<td></td>
</tr>
<tr>
<td>Nankai University</td>
<td>Tianjin</td>
<td></td>
</tr>
<tr>
<td>Zhongshan University</td>
<td>Guangzhou</td>
<td></td>
</tr>
<tr>
<td>Chinese Printing Technology Research Institute</td>
<td>Beijing</td>
<td></td>
</tr>
<tr>
<td>Institute of Modern Physics, Academia Sinica</td>
<td>Lanzhou</td>
<td>EB Curable Surface coating</td>
</tr>
<tr>
<td>Sichuan Union University</td>
<td>Chengdu</td>
<td>Plaster Board</td>
</tr>
<tr>
<td>Beijing Eastern Chemicals Works</td>
<td>Beijing</td>
<td></td>
</tr>
<tr>
<td>Tianjin Chemical Reagent Institute</td>
<td>Tianjin</td>
<td></td>
</tr>
</tbody>
</table>

5. China has lagged behind in the development of radiation curing technology

As a developing country, China has lagged behind in the development of radiation curing technology. Briefly, the development is classified as four parts: basic research, development of new products, production of raw materials and equipment research. However, the exploitation is at different stage in various regions and mainly distributed in the following regions.

In the Beijing-Tianjin areas, significant progresses were made in basic research, products exploitation, raw material manufacturing and equipment. Tsinghua University, Beijing University, Beijing Normal University, Beijing University of Chemical Technology, Institute of Photographic Chemistry and Tianjin Institute of Synthetic Reagent, and Tianjin Ink Inc. are
now developing radiation cured products. Beijing Institute of Automotive Technology and Radiate. Tech. Inc. are devoted to the research and production of UV/EB equipments.

In eastern, southern, southeastern and northwestern of China, some key research institutes, universities and companies listed above are engaging in development and production of UV/EB curing products, raw materials, and equipment (accelerator and UV light). The progress made in EB curing is not the same as in UV curing field in China. Recently, an electron curtain curing line manufacturing gypsum plaster board was constructed by the Institute of Lanzhou Modern Physics of Chinese Academy of Sciences. The products have gone on the market. Progress was made in EB curing coating for wood board by mutual cooperation of Radiate. Tech. Inc. and Beijing University. The result has been applied for a Chinese patent.

Although the research and manufacture of oligomer, photoinitiator, multifunctional acrylic acid, formulated ink, coating and photoresists have achieved certain scale, the research and manufacturing capacities in China are unable to meet the rapidly increased requirements of domestic markets. A lot of raw materials and formulated products with novel properties used in some critical circumstances are entirely dependent on importation.

6. RadCure China takes considerable effect of bridge for the development of radiation curing

RadCure China, the professional organization of Chinese radiation curing sector, was founded in May, 1993 under the supervision and support of CIRA. RadCure China has not only played significant role on strengthening the communication exchange and connections among the persons of same occupation, and making training of personnel engaged in radiation curing technology in China, but enhancing international exchange as well as market exploitation. It is being recognized by more and more individuals, companies and organizations. As the president of RadCure China, I hope to actively promote and enhance the development of radiation curing in China.

As mentioned above, recent trends in 1990s indicate that a close relationship among research, development, manufacturing, and marketing of radiation curing products has been established. In the last 10 years, China has increased communications with foreign academic and industrial organizations in an effort to improve the status of radiation curing technology in China. You are warmly welcome to China to exploit the greatest potential radiation curing market in the world.
THE ROLE OF PHOToinitiators IN LIGHT CURING FORMULATIONS

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ABSTRACT
This paper gives guidelines for a selection of photoinitiators by explaining their chemical and physical properties and also renders useful data for the formulator. Skilful formulation is a good combination of the physico-chemical background of the ingredients combined with experience. Hydroxyketones, Aminoketones and Acylphosphineoxides are described as effective solutions to various practical problems.

INTRODUCTION
The need for photoinitiators is well known to everybody dealing with radiation curing processes in different industries. Photoinitiators have a major impact on curing properties such as line speed, adhesion or mechanical performance of the cured film. With price differences of more than 10 times compared to each other, they can be a cost determining component of your products. Photoinitiators are an essential part of a photocuring formulation and not "just another additive." Facing the large number of available products, the right choice of photoinitiators or photoinitiator combinations can be the key to your success.

CLEAR COATINGS
Clear coatings encompass a range of applications including metal, wood, glass and plastic. Coating thickness can range from 5 μm for over print varnishes to 100 μm or more for floor tile and fibre optics. To improve weatherability of UV cured clear coatings, hindered amine light stabilisers (HALS) have proven useful, as they do not interfere with the UV cure process. Hydroxybenztriazole UV Absorbers (BTZ) can be used as well to improve substrate stability when used in combination with photoinitiator blends of α-Hydroxyketones (α-HK) and Bisacylphosphineoxides (BAPO).¹

Over Print Varnish
UV-Curing of clear coatings is a well-established technology in graphics. A large number of formulations are using Benzophenone/Amine combinations as cheap and well performing initiators. The major advantage of such bimolecular initiators is (beside their low cost) a fast surface cure. Negative properties such as yellow discolouration, offensive odour or weak abrasion resistance can be improved by adding high performing initiators.

Short wavelength absorbing α-Hydroxyketones (α-HK) are known as such highly reactive, non yellowing photoinitiators. They can be used alone or in combination with Benzophenone/Amine.
α-Hydroxyketones provide better colour properties when compared to a Benzophenone (BP) / Amine (A) mixture in an epoxyacylate overprint varnish. An overall lower photoinitiator concentration improves odour properties as well. Fig. 1 shows the yellowness-indices (YI) with both initiator types at different curing speeds.

**Fig. 1 The Yellowness Indices (YI) of Clear Over Print Varnishes**

Addition of small quantities of α-Aminoketones (α-AK₁) (approximately 0.5%) can improve the abrasion resistance of an over print varnish.

**Clear Furniture Coating**

Benzildimethylketal (BDK) is widely used as the standard photoinitiator for unsaturated Polyester (UPES)/Styrene furniture coatings. BDK provides a good body cure and thus is state of the art in UPES/Styrene despite its strong yellow discolouration properties. Recently we found out that a mixture of α-Hydroxyketone 1, with 5 parts Bisacylphosphine oxide (95 parts α-HK₁+ 5 parts BAPO) gives a similar curing performance as BDK but considerably less yellowing (see Fig. 2). This blend is liquid and easier to mix with the viscous resin than the solid Benzildimethylketal.

**FIG. 2 Yellowness Indices of a UPES/Styrene Furniture Clear Coating**

**Clear Coatings on Plastic**

Clear varnishes for plastic material are very common for typical uses such as hard coatings for rigid substrates (e.g., headlight lenses) as well as more flexible formulations for PVC floor tiles or cushion
vinyl sheets. A complete body cure (Body cure = maximum crosslink density at the interface between coating and substrate) provides the good adhesion in these very often heavy duty applications.

Recently it was found, that body cure of acrylate coatings was improved by blending 95 parts of α-HK₁ with 5 parts of BAPO. The through curing performance is determined by the measurement of the maximum cured thickness. A thick layer (1 mm) is exposed to one 80 W/cm medium pressure Mercury (Hg) lamp at a high cure speed, thus forming a cured film on top of uncured resin. The thicker this film, the better the photoinitiator is at achieving through cure and hence providing improved adhesion as measured by crosshatch test. A compact disc coating formulation (results in Fig. 3) was tested as an example of an industrial acrylate hard coat formulation. Two different α-Hydroxyketones (α-HK₁, α-HK₂) were used alone and together with 5 parts BAPO. An oligomer α-Hydroxyketone (oligom. α-HK) and Phenylmethylglyoxylate (PMG) were included as references.

Fig. 3 Body Cure of a PC Hard Coating

An industrial PVC coating for flooring shows similar body cure improvement as well (results in Fig. 4).

Fig. 4 Body Cure of a Clear Varnish for PVC Flooring

The body cure improvement by BAPO is quite effective, as already very small concentrations provide a dramatic increase in curable film thickness.

PIGMENTED COATINGS

Early photoinitiators were not very effective in the through cure of pigmented systems. However developments in the last decade, coupled with continuous research on these systems, have yielded photoinitiators that can successfully be used in the graphics industry.
White Pigmented Furniture Coatings

Liquid α-Hydroxyketone blends with higher amounts of Phosphineoxide type initiators show excellent properties in pigmented furniture coatings. The formulations are based on unsaturated Polyesters and Acrylates. The Phosphineoxides provide body cure and the Hydroxyketones enhance surface cure.\(^3\)

For lower pigment concentrations in the range of 5 to 15% TiO\(_2\) a Monoacylphosphineoxide (MAPO) blend (50 parts α-HK\(_1\) + 50 parts MAPO) is widely used. To completely exploit this technology, a pre-gellation step using a pre-exposure under TL 40W/03 fluorescent lamps is needed.

The use of MAPO limits the technology to the concentration range mentioned above. A BAPO-blend (75 parts α-HK\(_1\) + 25 parts BAPO) can cure a formulation containing much higher pigment loads. A pre-gellation step is not needed. BAPO-blends provide an additional opportunity for those end users, that are not equipped with a space consuming pre-gellation unit to cure pigmented coatings.

The following results show a comparison between the BAPO and the MAPO blends in UPES and UPES/Epoxyacrylate white wood finishes. Both formulations contain 25% titanium dioxide (rutile modification) as the pigment. The pendulum hardness indicates the reactivity of photoinitiators with and without pre-exposure (results see Fig. 5).

**Fig. 5 Pendulum Hardness of a White furniture Coating**

![Pendulum Hardness Graph](image)

A sufficient through cure with a MAPO blend was only possible with pre-gellation. Without pre-gellation a rapidly shrinking film is formed at the surface, thus leading to a problematic wrinkling phenomenon. The layers of the coating below the surface remain uncured beneath the wrinkled skin. Using a BAPO blend a white coating can be cured in the same way as a clear varnish, using a standard exposure unit. Spray application is possible as well. UV Curing of highly pigmented furniture coating using BAPO-blends can be a cost saving alternative to highly pigmented PUR-formulations.

The higher the concentration of pigment used, the greater the benefits of BAPO blends.

BAPO- and MAPO-blends were compared in a Polyesteracrylate (PEA) and a Urethaneacrylate (URA) white formulation containing the very high concentration of 50% TiO\(_2\). Using these more reactive resin systems the wrinkling phenomenon is not an issue; however, only the BAPO blends yield a cured coating with sufficient pendulum hardness. (see Fig. 6).
Screen Printing Applications
Curing white pigmented inks is a challenge because of the absorption of light by TiO$_2$, a dominant white pigment that absorbs in the UV region up to 380 nm. The trend is for faster curing white screen inks to be used in modern rapid rotary screen presses for label printing.

Phosphinoxide blends are recommended to cure white screen inks. In a recent experiment two different BAPO blends were compared with a MAPO blend (see Fig. 7). The reactivity was evaluated as the maximum cure speed for a tack-free and scratch resistant surface. Separately the adhesion (body cure) was measured by tape test.

BAPO-blends provide excellent surface cure and adhesion properties. The recently developed solid blend with BAPO and $\alpha$-HK$_2$ can improve the odour of cured inks as well.

Offset Printing Applications
$\alpha$-Aminoketones ($\alpha$-AK) are the state of the art photoinitiators for today's UV offset ink formulations, providing rapid cure speed across the range of pigments. $\alpha$-Aminoketones are very often used in combination with other initiators such as $\alpha$-Hydroxyketones or Benzophenone/Amines. Generally a photoinitiator concentration in the range of 1-4% is suggested.

Sensitisers such as Isopropylthioxanthone (ITX) can enhance the performance of $\alpha$-AK, significantly. It is also known that $\alpha$-AK exhibits excellent surface cure due to its high extinction coefficients at the major emission lines of industry standard UV curing lamps.

Due to its red shifted absorption spectrum $\alpha$-AK is especially suitable for dark pigmented systems.
\( \alpha \)-AK_2 also exhibits low volatility.

\( \alpha \)-Aminoketones split into two radicals when exposed to UV light (Monomolecular \( \alpha \)-cleavage mechanism). Bimolecular photoinitiators like sulphur substituted Benzophenones (SBP) or Isopropylthioxanthone (ITX) / Amine (A) combinations create radicals by a hydrogen transfer reaction. The latter reaction provides a good resistance to oxygen inhibition, but is slower than an \( \alpha \)-cleavage process.

In the following experiment two \( \alpha \) Aminoketones (\( \alpha \)-AK_1 and \( \alpha \)-AK_2) are compared with two bimolecular initiators (SBP/A, ITX/A) in a blue offset printing ink. Again the surface and through cure are determined separately.

**Fig. 8 Photoinitiator Performance in a Blue Offset Ink**

Thick section curing covers many applications: sealants, adhesives, printing plates, optical lenses and potting compounds. The polymer in most of these applications must have a relatively long dwell time under the UV light source to achieve the desired level of cure. Blends of BAPO with \( \alpha \)-Hydroxyketones with their red shifted absorption spectra and their photobleaching property match these requirements.

**Composites**

The manufacturing of composite material is a special thick section application for photoinitiators. Composites often consist of unsaturated polyesters, styrene and glass fibre materials. Because of their high stability and low specific weight composites are used in various construction elements (e.g., pipelines, tubes, walls, roofing, honey-comb structures).

The conventional thermally curing process for composites initiated by the decomposition of peroxides, suffers from styrene emission. UV curing eliminates the emission problem by rapidly closing the surface. The use of phosphine oxide initiators allows the curing of very thick layers of composites^9. Typically 0.5% of an \( \alpha \)-Hydroxyketone/BAPO blend is mixed with the resin. Laminates can be prepared by soaking several layers of the glass fibre material with such a mixture. The curing process is performed with fluorescent lamps.

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WEATHERING RESISTANT OLIGOMERS

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ABSTRACT

A series of aliphatic urethane acrylate oligomers were UV cured and their accelerated weathering performance studied. Gloss retention, yellowing index, tensile strength, break elongation, and tensile modulus were determined as a function of accelerated weathering length. Preliminary spectroscopic data will also be presented. Several high performance oligomers passed 3000 hours QUV test with excellent retention of both physical appearance and mechanical properties. Possible degradation mechanisms in weathering will be proposed and related to chemical structures of these oligomers.

INTRODUCTION

Even still a relatively new technology, Ultraviolet (UV) and Electron Beam (EB) curing has already enjoyed a healthy growth in numerous industrial segments such as coatings, adhesives, inks, and electronics in recent years. Fast curing (usually less than 1 second), excellent film properties, essentially no volatile organic compounds (VOC) are the major benefits among many other advantages compared with conventional solvent-borne thermal curing process which is under increasing pressure from regulatory agencies to limit the amount of solvents emitted into the environment. In recent years, major advances have been made in raw materials and equipment designs which make this unique technology available for more and new industrial applications. Accompanied by the exciting development in low skin reaction acrylate monomers, low viscosity oligomers, cationic chemistry, and kinetic monitoring of the polymerization process, a theme of increasing interests in current UV/EB curing industry is the study of the weathering resistance of radiation-cured films. By careful experimental design and systematic evaluation, highly weathering resistant oligomers, monomers, photoinitiators, and stabilizers package can be identified. Based on better understanding of the chemical and mechanical changes during the complicated weathering process, UV/EB cured coatings for long term exterior applications can be realized.

A laboratory accelerated QUV weathering device was used in this study. In coatings industrial, the most reliable and widely accepted weathering data is gathered by exposure of up to five years in harsh outdoor environment (e.g., Florida or Arizona). However, the long exposure time required to evaluate coatings durability directly conflict with the need to study the chemical changes with a wide range of formulation components. As a result, it is a common practice in today’s coating industry to develop new chemistry and make significant formulation modification based on the data from laboratory accelerated weathering test.

The very nature of high density crosslink makes UV cured films in general resistant to radiation, chemical and thermal treatment. From previous work by other investigators on the weatherability of UV cured coatings, the following general observation can be made: (1) Aromatic epoxy and aromatic urethane acrylates are inferior to aliphatic urethane acrylates in weathering resistance. (2) The photo resistance of UV cured films can be markedly enhanced by the addition of adequate photostabilizers, mainly UV absorbers and HALS. (3) Low functionality and non ether-containing monomers have better gloss retention. (4) Photoinitiators of α-hydroxyacetophenone derivatives offer high reactivity in photocuring and low color development. (5) For non light-absorbing polymers, backbone chemical structure greatly influences a coating’s weathering pattern. Radical induced oxidation and photolysis have been proposed as two of the major mechanisms accounting for the degradation.
This paper will focus on the accelerated weathering performance of a series of commercial aliphatic urethane oligomers with vastly different backbone structures. Results of the evaluation will provide further insights into understanding the fundamentals of the weatherability of UV cured coatings.

EXPERIMENTAL

QUV Accelerated Weathering Tester

A QUV Accelerated Weathering Tester equipped with QFS-40 lamps (UV-B) from Q-Panel Company was used in this study. The QFS-40 lamps have substantially high energy output between 270 nm and 323 nm compared with the spectrum of natural sunlight.

The QUV is programmed to operate in a cycle of 8 hours UV radiation at 60°C followed by 4 hours dark condensation at 40°C. Lamps are replaced after 400 service hours to ensure constant UV radiation dosage.

Formulation and Materials

Totally 12 oligomers were used in the weathering study. The general backbone structures and physical properties for these oligomers are listed in Table 1. The typical formulation for all the oligomers studied is as following:

<table>
<thead>
<tr>
<th>Component</th>
<th>Oligomer</th>
<th>SR238 (HDDA)</th>
<th>KIP-100F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight %</td>
<td>80</td>
<td>20</td>
<td>5</td>
</tr>
</tbody>
</table>

Where HDDA, hexanediol diacrylate is a difunctional monomer with excellent solvency and weathering resistance as concluded from previous study. KIP-100F, (oligo[2-hydroxy-2-methyl-1-[4-methylvinyl] phenyl] propanone), is an α-hydroxy-acetophenone type unimolecular photoinitiator known for its non-yellowing properties. HDDA, KIP-100F and all oligomers are commercial products from Sartomer Company.

Wet Films Preparation
Both 0.5 mil and 5 mil wet films were cast on mill finished aluminum Q-Panels by using different drawdown rods. Great care was taken to obtain films with uniform and constant thickness. This is very important because film thickness is a very important factor in determining a coating's weathering performance.

**UV Curing System**

A Fusion Model F440 UV curing unit was used. For gloss and yellowing measurement, both 0.5 mil and 5 mil samples were cured by passing one 300 W/in “D” bulb followed by one 300 W/in “H” bulb at a conveyor speed of 50 fpm (feet per minute). Each sample passed twice under this curing condition. For mechanical properties and spectroscopic measurements, 5 mil wet films were cast on aluminum Q-Panel and initially cured under one 300 W/in “H” bulb at 200 fpm. The semi-cured films were then cut into 0.5 inch wide strips. Finally, fully cured films were obtained by passing the stripes under one 300 W/in “D” bulb followed by one 300 W/in “H” bulb at a conveyor speed of 50 fpm. Again, a total of two passes were used under this curing condition.

**Gloss Measurement**

60C gloss were measured by using a Micro-Tri-Glossmeter from BYK-Gardner. Gloss retention was calculated by dividing gloss reading at certain time by gloss reading at time zero.

**Yellowing Measurement**

Yellowing property of a film is expressed by yellow index which is calculated by following equation.

\[
YI = [(1.28 \times X - 1.06 \times Z) / Y] \times 100
\]

where X, Y, Z are the tristimulus coordinates. The value for X, Y, and Z were obtained from a Hewlett Packard 8452-A Diode Array UV-Vis Spectrometer equipped with a Reflectance Spectroscopy Accessory from LapSphere. The UV-Vis is operated by a Window Color software program which gives tristimulus, Hunter Lab, CIELAB, and POLAR Coordinates.

**FTIR**

A Nicolet Magna 550 FTIR Spectrometer equipped with a Baseline Horizontal ATR accessory was used. 5 mil film strips were used for data collection.

**Mechanical Properties Test**

Tensile strength, break elongation, and tensile modulus were determined with a Thwing-Albert tensile tester with a strain rate of 0.5 in/min. For each sample, at least 5 specimens were tested and average value was reported.

**RESULTS AND DISCUSSION**

**Weatherability of Aliphatic Urethane Acrylates with Polyester Backbones**

Oligomers CN963, CN964, CN965, and CN966 belong to same class of aliphatic urethanes which are extended with same class of branched polyester polyol with only the molecular weight of the polyol changing. The ratio of molecular weight for CN963, CN964, CN965, and CN966 is 1:2:3:5. Because polyol backbone is the only variable, this class of oligomers provides a good base to study the effect of polyol backbone structure on the weathering performance of the films. Figure 1 gives gloss retention vs QUV exposure time for this class of oligomer. The very clear pattern from the graph shows a dramatically improved gloss retention as the molecular weight of polyester polyol decreases. This observation is in total agreement with previous findings from this laboratory in a closely related system studied.
To explain this observation, it is necessary to carefully examine possible modes of chemical modification occurring both in the film's surface and bulk. In a QUV accelerated weathering chamber, high energy UV radiation, moisture, oxygen and temperature are the primary factors for film degradation. The combination of these factors could result in complex degradation pathways. From a macroscopic point of view, chain scission and crosslinking (Scheme 1) are mainly responsible for change in a polymer's physical properties in weathering. Chemically, both free radical induced and non-free radical reactions such as hydrolysis of ester linkage could be the cause for chain scission and crosslinking. Scheme 2 is a typical free radical photooxidation process. The primary step in weathering induced degradation of aliphatic urethane acrylates involves the formation of free radicals by the interaction of crosslink matrix with light or heat. Residual free radicals from UV curing process could also be a source of free radical. Once these free radicals have been formed, they react with oxygen to form peroxy radicals. Peroxy radical can abstract hydrogen from polymer matrix to form hydroperoxide and a new carbon-centered free radical. This cyclic process will continue until two free radicals are coupled. This coupling termination causes excessive surface crosslinking. Some of the ultimate products of photooxidation reactions are alcohol, ester, acid and other carbonyl compounds. As a result, chain scission and crosslinking occur.

Above analysis based on previous studies by others suggests two possible factors contributing to the gloss and yellow index change for this class of oligomers. First, the degree of crosslinking in a UV cured film is partially affected by the concentration of acrylate functionality in a formulation. On a unit volume basis, the lower molecular weight CN963 has a higher acrylate concentration, thus a higher degree of crosslinking upon curing. This highly crosslinked network greatly reduces the rate of oxygen and moisture uptake and retards the rate of surface oxidation and photolysis. Degree of possible ester hydrolysis is also low. This is evidenced by a much smaller number of water spots for CN963 and CN964 compared with their higher molecular weight counterpart.
CN965 and CN966. As a result, great gloss was retained even after 3000 hours QUV exposure. Secondly, with a long branched polyester polyol. CN966 has more secondary and tertiary hydrogen available for abstraction by radicals. This hydrogen abstraction process may cause radical coupling between polymer chains and lead to excessive crosslinking at the film surface causing micro-cracks. These micro-cracks change the surface morphology and result in lower gloss readings.

For the same class of oligomers, the yellow index data follows a similar trend. For half mil films, CN963 retains a very low yellow index over the course of weathering while CN966 reaches a fairly high value (Figure 2). In such an inherently non-light-absorbing system, both oxidation and photolysis are important degradation processes. Chromophores such as hydroperoxides or ketones formed during oxidation could be UV sensitized and react with other labile hydrogen source in the presence of oxygen resulting in the formation of highly colored quinoid (by oxidation, as presented in Scheme 3) and conjugated products (by coupling). In CN963, the low molecular weight polyester backbone provides limited number of labile hydrogen for abstraction. The high crosslink density also slows down the migration of the residual photocurable groups onto the film surface. These all help keep yellowing to a minimum.

Figure 2. Effect of molecular weight on yellowing

Yellow Index vs Time
80% Oligomer + 20% HDDA + 5% KIP100F

Figure 3. Effect of molecular weight on tensile strength

Tensile Strength vs Time
80% Oligomer + 20% HDDA + 5% KIP100F
Film Thickness: 5 mil

Scheme 3. Formation of colored quinoid

Scheme 4. Oxidation and crosslinking of ether linkages

R, R': Labile H containing species
Figures 3, 4, 5 give tensile strength and elongation data vs QUV exposure time. All oligomers show increase of tensile strength upon aging. This is due to the well known fact that even in fully cured films, there are still substantial residual acrylate double bonds. Upon QUV weathering, these residual acrylates continue to crosslink. This contributes to the increase of tensile strength. It is interesting to note that for CN963, the tensile strength starts declining and eventually levels off after the first 500 hours increase. Similar trend was observed for other oligomers in this series. This could well be that crosslinking of residual double bonds dominated in the initial QUV exposure. As the double bond concentration decreased, the other competing degradation mechanisms started dominating and determined physical properties change at later stage of weathering. On the other side, flexibility suffered from this same crosslinking, hence, films broke at a lower elongation. Compared with polyether polyol urethane acrylates which will be discussed later, the change of elongation (for CN964, from 28% at initial to 22% at 3000 hours QUV) for this class of oligomers is still very gradual. Significant elongation was still conserved. The impact resistance follows the same trend as shown in Figure 5 for tensile modulus vs time.

**Figure 4. Effect of molecular weight on elongation**

![Graph showing Break Elongation vs Time for different oligomers](image)

**Figure 5. Effect of molecular weight on tensile modulus**

![Graph showing Tensile Modulus vs Time for different oligomers](image)

Figure 6 shows FTIR spectrums for CN964 both before weathering and after 1000 hours in QUV. The increase of peak around 3600 cm⁻¹ and broadened peak at 1750 cm⁻¹ suggested the formation of hydroxyl and carbonyl groups resulting from the radical photooxidation process. Hydrolysis of ester backbone is not likely a major process. Otherwise, a reduction in tensile strength due to chain scission should be observed. The fairly significant peak shifts around 1000 cm⁻¹ and 1500 cm⁻¹ also suggest the modification of polyester backbone. Work is undergoing to provide possible chemical modification mechanisms.

**Figure 6. FTIR spectrum of CN964 before and 1000 hours after QUV**

![FTIR spectrum graph](image)
Finally, film thickness also plays a very important role in the accelerated weathering. Take CN965 and CN966 as examples, as shown in Figure 7 and Figure 8, thick film has better gloss retention but poorer yellowing resistance than its respective thin film. The higher photoinitiator concentration in thick films explains the color development. The mechanism for the difference in gloss retention still remains unclear.

It should be made clear that the designed QUV test length for all films were 3000 hours. However, some films failed at earlier stage. The films either delaminated or degraded so severely that no meaningful data could be collected, thus test stopped.

It can be tentatively summarized that weathering degradation is really a multi-mechanism chemical process. The observed physical properties at certain stage of weathering are likely to be the overall collective effect of several competing mechanisms. Much more work need to be done to gain a quantitative understanding of the multi-mechanism degradation process.

**Figure 7. Effect of film thickness on gloss retention**

**Gloss Retention vs Time**

\[ 80\% \text{ Oligomer} + 20\% \text{ HDDA} + 5\% \text{ KIP100F} \]

**Figure 8. Effect of film thickness on yellowing**

**Yellow Index vs Time**

\[ 80\% \text{ Oligomer} + 20\% \text{ HDDA} + 5\% \text{ KIP100F} \]

**Weatherability of Aliphatic Urethane Acrylates with Ether or Ether/Ester Polyol Backbones**

CN980, CN981, and CN982 are aliphatic urethane acrylates where CN980 has pure polyether polyol backbone and CN981 and CN982 have ether and ester polyol backbones. As shown in Figure 9, Both CN981 and CN982 have excellent gloss retention. CN982 already passed 3000 hours QUV. CN981 passed 2400 hours with 90% gloss retention and is expected to reach 3000 hours with great film properties. This weathering resistant oligomer also has unique properties such as low viscosity, fast curing, and good pigment wetting.

**Figure 9. Effect of ether/ester polyol on gloss retention**

**Gloss Retention vs Time**

\[ 80\% \text{ Oligomer} + 20\% \text{ HDDA} + 5\% \text{ KIP100F} \]

**Figure 10. Effect of ether/ester polyol on tensile strength**

**Tensile Strength vs Time**

\[ 80\% \text{ Oligomer} + 20\% \text{ HDDA} + 5\% \text{ KIP100F} \]

Film Thickness: 5 mil
CN980, with pure ether backbone shows a rapid loss in gloss retention even the film is still surviving after 2200 hours. α-hydrogen of ether is well known to be labile for abstraction by radical. The high content of ether linkage in CN980 causes excessive surface crosslinking (Scheme 4) and micro-crack which leads to lower gloss reading. Data from Figure 10 also show increase of tensile strength for all three oligomers which again is due to the crosslinking of residual double bonds. It is worth to point out that upon weathering, this class of oligomers become rigid more rapidly than their ester counterpart. All three oligomers starts with great than 30% elongation. Elongation quickly dropped to less than 5% after 500 hours (Figure 11). Extra crosslinking due to the ether linkage is the major cause for the dramatic loss of flexibility.

Preliminary Weathering Evaluation of Some New Specialty Oligomers

CN983 is a low viscosity pure urethane acrylate. CN132 and CN133 are aliphatic difunctional and trifunctional acrylates, respectively. Both are very low viscosity. Without ester or ether backbone, these new generation of oligomers are expected to have superior weathering performance provided the oligomers are formulated properly.

Compared with CN963, the best weathering resistant oligomer in this study, CN132, CN133, and CN983 show very little color development. This is shown in Figure 12. For comparison, CN120, an aromatic epoxy acrylate, shows substantial color development as expected. Thin films of CN132, CN133 and thick film of CN983 cracked or delaminated at early stage of QUV exposure due to embrittleness. This problem can be solved by modifying the formulation to increase film’s inherent flexibility.

CONCLUSION

Weathering is a multi-mechanism degradation process. Aliphatic urethane acrylates show great resistance to accelerated weathering. For polyester polyol extended acrylate, low molecular weight oligomer, namely CN963, give higher gloss retention and great yellowing resistance. The mechanical properties of this class of oligomers are also well conserved during accelerated weathering. Aliphatic urethane acrylates with properly balanced ether and ester polyols such as CN981 and CN982 also perform well in the 3000 hours QUV test. Preliminary data indicates the new generation of low viscosity aliphatic oligomers show superior weathering resistance. It can be concluded that with a judicious selection of formulation components, UV curable coatings with excellent weathering resistance can be achieved. Work is undergoing in this lab to systematically study the effect of structure as well as component ratio on weathering performance.
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RECENT ADVANCES IN CATIONIC PHOTOINITIATORS
Application to the Photopolymerization of Epoxides and Vinyl Ethers

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ABSTRACT

The rate constant of polymerization of different vinyl ethers have been evaluated by differential
photocalorimetry DPC and compared to epoxide using various cationic photoinitiators.

INTRODUCTION

Over the last twenty years there has been constant development in the use of photochemistry as
applied to monomers or multi-functional oligomers (1, 2). UV curing technology has led to materials
which are not new, however the process of obtaining them presented numerous advantages,
especially for thin film applications.

The use of photochemical process (3) i.e. the use of UV/visible light has made it possible to dispense
with the thermal effect which is inhibiting for certain applications such as wood coating or paper
release. This has thus made it possible to develop certain new concepts of photosensitive
formulations, in particular relevant to microelectronics (photoresists), one relevant to inks, varnishes,
paints, resins or ever one relevant to dental materials.

A photosensitive formulation is somewhat complex and composed of apart from mono and
multifunctional monomers and/or oligomers, photoinitiator, photosensitiser and some additives such
as inhibitors (thermal and oxidative), pigments, dyes, stabilizers, plasticizers....
Thus it is essential to be able to control each of the compounds of the formulation and particularly to
know the nature of their response to a photochemical event as well as their influence on the different
partners of the composition. Very often the photoreactive formulations used are much more the
concern of empirical approach, based essentially on experience and closely guarded know-how than
on a rational and scientific procedure.

Cationic Polymerization

In most photocuring reactions, cross-linked polymer networks are formed by irradiation of
monomers and/or functional oligomers that contain at least two reactive functionalities in their
structural unit. Since these monomers do not produce initiating species with a sufficiently high yield
upon UV exposure, it is necessary to introduce a photoinitiator that will absorb effectively the
incident radiation and generate ions with a high quantum yield. The rate of initiation \( \tau_i \) is directly
related to the intrinsic absorbance \( \alpha \) of the photoinitiator, to the quantum yield for the primary
radical production \( \phi_R \), and to the efficiency \( \psi \) of the radicals in starting polymer chains:

\[
\tau_i = \phi_R \epsilon \Gamma_o \left( 1 - \exp(-\alpha) \right)
\]

where \( \Gamma_o \) is the fluence rate (light intensity) of the incident radiation. Compared to thermal
polymerisation, photoinitiation allows the attainment of very high values of \( \tau_i \) which in addition can
be varied throughout a large range by simply controlling the fluence rate.
While photoinduced radical polymerizations have been known and investigated for a considerable length of time, the corresponding photoinduced ionic polymerizations have received little attention. However, within the past few years and thanks to the works of Crivello et al. considerable progresses have been made, especially in the development of new photoinitiators for cationic polymerizations.

Most of photoinitiators for cationic polymerization are essentiallyonium salts with complex metal halide anions. A key feature of such a technology is based on the low nucleophilicity of the anion which reduces termination processes and allows ambient temperature cationic polymerization to proceed. The absence of air inhibition represents a distinguishing feature of cationic as compared to radical polymerizations. Commercially significant photoinitiators for UV curing by cationic polymerization are essentially based on diaryl iodonium and triaryl sulfonium hexafluoroantimonates or hexafluorophosphates (4, 5).

The photolysis mechanism proposed for these salts are more or less complex with major and minor reactions. For example, for sulfonium salts the excited state causes the heterocyclic rupture of the C-S bond giving a Ph₂S⁺⁺ ion radical; the hydrogen transfer between the latter and YH (solvent or monomer) leads to a proton according:

\[
\begin{align*}
\text{Ph₃S}^+\text{MXn}^- & \Rightarrow [\text{Ph₃S}^+\text{MXn}^-]^+ \
\text{Ph₂S}^++\text{YH} & \Rightarrow \text{Ph₂S}^+\text{H}+\text{Y}^-
\end{align*}
\]

We have to point out that beside the liberation of Bronsted acid, highly reactive radicals and radical cations may escape from the cage to undergo radical reactions with functional monomers.

It is interesting to note that commercially available sulfonium salts are complex mixtures that contain substantial quantities for 1 as well as the bis salt 2.

\[
\begin{align*}
\text{Ph₂S}^+\text{-Ar-S}-\text{Ph} & \quad \text{Ph₂S}^+-\text{-Ar-S}-\text{Ar-S}^+\text{Ph}_2 \\
1 & \quad 2
\end{align*}
\]

Therefore Cyracure® UVI from Union Carbide is a 50% mixture of 1 and 2 structures in propylene carbonate, respectively.

LEMP/MAO - Université Montpellier 2 - Case courrier 21 - 34095 Montpellier CDX 5 - FRANCE
Cyracure® UVI 6974 (with $X^* = \text{SbF}_6^-$)
Cyracure® UVI 6990 (with $X^* = \text{PF}_6^-$)

Degussa produces under 3M licence Degacure® KI 85 which is the bis salt (structure 2) with $X^* = \text{SbF}_6^-$ as counter ion.

In fact it was shown that polymerization strongly depends on the chemical nature of the non nucleophile counter ion and gives for cyclohexane oxide the following order of reactivity (8):

$$\text{SbF}_6^- > \text{AsF}_6^- > \text{PF}_6^- > \text{BF}_4^-$$

For epoxy functional silicone release coatings, diaryliodonium salts are preferred. In addition to enhancing solubility in the silicone formulations, long chain substituted diaryliodonium salts such as bis (4-dodecylphenyl)iodonium 3 and/or 4-octyloxylphenyl phenyliodonium 4 are used.

$$\text{(C}_{12}\text{H}_{25}\text{-Ar})_2\text{I}^- \quad \text{C}_{8}\text{H}_{17}\text{-O-Ar}-\text{I}^-\text{-Ph}$$

UV 9310C from General Electric has the structure 3 (the anion is not known).

Very recently Rhône-Poulenc (9) has patented a new type of iodonium salt which differs from the others by its counter ion, an ionium borate $[\text{BX}_a\text{R}_b]$ where $X$ represents an halogen atom ($\text{Cl}$, $\text{F}$) or a OH group, $R$ an aryle radical substituted by at least two halogen atoms.

$$\text{(R-Ar)}_2\text{-I}^+\text{B(C}_6\text{F}_5)_4^-$$

This new photoinitiator seems to be much more reactive that those made by GE and are especially characterized by a very high solubility in silicon oils (10) compared with other products on the market i.e. iodonium salts from GE or sulfonium salts from Degussa or Union Carbide.

Beside iodonium and sulfonium salts which are widely commercially used, we have to mention the ferrocenium salts which have been primarily developed by Ciba-Geigy (11). Similar to onium salts, these arene salts absorb in the deep UV but also in the visible range (violet or blue) more or less strongly, depending on the nature of the arylic group. Their photolysis differs strongly from that of other photoinitiators. After absorbing a proton, the ion aromatic complex loses the aromatic ligand neutral $\text{Ar}$ and releases a coordinatively unsaturated Lewis acid which forms a new saturated complex in the presence of a ligand. However the free Lewis acid must be thermally activated to polymerize epoxies. Irgacure® 261 produced by Ciba-Geigy is a cumene hexafluoroantimonate Iron II cyclopentadienyle.
Discovery of cationic photoinitiators have broadly extended the interests of UV curing technology, almost exclusively oriented by monomers which are sensitive to radical polymerization, particularly acrylates and methacrylates. The use of cationic photoinitiators allowed to activate monomers which are sensitive to cationic polyaddition mechanisms; among these monomers one can cited cyclic ethers, lactones, cyclic formals and acetals, vinyl monomers like vinyl pyrolidone, vinylcarbazole, and particularly, vinyl ether and epoxy family (alcohols, di and multifunctional monomers/oligomers).

We report a comparative kinetic study of vinyl ethers and epoxies.

EXPERIMENTAL

Different cationic photoinitiators have been used i.e. Cyracure® UVI 6974 & 6990, Degacure® KI 85, to crosslink mono and disfunctionnal vinyl ether or epoxy monomers and their mixture.

Two vinyl ethers from GAF have been tested, Rapi-Cure® DVE-3 and CHVE and compared with diepoxy carboxylate ERL 4221 from Union Carbide.

CH2=CH-O-(CH2-CH2-O)3-CH=CH2  CH2=CH-O-CH2-O-CH=CH2
Rapi-Cure® DVE-3  Rapi-Cure® CHVE

ERL 4221

Photocrosslinking reactions are evaluated and studied by Differential Photocalorimetry Technique with a DuPont DPC model 930 (12).

RESULTS AND DISCUSSION

The general kinetic equation for the photochemical reaction is given by the general equation (13).

\[ R(T) = \frac{d\alpha(t,T)}{dt} = k(T) \alpha^m (1 - \alpha)^n \left[-\ln(1 - \alpha)\right]^p \]

where \( \alpha \) is the degree of conversion; \( k \) the rate constant; \( m, n \) and \( p \) the orders of reaction, \( m \) for initiation, \( n \) for propagation and \( p \) the termination. Assuming that we consider the reaction just at the beginning, termination reactions can be neglected, i.e. \( p = 0 \). The autocatalytic equation gives:

\[ R(T) = \frac{d\alpha(t,T)}{dt} = k(T) \alpha^m (1 - \alpha)^n \]

with \( k = A \exp(-E/RT) \)

From the photogramme (Fig. 1), different parameters might be calculated, particularly the enthalpy \( \Delta H \) (J/g), the percentage conversion of monomer up to the maximum of the peak, the induction time corresponding to 1% of monomer conversion and the rate constant \( k \) as above defined.

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Among all the photoinitiators used, Cyracure® UVI 6974 (with SbF$_6^-$ as counter ion) is the most reactive compared to Cyracure® UVI 6990 or Degacure® KI 85 (both with PF$_6^-$ as counter ion) - see Table 1.

<table>
<thead>
<tr>
<th></th>
<th>UVI 6974</th>
<th>UVI 6990</th>
<th>KI 85</th>
</tr>
</thead>
<tbody>
<tr>
<td>DVE-3</td>
<td>57.6</td>
<td>57.3</td>
<td>46.2</td>
</tr>
<tr>
<td>CHVE</td>
<td>22.9</td>
<td>17.9</td>
<td>17.3</td>
</tr>
<tr>
<td>ERL 4221</td>
<td>18.9</td>
<td>16.4</td>
<td>11.8</td>
</tr>
</tbody>
</table>

Table 1: Rate constant k (1/min) for vinyl ethers and epoxy.

For the vinyl ethers the photoreactivity of Rapi-Cure® DVE-3 is twice higher than Rapi-Cure® CHVE. This effect may be attributed to the presence of oxygen bond in the chain of DVE-3 which gives a higher degree of liberty to the vinyl ether function, compared to the aromatic ring in CHVE. We also note that epoxy functions in ERL 4221 exhibit a low reactivity compared to vinyl ethers (Fig.2 & 3). This explain why vinyl ethers are used as solvent of epoxies not only to decrease the viscosity of the formulation but also to increase the photoreactivity of the system.

Operating at different temperatures allows to reach Arrhenius parameters $E_a$ and $A$: $E_a$ values calculated - Table 2 - confirm that DVE-3 initiated by Cyracure® UVI 6974 gives the highest photoreactivity.
Figure 2: Comparative cure rate versus degree of conversion of vinyl ethers and epoxy.

Figure 3: Comparative cure rate versus time of vinyl ethers and epoxy.
Table 7: Activation energy $E_a$ (kJ/M) for vinyl ether and epoxy.

<table>
<thead>
<tr>
<th></th>
<th>UVI 6974</th>
<th>UVI 6990</th>
<th>KI 85</th>
</tr>
</thead>
<tbody>
<tr>
<td>DVE-9</td>
<td>2.8</td>
<td>4.0</td>
<td>3.8</td>
</tr>
<tr>
<td>ERL 4221</td>
<td>4.3</td>
<td>7.3</td>
<td>9.5</td>
</tr>
</tbody>
</table>

CONCLUSIONS

From the different formulation which has been investigated, CyraCur® UVI 6974 has proved to be the most efficient cationic photoinitiator. The highest photoreactivity is obtained with vinyl ether monomers compared to epoxies, particularly with Rapi-Cure® DVE-3; its high response is due to the flexibility of the chain thanks to the presence of ether bond.

Other assets are also implicit in photoinitiated cationic polymerizations. One of these is the insensitivity of cationic polymerizations to oxygen.

Finally these commercial products (vinyl ethers and epoxies) can be formulated to provide a wide range of mechanical and chemical properties in the cured resins.

REFERENCES


(3) V.V. Kronganz, A.D. Trifunac, Processes in Photoreactive Polymers, Chapman & Hall Ltd., 1995.


ABSTRACT

There is an increasing demand for UV/EB formulations without monomers. Water dilutable oligomers offer one approach to formulations of this type.

In this paper several ways to use water as a primary means of reducing oligomer viscosities are reviewed.

A number of new water dilutable acrylated resins were prepared having different functionalities and properties.

Depending on the structure, viscosity decreases significantly by adding water. Good reactivity, solvent and water resistance were achieved after curing.

INTRODUCTION.

One of the main advantages of radiation curable coatings is the fact that they are solvent free and thus non-polluting. The resins used in the formulations are often high viscosity and as such difficult to supply.

In order to get the right properties (viscosity, rheology) to allow application, diluting monomers are added. These products bearing reactive groups are incorporated in the network. Some of the more effective viscosity reducers, although not toxic may cause skin irritation and sensitization.

This fact limits the use of radiation curable formulations in spray applications due to the unavoidable formation of clouds of fine liquid particles that may provoke irritation of the worker's skin.

Another drawback of some reactive diluents of low molecular weight comes from the fact that they are easily absorbed by porous substrates like textiles, non woven articles, fibre-cement slates, unsealed paperboards, etc.. On such substrates it has been shown that during the time between application and curing some diffusion of the low
viscosity reactive diluents occurs into the core of the substrate. These diluents being shielded from the UV-light by the upper layers of the substrates are not photopolymerized and remain unreacted. This behaviour impart unpleasant odour to the finished goods and may also adversely influence some physical and chemical properties of the coating e.g gloss, solvent resistance etc...

Urethane acrylates developed to give flexible coatings are normally high in viscosity. The diluents added to reach the application viscosity will strongly influence the final properties. The coating becomes less flexible, which makes it totally unacceptable for coatings on flexible substrates.

Obviously, the most efficient way to get high performance coatings is to blend the acrylated oligomers with inert solvents, which is commonly practised for some applications where outstanding abrasion resistance is required e.g. varnishes for the protection of plastic helmets.

However using this approach, we are losing 2 main advantages of the Radcure technology: the absence of solvent emission which makes it ecologically acceptable and consequently its low flammability potential which is a major concern for the printing and coatings industry.

Taking these considerations in mind, a large amount of research has been devoted in order to use water as the diluent in radiation cure systems.

If compared to 100% organic radiation curable systems, those containing water may have advantages with respect to the control of rheology and film thickness. However, it is obvious that its use always bring drawbacks such as the necessity to introduce a water removable step prior to radiation curing or, in certain cases, imparts a low water resistance of the cured film. Some systems may still contain small amounts of organic volatils (amine or glycol ethers that help wetting or film formation).

Applications where water based radiation curable systems can be used, or asked are:

- wood coatings
- screen inks / varnishes
- electronics
- flexo plates
- textile printing / coatings
- flexo inks
- general overprint varnishes

It is the purpose of this work to explore approaches for using water as a primary means
of reducing oligomer viscosities for UV-curable coatings systems.

**RADIATION CURABLE EMULSIONS**

- Mechanical emulsification of lipophillic resins with external emulsifiers and/or protective colloids in order to manufacture oil in water emulsions is a possibility. This technic allows to use chemical structures which are very similar to those currently used in the radiation curable chemistry.

- Particularly it is possible to use oligomers of low thermoplasticity and thus structures exhibiting low film formation temperature. Oligomers bearing hydroxyl groups (like epoxy acrylates) are the most easable resin to disperse. However with this kind of process the quality of the applied and cured film depends greatly on the manufacturing procedure which influences the mean droplet size and the particle size distribution. These parameters have an impact on film formation behaviour which in turn influences properties such as drying time, water vapour permeability, water resistance, gloss, pigment hiding capacity, etc...

- Emulsion polymerization of acrylates bearing free unsaturated double bounds are also known. These products can be used as a primer, but due to the low unsaturation functionality introduced in the backbone, inherent to the synthesis and the chemical process, the hardness of the cured film is too low for their use as top coat if no multifunctional monomers are used as coalescing aid.

Table 1 gives an overview of the different emulsified acrylated resins with their nature and their basic properties, available by UCB Chemicals.

**WATER SOLUBLE ACRYLATES.**

*Non ionic hydrophilic groups.*

These groups may induce water solubility or dispersibility through hydrogen bounding with water molecules. Such groups are e.g. ether or amide. Ether groups are easily built into the structure through polyethylene glycol or polypropylene glycol which are commercially available in a full range of molecular weights. This building block can be used in the structure of urethanes along with other macromols or reacted with acrylic acid. With this kind of structure, the water sensistivity is built inherently into the cured film and to compensate for this drawback a highly crosslinked network of the cured film has to be obtained.

P.S Beside the non ionic groups, there are the ionic groups using amines as counter
In this paper will only intend to discuss the acrylated water soluble resins containing non-ionic hydrophilic groups.

**ADVANTAGES OF WATER BASED RADIATION CURE TECHNOLOGY:**

Currently, coatings are going through a major evolution. Low solids, solvent containing paints with high VOC are decreasing in importance due to environmental regulations.

When possible water based or solventless systems are used now. The growth of the use of powder coatings, the UV-and EB technology are not only justified for environmental reasons but also because they permit achievements of outstanding performances in such area as metal protection and printing inks.

Taking in account the main advantages of UV-curing systems which contain only reactive oligomers and diluents allowing high speed of transformation and requiring low energy, it may seen contradictory to introduce water in such a composition. Indeed water is a poor solvent having a high internal cohesive energy and a high surface tension. Consequently a lot of energy is required for its evaporation and the wetting of polar materials is also problematic.

**WHY COMBINE WATER WITH RADIATION CURE FORMULATIONS ?**

1. The prepolymeres used in radiation cure formulations are often very viscous. Therefore it is difficult to apply them with the equipment such as curtain coaters, spray guns and roller coaters when thin layers have to be applied as in the case of photodurable flexographic inks. In order to get the appropriate rheological behaviour, oligomers are diluted with low viscosity reactive mono- or multifunctional monomers. Some of these viscosity reducers, although not toxic may cause skin irritation or sensitization. Reactive diluents are also a part of the film structure which in some cases may unfavourably influence the properties. If water could be used as the diluent, these drawbacks would of course be eliminated.

2. High levels of reactive diluents induce shrinking of the cured film which generates internal stress which adversely influence the adhesion. In certain cases the level of crosslinking density which results from the high concentration of unsaturations, induces an undesirable rigidity of the film.

3. With water as a diluent it is possible to adjust the thickness of a film by varying the solid contents of the formulation.

4. Water soluble radiation curable products can also be used in special applications such as photoimagable solder resists for the electronic industry.
After UV-exposure through a mask, the unexposed resin is washed away with water or an alkaline solution.

**PREPARATION METHODS FOR RADIATION CURE WATER THINNABLE RESINS.**

Different methods have been described to prepare a water-compatible photocurable material:

1. Mechanical dispersion under heavy shear conditions of any conventional epoxy-urethane- or polyester acrylate with the help of external emulsifiers or non-ionic protective colloids such as PVA or PEG-PPG block copolymers. In order to get a stable oil in water system and good film forming characteristics, the particle size distribution has to be carefully controlled. Epoxy acrylates bearing secondary hydroxyl groups are the most easily dispersable oligomers. Like conventional emulsions the Tg of the oligomer influences its TMF, and consequently the conditions of the predrying step play an important role for the cured film properties.

   The main drawback of such a method is the permanent water sensitivity induced by the non reactive hydrophilic emulsifying compounds.

2. Conventional vinyllic and acrylic structures in which free double bounds are left unreacted. This technic offers a broad latitude in the design of the chemical structures. However due to the fact that only a limited amount of unsaturated functionality can be introduced in the backbone to avoid intramicellar crosslinking such system exhibit low reactivity and are mainly used as a primer for wood coatings.

3. Modification of structures by introducing polyoxyalkylene glycol portions of various molecular weights and molar ratios in order to increase the hydophilic nature of the resin is used to make a water compatibility through hydrogen bonding with water molecules. To obtain a stable emulsion or a solution, the level of oxygen atoms in the backbone has to be relatively high. This means the cured film remains inherently water sensitive and a high level of unsaturations has to be introduced in the oligomer to counteract this drawback. The mechanical properties of the cured film depend on the length of the polyoxyethylene moiety and on the degree of branching. In order to improve the water solubility or dispersibility, low molecular weight polyethylene glycol diacrylates (e.g. Ebecryl 11) may be added to the oligomer. Such compounds significantly reduce the viscosity of the diluted solution without significantly affecting the reactivity.

4. Another way to solubilize organic polymers into water is to introduce hydrophilic ionic groups which can undergo neutralization.
EXAMPLES OF WATER THINNABLE RADIATION CURE RESINS.

A. POLYESTER ACRYLATE BASE
Based on the methods described in the previous section, various structures and formulations were prepared. In many cases there is a need for a good water solubility before cure and good water resistance after the curing step. Apart from the type and the amount of water soluble groups used in the product, the overall structure also plays an important role as is shown in table 2 for water soluble polyester acrylates.
The formulations were cured by adding 5 % Irgacure 500 (CIBA) and 3 % of Ebecryl P115 (UCB). The coating thickness was 10g/m2 and cured under a medium pressure mercury lamp of 80W/cm.

B. URETHANE ACRYLATE BASE
Table 3 gives an overview of different water dilutable urethane acrylates, while Fig 1 shows the dilution characteristics of the different oligomers.
Table 4 shows the cure performance of the formulations.

WATER THINNABLE RADIATION CURABLE PRODUCTS USED IN SCREEN PRINTING.
The water present in the formulation permits the right viscosity and rheology to control the dry coating weight applied. In order to reach the right "touch" a coating weight of 15 g/m2 is needed (for textile printing). The best results for the screen printing process are obtained with a formulation containing 20 % of binder in combination with a water-thickener solution. The thickener solution is needed to get the appropriate rheology for the screen printing. Lower binder concentrations are not suitable because of too low coverage of the substrate. The pigment concentration is also very important. High pigment concentrations (> 10 %) lead to decreased cure and rub fastness. By combining printing parameters such as the type of screen, squeegee pressure and angle, it is easy possible to reach a coating weight of 20 g/m2.
A typical formulation and its performance is shown in table 5.

CONCLUSIONS / CONSIDERATIONS.
Water dilutable radiation curable formulations offer new possibilities for the printing industry as they allow reduction of coating weight without using solvents. The results indicate that overall properties can be obtained with high productivity and low energy requirements.
An important consideration we all (printers included) have to make is the fact that these water soluble resins and inks will provoke ecological considerations. Being water soluble, man should avoid cleaning the equipment with water and drain the with resins polluted water into the sewage. Collect and incenerate the remainings as they do with solvent based resins is the best solution.
Unlegal disposals will create an negative image of a such evolved new technology.
References.

1. Radiation Curable Water soluble Polyester Acrylates
by: Dr. R. Destexhe, Dr. JM Loutz, Dr. S. Peeters, Dr. M. Philips, Mr. L. Lindekens.
UCB Chemicals, Business Unit Radcure
1620 Drogenbos Belgium

2. Waterborne UV-Curable materials for textile printing.
by: Dr. S. Peeters, Dr. JM. Loutz, Mr. L. Lindekens
UCB Chemicals Business Unit Radcure
1620 Drogenbos Belgium
### Emulsions - Monomer Free

<table>
<thead>
<tr>
<th>Viscosity mPa.s @ 22°C</th>
<th>Wood Applications</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>RR 192 fast cure, rigid UA</td>
<td>hard, brittle coatings</td>
<td>4.6</td>
</tr>
<tr>
<td>RR 193 flexible UA</td>
<td>soft, non sandable base coat</td>
<td>5.4</td>
</tr>
<tr>
<td>RR 194 epoxy acrylate</td>
<td>typical properties is an EA-coating</td>
<td>5.5</td>
</tr>
<tr>
<td>RR 195 polyester acrylate</td>
<td>typical properties is an PEA-coating</td>
<td>2.2</td>
</tr>
<tr>
<td>RR 196 flexible UA</td>
<td>soft and flexible coating</td>
<td>7.4</td>
</tr>
<tr>
<td>RR 197 flexible EA</td>
<td>very hard, chemical resistant coating</td>
<td>6.4</td>
</tr>
<tr>
<td>RR 198 flexible PEA</td>
<td>overall best compromise</td>
<td>5.8</td>
</tr>
</tbody>
</table>

### Water Thinnable Polyester Acrylates

<table>
<thead>
<tr>
<th>Viscosity mPa.s (+10% water)</th>
<th>MW</th>
<th>Function.</th>
<th>Reactiv. (m/min)</th>
<th>Acetone rubs</th>
<th>Water resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000</td>
<td>640</td>
<td>2</td>
<td>11</td>
<td>40</td>
<td>-</td>
</tr>
<tr>
<td>2500</td>
<td>670</td>
<td>2.5</td>
<td>11</td>
<td>&gt;100</td>
<td>+</td>
</tr>
<tr>
<td>47500</td>
<td>1600</td>
<td>3</td>
<td>50</td>
<td>&gt;100</td>
<td>+</td>
</tr>
<tr>
<td>1130</td>
<td>2950</td>
<td>2.5</td>
<td>0.5</td>
<td>10</td>
<td>-</td>
</tr>
</tbody>
</table>

| | | | Water resistance |
|------------------------------|--------------|-----------------|
| | | | To h |
| | | | T24h |

- +
## Water dilutable radiation cure resins

<table>
<thead>
<tr>
<th>Prod. name</th>
<th>Prod. family</th>
<th>Function</th>
<th>Water uptake %</th>
<th>Viscosity mPa.s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ebecryl 11</td>
<td>PEG-DA</td>
<td>2</td>
<td>&gt;90</td>
<td>110 @ 25°C</td>
</tr>
<tr>
<td>IRR 143</td>
<td>Aliph. UA</td>
<td>2</td>
<td>15</td>
<td>4000 @ 60°C</td>
</tr>
<tr>
<td>IRR 210</td>
<td>Polyest. Acr.</td>
<td>3</td>
<td>45</td>
<td>150 @ 25°C</td>
</tr>
<tr>
<td>IRR 213</td>
<td>Aliph. UA</td>
<td>2</td>
<td>60</td>
<td>70000 @ 25°C</td>
</tr>
<tr>
<td>IRR 221</td>
<td>Aliph. UA</td>
<td>2.5</td>
<td>&gt;90</td>
<td>7000 @ 60°C</td>
</tr>
<tr>
<td>IRR 222</td>
<td>Aliph. UA</td>
<td>2.5</td>
<td>&gt;90</td>
<td>70000 @ 25°C</td>
</tr>
</tbody>
</table>

Water uptake: maximum quantity of water giving a clear solution and a good stability.

### Viscosity Profile

Viscosity mPa.s (x thousand)

![Viscosity Profile Graph]

- [ ] IRR 213/221
- [ ] IRR 222

% Water

---

67
## Cure performance of water dilutable oligomers

<table>
<thead>
<tr>
<th>Product</th>
<th>Cure speed (m/min)</th>
<th>Water resistance</th>
<th>Acetone double rubs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dry</td>
<td>Talc speed (*)</td>
<td>Water double rubs</td>
</tr>
<tr>
<td>IRR 143</td>
<td>40</td>
<td>20</td>
<td>2</td>
</tr>
<tr>
<td>IRR 213</td>
<td>5</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>IRR 221</td>
<td>45</td>
<td>20</td>
<td>2</td>
</tr>
<tr>
<td>IRR 222</td>
<td>30</td>
<td>30</td>
<td>2</td>
</tr>
</tbody>
</table>

**Formulation:**
- Resin: 90 parts
- Water: 10 parts
- Darocur 1173: 5 parts
- IRR 154 (slip agent): 2 parts

**Cure conditions:** 1 MPM - lamp 80 W/lcm
 thickness: 10g/m2

**Substrate:** paper

(*) Visual observation after contact with water
- 1: very good
- 4: very bad

(table 4)
NOVEL ADDITIVES IN RADIATION POLYMERISATION PROCESSES. SIGNIFICANCE OF MOLECULAR WEIGHT DATA IN THEIR APPLICATION TO GRAFTING, CURING AND COMPOSITE FORMATION

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ABSTRACT

The role of additives in accelerating rates of reaction has been investigated in the following related radiation polymerisation processes, ie simple homopolymerisation, grafting, WPC formation and curing. Additives used include mineral acid, polyfunctional monomers, urea and thermal and photochemical initiators. Molecular weight analysis carried out on the polymers formed in the presence of the additives indicate that both chemical and physical processes are involved in the mechanism of the polymerisation reaction. Chemical processes (free radicals) lead to an enhancement in initial rate of polymerisation whilst the physical parameter involves partitioning of reagents during reaction. Both chemical and physical processes are shown to act in concert to influence both polymer yield and properties.

INTRODUCTION

The role of additives in polymerisation process is important. In radiation induced systems, they can be used to accelerate rates of polymerisation. Certain types of additives can induce novel properties which may be common to particular groups of radiation polymerisation processes. One such group which will be treated in this paper is homogeneous monomer polymerisation, grafting, curing and wood plastic composite (WPC) formation.

In previous polymerisation and grafting studies, additives have been used to increase yield. In curing, additives are essential to achieve fast polymerisation, gloss, slip, adhesion and hardness of film. With WPC, additives can increase both polymer loading (PL) and tensile strength (Tf). In the present paper, additives for accelerating simple radiation polymerisation of monomers like styrene and methyl methacrylate (MMA) will be reported. The application of this concept to related radiation polymerisation systems like grafting, curing and WPC formation will be demonstrated. The mechanistic significance of the effect of additives on molecular weight data in the radiation polymerisation systems will be discussed. A theory to explain the role of these additives in the radiation processes will be proposed.

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EXPERIMENTAL

The polymerisation and grafting procedures were similar to those previously described\(^1\). The techniques used in the WPC experiments were modifications of those already published\(^3,4\) with pinus radiata as the timber substrate. For the molecular weight determinations, polymer samples were analysed in equipment supplied by Polymer Laboratories with accessories from GBC.

RESULTS AND DISCUSSION

1. Additive Effects in Radiation Polymerisation

The data in Table 1 demonstrate that inclusion of mineral acid in dioxan solutions of styrene leads to an enhancement in polystyrene yield at all monomer concentrations studied with a Trommsdorff peak being observed at 40-60\% monomer concentration. Very importantly, addition of mineral acid results in a significant reduction in Mn values at each monomer concentration studied. When MMA replaces styrene, the effect of acid is even more dramatic in enhancing polymer yields and also reducing the Mn value. The solvent chosen for these studies, dioxan is a non-precipitating solvent for the polymer formed, thus avoiding potential problems with phase separation during polymerisation.

Table 1 Polymer Yields and Molecular Weights from Solution Polymerisation of Styrene and MMA in Dioxan in Presence of Acid Additives\(^a\)

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Monomer (%) (v/v)</th>
<th>Polymer Yield (%)</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>N.A. H(^+)</td>
<td></td>
</tr>
<tr>
<td>Styrene</td>
<td>20</td>
<td>10.9 14.9</td>
<td>17,900</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>10.5 14.8</td>
<td>37,400</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>9.7  14.1</td>
<td>58,600</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>8.9  12.3</td>
<td>84,400</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>7.8  11.0</td>
<td>112,600</td>
</tr>
<tr>
<td>MMA</td>
<td>30</td>
<td>0.8  10.5</td>
<td>90,000</td>
</tr>
</tbody>
</table>

\(^a\) Dose rate 3.3 x 10\(^2\) Gy/hr; N.A. = no additives; T = 25\(^\circ\)C; Data from Garnett and Jankiewiez\(^5\)

\(^b\) Dose 1.5 x 10\(^4\) Gy, H\(^+\) = 0.1M

\(^c\) Dose 2.0 x 10\(^3\) Gy, H\(^+\) = 0.2M

2. Additive Effects in Radiation Grafting

(a) Acid - The acid enhancement effect in radiation grafting is applicable to a wide range of monomers and substrates\(^6-11\), the data in Table 2 for the grafting of styrene and MMA in two different solvents to polypropylene confirming typical information which can be obtained. The types of solvents used can be important since in this instance, of the two, methanol is a precipitant of the polymer formed whereas dioxan is not. Other significant features of the
data are that, in the presence of acid, grafting is enhanced at all monomer concentrations studied. With styrene, the percentage increase is highest at the lowest monomer concentration reported. The acid effect is more pronounced with the MMA in methanol system, no grafting being observed at three monomer concentrations unless acid is present, the yield being extremely large at 60% monomer concentration.

**Table 2** Grafting of Styrene and MMA in Methanol and 1,4-Dioxan to Polypropylene with Acid Additive

<table>
<thead>
<tr>
<th>Monomer Solvent (%)v/v</th>
<th>MMA in Methanol</th>
<th>Graft (%)</th>
<th>Styrene in Methanol</th>
<th>Graft (%)</th>
<th>Styrene in 1,4-Dioxan</th>
<th>Graft (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N.A.</td>
<td>0.2M H⁺</td>
<td>N.A.</td>
<td>0.2M H⁺</td>
<td>N.A.</td>
<td>0.2M H⁺</td>
</tr>
<tr>
<td>20</td>
<td>6</td>
<td>1</td>
<td>29</td>
<td>214</td>
<td>6</td>
<td>14</td>
</tr>
<tr>
<td>30</td>
<td>-</td>
<td>-</td>
<td>94</td>
<td>151</td>
<td>12</td>
<td>23</td>
</tr>
<tr>
<td>40</td>
<td>0</td>
<td>302</td>
<td>50</td>
<td>86</td>
<td>15</td>
<td>30</td>
</tr>
<tr>
<td>50</td>
<td>0</td>
<td>196</td>
<td>37</td>
<td>56</td>
<td>17</td>
<td>33</td>
</tr>
<tr>
<td>60</td>
<td>0</td>
<td>1010</td>
<td>36</td>
<td>48</td>
<td>19</td>
<td>37</td>
</tr>
<tr>
<td>70</td>
<td>198</td>
<td>278</td>
<td>35</td>
<td>42</td>
<td>21</td>
<td>39</td>
</tr>
</tbody>
</table>

Radiation dose rate 4.0 x 10^2 Gy/hr to 3.0 x 10^3 Gy except for MMA (2.0 x 10^3 Gy); H⁺ = H₂SO₄; N.A. = no additive

(b) **Polyfunctional Monomers** - A second important class of additives of significance in radiation grafting are the polyfunctional monomers, especially the multifunctional acrylates and methacrylates like trimethylol propane triacrylate (TMPTA). When such monomers are included in a grafting solution like styrene in methanol, an enhancement in copolymerisation yield to a substrate such as polyethylene is observed. The used of these multifunctional acrylates for this purpose has previously been reported [1,11], the data in Table 3 indicating the type of reactivity to be expected for such systems. A non-acrylate polyfunctional monomer such as divinyl benzene (DVB) is seen to act in a similar manner to TMPTA. When acid is included with the polyfunctional monomer, a synergistic effect in grafting is observed.

(c) **Thermal and Photoinitiators** - A final group of additives which are useful for accelerating these radiation grafting processes is reported for the first time in Table 4 where MMA in methanol is grafted to cellulose using the styrene comonomer technique to overcome homopolymerisation [1,11]. In practice, it is difficult to use radiation doses above 2.0 kGy with MMA alone because of severe homopolymer formation, however with the styrene comonomer technique, high doses of radiation can be utilised with low homopolymer formation thus permitting high grafting yield (Table 4). Although there is a percentage of styrene in the monomer feed in the comonomer solution, the resulting grafting is not only high in MMA at most monomer concentrations, it also possesses the properties essentially of polymethyl methacrylate.

Of the additives used in Table 4, the photoinitiator, BEE, has previously been reported to accelerate styrene grafting [12] but this is the first report of its use with the radiation grafting of MMA. Analogous studies with the thermal and photoinitiator, AIBN, have also been published, again only with styrene [13]. However the new Ciba Geigy initiator C-1700 and
AMBN have not previously been used in this work. The data show that all four initiators are very active in accelerating the grafting of MMA in methanol to cellulose.

Table 3 Grafting of Styrene in Methanol to Polyethylene Using Acid, DVB and TMPTA as Additives

<table>
<thead>
<tr>
<th>Solvent + Additive</th>
<th>Graft (%)</th>
<th>Styrene (% v/v)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>N.A.</td>
<td>14</td>
<td>37</td>
</tr>
<tr>
<td>H⁺ (0.2M)</td>
<td>19</td>
<td>51</td>
</tr>
<tr>
<td>DVB</td>
<td>15</td>
<td>41</td>
</tr>
<tr>
<td>DVB + H⁺</td>
<td>27</td>
<td>58</td>
</tr>
<tr>
<td>TMPTA</td>
<td>-</td>
<td>39</td>
</tr>
<tr>
<td>TMPTA + H⁺</td>
<td>-</td>
<td>54</td>
</tr>
</tbody>
</table>

* DVB = divinyl benzene; TMPTA = trimethylol propane triacrylate; Dose = 2.4 x 10³ Gy; dose rate 4.1 x 10² Gy/hr; DVB, TMPTA at 1% v/v with polypropylene film (0.12 mm)

Table 4 Effect of Thermal and Photoinitiators as Additives in Radiation Grafting MMA to Cellulose using Styrene Comonomer Technique

<table>
<thead>
<tr>
<th>MMA ALONE*</th>
<th>MMA COMONOMER TECHNIQUE^</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMA in MeOH (% v/v)</td>
<td>Graft (%)</td>
</tr>
<tr>
<td>N.A.</td>
<td>BEE</td>
</tr>
<tr>
<td>100</td>
<td>3.1</td>
</tr>
<tr>
<td>80</td>
<td>6.3</td>
</tr>
<tr>
<td>60</td>
<td>21</td>
</tr>
<tr>
<td>50</td>
<td>21</td>
</tr>
<tr>
<td>40</td>
<td>16</td>
</tr>
<tr>
<td>20</td>
<td>2.1</td>
</tr>
</tbody>
</table>

* Dose 2.0 x 10³ Gy at 5.0 x 10² Gy/hr
^ Dose 8.0 x 10³ Gy at 5.0 x 10³ Gy/hr
£ N.A. = No additive; BEE = benzoin ethyl ether; TFI = C-1700 (25% bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphineoxide and 75% 2-hydroxy-2-methylphenyl-propan-1-one) (Ciba); AIBN = azoisobisbutyronitrile; AMBN = methyl analogue of AIBN (all additives 1% w/v monomer)


WPC formation is effectively an extension of radiation polymerisation, since wood is impregnated with monomers such as MMA which is then subsequently polymerised in situ. The data in Table 5 list a range of additives which accelerate the polymerisation process and
yield significant increases in polymer loading (PL). Of these additives, DVB (Table 3), also AIBN and AMBN (Table 4) have been shown to accelerate analogous radiation grafting processes as has urea\textsuperscript{14} and DEGDMA which is representative of many of the multifunctional acrylates and methacrylates previously used in the grafting studies. Urea has also been utilised in preliminary early studies to enhance PL values in WPC\textsuperscript{15}, however this additive has never previously been combined with the other additives reported in Table 5. When the most effective of the additives in System I, Table 5 are combined, synergistic effects in PL are observed, the combination of urea with AIBN and AMBN being particularly effective.

Table 5 Effect of Additives on Polymer Loading (PL) in Wood Plastic Formation

<table>
<thead>
<tr>
<th>SYSTEM I</th>
<th>ONE ADDITIVE</th>
<th>PL (%)</th>
<th>SYSTEM II</th>
<th>TWO ADDITIVES</th>
<th>PL (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N.M</td>
<td>0.4</td>
<td></td>
<td>N.M.</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>N.A.</td>
<td>90</td>
<td></td>
<td>N.A.</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>U</td>
<td>94</td>
<td></td>
<td>U + AIBN</td>
<td>194</td>
</tr>
<tr>
<td></td>
<td>DEGDMA</td>
<td>97</td>
<td></td>
<td>DEGDMA + AIBN</td>
<td>124</td>
</tr>
<tr>
<td></td>
<td>DVB</td>
<td>115</td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>AIBN</td>
<td>116</td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>AMBN</td>
<td>144</td>
<td></td>
<td>U + AMBN</td>
<td>171</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Dose 2.0 \times 10^4 \text{ Gy at 4.0 \times 10^3 Gy/hr}; N.M. = no monomer; N.A. = no additive; U = urea; DEGDMA = diethylene glycol dimethacrylate; DVB = divinyl benzene; AIBN = azoisobutyronitrile; AMBN = methyl analogue of AIBN (all additives 1\%w/v monomer); timber used was pinus radiata.


\(\bar{M}_n\) values for MMA polymerised under various experimental conditions in the presence of a number of additives are shown in Table 6. These results complement the acid data in Table 1 for both MMA and styrene. Previous preliminary work with acid was reported only with styrene in dioxan at 30\% monomer concentration and at different acidities\textsuperscript{16}. The present more comprehensive information covers a range of styrene concentrations and also MMA. As mentioned in Section 1, acid increases polymer yields and leads to a reduction in \(\bar{M}_n\) under the experimental conditions used. In a similar manner, when AIBN is used as additive in the polymerisation of neat MMA, there is a large reduction in \(\bar{M}_n\) in the polymethyl methacrylate obtained. Analogous data are also obtained with AMBN however the magnitude of the reduction is lower (Runs 1-3). When the homopolymer from the grafting of styrene (60\%) in methanol to cellulose reported in Table 4 is analysed (Table 6, Runs 4 & 5), inclusion of AIBN in the monomer solution again leads to a lowering of \(\bar{M}_n\) of the polymethyl methacrylate homopolymer. When the homopolymer samples from the AMBN and BEE additive experiments reported in Table 4 are analysed (Table 6, Runs 6 & 7), the \(\bar{M}_n\) value for the polymer with BEE is lower than from AMBN. It is significant that all of the additives reported in Table 6 form free radicals in the presence of ionising radiation.
Table 6 Molecular Weight (Mn) Data for Radiation Polymerisation of MMA in Presence of Additives

<table>
<thead>
<tr>
<th>Run No</th>
<th>Monomer</th>
<th>Solvent</th>
<th>Additive (1%)</th>
<th>Dose (Gy)</th>
<th>Dose Rate (Gy/hr)</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MMA</td>
<td>Nil</td>
<td>Nil</td>
<td>3.0 x 10^4</td>
<td>4.0 x 10^3</td>
<td>1.35 x 10^5</td>
</tr>
<tr>
<td>2</td>
<td>MMA</td>
<td>Nil</td>
<td>AIBN</td>
<td>3.0 x 10^4</td>
<td>4.0 x 10^3</td>
<td>2.30 x 10^4</td>
</tr>
<tr>
<td>3</td>
<td>MMA</td>
<td>Nil</td>
<td>AMBN</td>
<td>3.0 x 10^4</td>
<td>4.0 x 10^3</td>
<td>1.17 x 10^5</td>
</tr>
<tr>
<td>4</td>
<td>MMA</td>
<td>MeOH (40%)</td>
<td>Nil</td>
<td>2.0 x 10^3</td>
<td>5.0 x 10^2</td>
<td>1.63 x 10^5</td>
</tr>
<tr>
<td>5</td>
<td>MMA</td>
<td>MeOH (40%)</td>
<td>AIBN</td>
<td>2.0 x 10^3</td>
<td>5.0 x 10^2</td>
<td>1.47 x 10^5</td>
</tr>
<tr>
<td>6</td>
<td>ST/MMA (1/3)</td>
<td>MeOH (40%)</td>
<td>BEE</td>
<td>8.0 x 10^2</td>
<td>3.0 x 10^3</td>
<td>2.60 x 10^4</td>
</tr>
<tr>
<td>7</td>
<td>ST/MMA (1/3)</td>
<td>MeOH (40%)</td>
<td>AMBN</td>
<td>8.0 x 10^2</td>
<td>3.0 x 10^3</td>
<td>1.35 x 10^5</td>
</tr>
</tbody>
</table>

^ Terminology as in footnote to Table 5; BEE = benzoic ethyl ether

5. Mechanism of the Additive Effect in Grafting - Chemical and Physical Parameters.

The simple radiation polymerisation of monomers and the process of grafting are mechanistically related. Because most of the basic work with the current additives has been performed with grafting, this system will be treated first then the concept applied to monomer polymerisation, using initially, acid as the representative additive followed by the others reported in this paper. Originally when the acid effect was first observed, a chemical process involving hydrogen atoms was proposed to account for the observed reactivity. However, with further work, the situation became more complicated, especially when acid enhancement effects were observed in non ionising radiation grafting systems such as UV work. At that time data available indicate that a physical phenomenon involving partitioning of reagents was responsible for the effect. With the present results, especially the Mn information, it is now proposed that both chemical and physical parameters act in concert to influence the grafting enhancement in different ways.

a) Chemical Process - The acid enhancement was originally attributed to a radiation chemistry phenomenon involving increased G(H) yields and thermalised electrons. The processes can lead to increased numbers of grafting sites by abstraction reactions with the backbone polymer. Three aspects of the present data enable the hydrogen atom proposal to be pursued further. Thus acid (i) enhances simple radiation polymerisation (ii) increases both grafting and homopolymer yields in a grafting system and (iii) leads to lower Mn values which are independent of the presence or polar nature of the grafting substrate. These results suggest that the trend in Mn values for the grafted copolymers should be similar to those found in analogous homopolymers and also in the simple radiation polymerisation of monomer. Thus, although the oligomer chains are shorter in acid grafting solutions, the number of these chains are higher and because of the smaller size, they can more readily diffuse into the trunk polymer. With respect to the other additives reported in the current work, a similar explanation for reactivity can be proposed for those which form free radicals in the presence of radiation (BEE, AIBN, AMBN, C-1700).

b) Physical Process - The explanation of the acid enhancement effect in terms of physical phenomenon relate to the concept of partitioning. Thus it has been shown that increased partitioning of monomer occurs in the graft region when ionic solutes are dissolved in the bulk...
grafting solution. Thus higher concentrations of monomer are available for grafting at a particular backbone polymer site in the presence of the acid additive.

Overall it appears that both chemical and physical processes influence the overall grafting pattern when the additives are included. The chemical process leads to high yields with change in $\bar{M}_n$ due to free radical reactions whilst the physical process leads to the supply of high monomer concentrations at a grafting site via a partitioning phenomenon and thus enhanced reactivity at that site. Of the remaining additives used in the current grafting work, data discussed elsewhere indicate that the multifunctional acrylates and methacrylates act via chain branching mechanism whilst urea is an inclusion compound, a property which should enhance the partitioning process.


Again using acid as the representative additive, the data from the simple polymerisation systems such as monomers in solvents can be interpreted in a similar manner to that of the grafting work, i.e., chemical and physical processes are involved. Thus, via the former mechanism, in the presence of acid, the polymer yield is increased and $\bar{M}_n$ is decreased, i.e., the polymer contains shorter chains but in greater numbers, a situation expected if the number of radicals in the system were increased presumably via enhanced $G(H)$ yields. High concentrations of H atoms would then lead to an increase in rate of chain initiation resulting in higher polymer yields with lower $\bar{M}_n$ values. In addition to the enhancement occurring via a chemical process involving free radicals, the physical concept of partitioning, similar to the grafting work, is also relevant. Recently Harwood proposed that partitioning could occur in solution polymerisation of monomers under homogeneous conditions. In a study of solvent effects in copolymerisation he proposed that monomers are distributed between free solvent and the domains of growing polymer radicals. As polymerisation increases the magnitude of the effect increases because of the size of the polymer radicals. Harwood referred to this concept as the boot strap effect which is analogous to the type of partitioning already established for grafting systems.

This discussion on additive effects in homogeneous monomer polymerisation is also relevant to WPC formation where the predominant reaction occurring is the homopolymerisation of monomer which fills the voids in the timber. Acid has previously been used as an additive in WPC formation where it was shown to increase PL but lowers the tensile strength, properties expected from data already presented where acid increases yields but lowers $\bar{M}_n$ in simple polymerisation process. The effect of other additives (AIBN, AMBN, U and DEGDMA) on the properties of WPC reported in Table 5 can also be expected via the mechanisms already proposed for these additives in the grafting section.

7. Extrapolation of Simple Polymerisation and Grafting Concepts to Curing.

Data obtained from simple radiation polymerisation and grafting is also relevant to radiation curing systems. The fact that multifunctional acrylates and methacrylates accelerate both of the processes is important in curing since these polyfunctional monomers are one of the major components in curing formulations. The data in this paper show that polyfunctional monomers not only speed up polymerisation (cure) and cross-linking, they can also markedly affect the occurrence of concurrent grafting with cure and thus improve adhesion. The current results also suggest that some of the current additives used (e.g. Table 4) may be beneficial in EB curing systems since they may not only speed up rates of
polymerisation, they may also alter the properties of the final film via changes in molecular weight.

CONCLUSION

A range of additives has been shown to accelerate rates of reaction in a group of radiation polymerisation processes including simple homopolymerisation, grafting, WPC formation and curing. Detailed studies of the molecular weights of the polymers formed in the presence of the additives indicate that both chemical and physical processes contribute to the mechanism of the reaction. The chemical process involves an enhancement in the rate of initiation of polymerisation due to an increase in free radical concentration whilst the physical parameter relates to a partitioning phenomenon involving reagents during reaction. The two processes are shown to act in concert to explain both yields and properties of the polymers obtained from the additive process.

Acknowledgements. The authors thank AINSE for the irradiations and Mike Zammit for assistance with the GPC determinations.

REFERENCES

ABSTRACT.

Acrylic acid (AA) was grafted to Polypropylene (PP) films and Polyethylene (PE) films by preirradiation grafting method using low energy electron beam (LEEB) and compared with the grafting using ^6^Co γ-ray. In the case of PP, the rate of grafting was higher by LEEB than by γ-ray and higher in OPP (oriented PP) than in CPP (casted PP). In the case of PE, the rate of grafting was higher by γ-ray than by LEEB and the rate was in the order of LLDPE (linear low density PE), LDPE (low density PE), HDPE (high density PE). The differences of grafting reactions among these films were discussed from the view points of crystallinity and dose rate. The degree of swelling in water of the modified PE films were measured. The modified films were treated with sodium hydroxide aqueous solution. The degree of swelling of the treated films varied with temperature.

INTRODUCTION

Polyethylene (PE) and Polypropylene (PP) have been widely used for many kinds of products as polymer materials. But, they have a weak point, that it is difficult to bond them with other materials or to print on them. This weak point is somewhat improved by corona discharge treatment, but it is not sufficient enough. The modification of PE and PP films by radiation-induced grafting method using γ-ray or high or middle range energy electron beam has been reported by many researchers. Low energy electron beam (LEEB) is usually used for radiation curing, but it is also useful as a small radiation source for material modification. K. Mori et al. reported on radiation-induced grafting using LEEB by simultaneous irradiation method. In this study, it has tried to improve surface properties of PE and PP films by radiation induced grafting of acrylic acid (AA) with LEEB and the grafting reaction has been compared with the case of γ-ray. Then the adhesive strength of the grafted films were measured. The degree of swelling in water of the AA grafted PE was measured by L. Ishigaki et al. F. Wen et al. treated AA grafted PE film with
NaOH aqueous solution and improved water absorbency. In this study, to improve water absorbencies of the modified PE films, bifunctional monomer was added into the monomer solution of grafting to make crosslinked structure and the degree of swelling was measured.

EXPERIMENTAL

Oriented polypropylene film (OPP), cast film of polypropylene (CPP) including 0.1% butyl hydroxy toluene (BHT) and those films treated with corona discharge were used as PP films. CPP includes 0.3% ethylene component. The thickness of the films was 25 μm. All of these films were supplied from TOKUYAMA Corporation.

As PE films, 30 μm-thick high density film (HDPE), low density film (LDPE) and Linear low density film (LLDPE) made by AICELO Chemistry Co Ltd. were used. These films were washed with benzene in the beaker equipped with magnetic stirrer for 48 hours and dried under reduced pressure to remove additives before the experiment.

Table 1. Molecular Weight and Crystallinity of Raw Materials

<table>
<thead>
<tr>
<th>Raw Materials</th>
<th>Weight Averaged Molecular Weight (x10^4)</th>
<th>Number Averaged Molecular Weight (x10^4)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPP</td>
<td>26.0</td>
<td>4.41</td>
<td>61</td>
</tr>
<tr>
<td>CPP</td>
<td>24.8</td>
<td>2.89</td>
<td>28</td>
</tr>
<tr>
<td>LLDPE</td>
<td>9.59</td>
<td>0.93</td>
<td>45.2</td>
</tr>
<tr>
<td>LDPE</td>
<td>8.24</td>
<td>2.74</td>
<td>50.1</td>
</tr>
<tr>
<td>HDPE</td>
<td>14.5</td>
<td>0.94</td>
<td>65.7</td>
</tr>
</tbody>
</table>

Table 1 shows molecular weights and crystallinities of PP and PE films. The molecular weight were measured by gel permeation chromatography (GPC) (Waters 150C was used) at 135 °C. The flow rate of solvent ODCB was 1.0 ml/min, the amount of injected sample was 400 μl, two of ultrastyragel linear columns (7.8 mm in diameter, 300 mm in length) connected in series were used. The molecular weights were calculated by universal method. The crystallinities of PP were measured by X-ray diffraction method. The crystallinities of PE were derived from the densities measured by areometer in water and isopropyl alcohol mixture. These samples were modified by the following 4 methods.

1. Thick paper was set on the tray for LEEB and the samples with the size of 10 cm x 10 cm were fixed on it and the tray was conveyed through the self-shield LEEB irradiation apparatus in nitrogen gas flow. The irradiation equipment was NHV Areabeam-type Curetron. The acceleration voltage was 200 kV, electron beam current was 6.4 mA and conveying speed was 35 m/min. The total dose was 10 or 20 kGy. Some samples were irradiated in the polyethylene bag filled with oxygen gas. 1 hour after irradiation, the samples were immersed in the monomer solution in nitrogen gas flow (200 ml/min) at 30 °C for a settled reaction time. The monomer solution was...
composed of distilled water and AA with a ratio of 1:1, including 7x10^-4 mol/l of Mohr's salt. The samples were extracted with distilled water by Soxhlet extractor for 24 hours after reaction, dried under reduced pressure and weighed. The degree of grafting was the percent of weight increase by grafting. The diagram of reaction apparatus is shown in Figure 1.

![Diagram of Reaction Apparatus for Grafting](image)

**Fig. 1. Diagram of Reaction Apparatus for Grafting**

(2) The samples with the size of about 5 cm x 10 cm were irradiated with $^{60}$Co $\gamma$-ray in air to a total dose of 10 kGy. The dose rate was 0.59 kGy/h. After irradiation, the sample was grafted by the same method as (1).

The adhesive tape (Scotch mending tape with the width of 15 mm was used) was pasted on the modified sample and peeling strength was measured with peeling angle of 180 degree and peeling speed of 20 mm/min. The tensile strength of the modified samples were also measured with an elongation speed of 100 mm/min using Shimadzu Autograph AG-100. The size of the measured part of sample was 5 mm (width) x 40 mm (elongation direction).

(3) The PE samples were irradiated with LEEB to a dose of 20 kGy and immersed in the monomer solution for grafting as (1). The monomer solution was composed of distilled water, AA and polyethylene-glycol-di-acrylate (PEGDA). The ratio of AA, PEGDA and water was varied from 1:0:1 to 9:1:10. The procedure after grafting was the same as (1). The modified samples were immersed in distilled water for 24 hours at 25 °C or 10 °C, then the surfaces of the samples were wiped with gauze and weighed. The swelling was expressed as the percent of weight increase in water. The samples were immersed in 1N NaOH aqueous solution for 24 hour, then washed with distilled water and dried. The swelling of the samples treated with NaOH was measured at 10, 20, 30, 40 and 50 °C.

**RESULTS**

The relation of the degree of grafting to the reaction time by LEEB preirradiation method of OPP and CPP films is shown in Figure 2. The same relation by $\gamma$-ray preirradiation method of OPP and CPP films is shown in Figure 3. When irradiated with LEEB in oxygen gas, the rate of grafting was higher compared with that irradiated in nitrogen gas flow, especially in...
The rate of grafting is higher in OPP than in CPP and by LEEB method than by γ-ray method.

The relation of the degree of grafting to the reaction time by LEEB preirradiation method in the case of PE films is shown in Figure 4. The same relation by γ-ray preirradiation method is shown in Figure 5. In Figures 4 and 5, LLDPEC means LLDPE treated with corona discharge. Contrary to PP, in the case of PE, the rate was higher by γ-ray method than by LEEB method. The difference of the degree of grafting among three films is larger by LEEB preirradiation method than by γ-ray. The rate of grafting is in the order of LLDPE, LDPE, HDPE.

Table 2 shows tensile strength and peeling strength of OPP films modified by the 2 methods.
Table 2. Change of properties by modifications (OPP)

<table>
<thead>
<tr>
<th>Method</th>
<th>Tensile Strength (kg/mm²)</th>
<th>Peeling Strength (kg/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>raw material</td>
<td>13.68</td>
<td>0.06</td>
</tr>
<tr>
<td>γ-ray preirrad. graft.</td>
<td>2.0 - 2.65</td>
<td>0.2 - 0.31</td>
</tr>
<tr>
<td>EB preirrad. graft.</td>
<td>1.23 - 1.68</td>
<td>0.19 - 0.55</td>
</tr>
</tbody>
</table>

Table 3. Peeling Strength of Modified PP Films (kg/cm)

<table>
<thead>
<tr>
<th>Method</th>
<th>OPP</th>
<th>OPPC</th>
<th>CPP</th>
<th>CPPC</th>
</tr>
</thead>
<tbody>
<tr>
<td>raw material</td>
<td>0.06</td>
<td>0.12</td>
<td>0.18</td>
<td>0.30</td>
</tr>
<tr>
<td>γ-ray grafting</td>
<td>0.24-0.31</td>
<td>0.24-0.41</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LEEB grafting</td>
<td>0.19-0.55</td>
<td>0.32</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3 shows the peeling strength of OPP and CPP films. In Table 3, OPPC and CPPC mean OPP and CPP treated with corona discharge. By these modifications, the peeling strength has increased to 2 ~ 9 times of those of raw materials. The tensile strength has decreased by the methods (1) and (2). There are no remarkable differences between OPP and CPP by grafting methods (1) and (2).

Table 4. Change of properties by modification (LLDPE)

<table>
<thead>
<tr>
<th>Method</th>
<th>Tensile Strength (kg/mm²)</th>
<th>Peeling Strength (kg/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>raw material</td>
<td>3.21</td>
<td>0.07</td>
</tr>
<tr>
<td>γ-ray irradiation</td>
<td>3.77</td>
<td>0.07</td>
</tr>
<tr>
<td>EB irradiation</td>
<td>3.76</td>
<td>0.07</td>
</tr>
<tr>
<td>γ-ray preirrad. graft.</td>
<td>3.01 - 3.95</td>
<td>0.09 - 0.28</td>
</tr>
<tr>
<td>EB preirrad. graft.</td>
<td>3.20 - 3.95</td>
<td>0.17 - 0.19</td>
</tr>
</tbody>
</table>

Table 4 shows the tensile strength and the peeling strength of modified LLDPE films. The peeling strength has increased 2 ~ 3 times. The tensile strength has not decreased by two methods.

Table 5. Peeling Strength of Modified PE Films (kg/cm)

<table>
<thead>
<tr>
<th>Method</th>
<th>LLDPE</th>
<th>LLDPEC</th>
<th>LDPE</th>
<th>HDPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>raw material</td>
<td>0.07</td>
<td>0.10</td>
<td>0.13</td>
<td>0.17</td>
</tr>
<tr>
<td>γ-ray irradiation</td>
<td>0.07</td>
<td>0.11</td>
<td>0.15</td>
<td>0.18</td>
</tr>
<tr>
<td>EB irradiation</td>
<td>0.07</td>
<td>0.10</td>
<td>0.12</td>
<td>0.18</td>
</tr>
<tr>
<td>γ-ray grafting</td>
<td>0.15</td>
<td>0.15</td>
<td>0.17</td>
<td>0.32</td>
</tr>
<tr>
<td>LEEB grafting</td>
<td>0.19</td>
<td>0.17</td>
<td>0.28</td>
<td>0.36</td>
</tr>
</tbody>
</table>

Table 5 shows the peeling strengths of 4 kinds of modified PE films. In Table 5, LLDPEC means LLDPE treated with corona discharge. There is no remarkable differences among various kind of PE.

The relation of the degree of grafting to the concentration of PEGDA in the monomer solution is shown in Figure 6. The degree of grafting decreases with the concentration of PEGDA. The relation of the degree of swelling at 30 °C to the degree of grafting is shown in Figure 7. The degree of...
swelling increases with the degree of grafting and the values of the samples treated with NaOH aqueous solution are higher than those not treated with NaOH. The effect of PEGDA on the degree of swelling was not detected. The variations of the degree of swelling with temperature are shown in Figure 8 (24 h immersing) and Figure 9 (1 h immersing). The degree of swelling is best at 30 °C in the case that immersing time is 24 hours, but it becomes best at 50 °C in the case that immersing time is 1 hour.

DISCUSSION

1. Grafting Reaction

The reactions induced by irradiation are thought to be expressed by the following equations.

In these equations, RH means PE or PP.

When samples are immersed in the monomer aqueous solution after irradiation, the following reactions are thought to proceed.
\[
\begin{align*}
\text{RH} & \quad \rightarrow \quad \text{R}^+ + \text{H}^- \\
\text{H}^- + \text{RH} & \quad \rightarrow \quad \text{R}^+ + \text{H}_2 \\
\text{R}^+ + \text{O}_2 & \quad \rightarrow \quad \text{ROO}^- \\
\text{ROO}^- + \text{RH} & \quad \rightarrow \quad \text{ROOH} + \text{R}^+ \\
\text{ROOH} & \quad \rightarrow \quad \text{R}_1\text{CHO} + \text{R}_2^+ + \cdot \text{OH} \\
\text{ROOH} & \quad \rightarrow \quad \text{R}_1(\text{C}=\text{O})\text{R}_2 + \cdot \text{OH} + \cdot \text{H} \\
\text{ROOH} + \text{Fe}^{3+} & \quad \rightarrow \quad \text{RO}^- + \cdot \text{OH}^- + \text{Fe}^{2+} \\
\text{RO}^- (\text{or R}^-) + \text{M} & \quad \rightarrow \quad \text{ROM}^- (\text{or RM}^-) \\
\text{ROM}^- (\text{or RM}^-) + \text{M} & \quad \rightarrow \quad \text{ROM}_2^- (\text{or RM}_2^-) \\
\text{ROM}_n^- (\text{or RM}_n^-) + \text{M} & \quad \rightarrow \quad \text{ROM}_{n-1}^- (\text{or RM}_{n-1}^-) \\
\text{ROM}_n^- (\text{or RM}_n^-) + \text{ROM}_m^- (\text{or RM}_m^-) & \quad \rightarrow \quad \text{ROM}_{n+m}^- \text{OR} (\text{or RM}_{n+m}^- \text{R})
\end{align*}
\]

In these equations, M means monomer. By equation (7), peroxide \(\text{ROOH}\) changes to radical \(\text{RO}^-\) and by equations (8) - (10), grafting reaction proceeds. Equation (11) expresses termination reaction of grafting chains.

The rate of grafting is thought to depend on the concentration of \(\text{ROOH}\), because \(\text{ROOH}\) produces \(\text{RO}^-\) radical, which initiates grafting as expressed by equation (8). When irradiated in \(\text{O}_2\) gas, \(\text{ROOH}\) is expected to be produced more and grafting rate be high. The crystallinity of CPP is low as shown in Table 1, the amorphous region is large and movement of polymer chain is thought to be frequent. Then reaction proceeds farther to equations (5) and (6) and the concentration of \(\text{ROOH}\) is thought to become lower than that of OPP. The authors did not measure the concentration of \(\text{ROOH}\), but observed \(\text{ROO}^-\) radical by ESR and measured the half lives in OPP and CPP to be 3 and 0.8 hour respectively. This indicates that \(\text{ROOH}\) is formed more in OPP than in CPP and the rate of grafting is higher in OPP than in CPP as shown in Figure 2. It is also thought that during long time irradiation with \(\gamma\)-ray, reaction proceeds farther to decompose \(\text{ROOH}\) expressed by equations (5) and (6) and the rate of grafting is higher by the method of LEEB than by \(\gamma\)-ray as shown in Figure 3.

Contrary to PP, \(\text{ROOH}\) is more stable in PE than in PP. \(\text{ROOH}\) is formed more on the condition that the \(\text{O}_2\) is sufficiently supplied. By \(\gamma\)-ray irradiation method, \(\text{O}_2\) is sufficiently supplied than by LEEB during long time irradiation. The supply speed of \(\text{O}_2\) also depends on crystallinity, because \(\text{O}_2\) enters into the amorphous region of PE, but cannot enter into crystalline region. In the case of low crystallinity as LLDPE shown in Table 1, amorphous region is large and \(\text{O}_2\) easily enters to amorphous region and more \(\text{ROOH}\) is formed. Corona treatment is thought to increase the concentration of \(\text{ROOH}\). Therefore, the rate of grafting becomes in the order of LLDPE, LDPE, HDPE, which is in reverse order of crystallinity. These explains the results shown in Figures 4 and 5.

By preirradiation grafting method ( (1) and (2) ), the tensile strength of PP films decreased as shown in Table 2, but those of PE films did not decrease as shown in Table 4. Therefore, PE film is desirable to modify by
preirradiation grafting methods.

2. Swelling

Only when PEGDA is added to the monomer solution without Mohr's salt, PEGDA was detected by ATR method of infrared spectroscopy in the grafted PE films. Therefore, PEGDA is thought to react only near the surface of the film and not to make effect on the grafting inner part of the film. The concentration of PEGDA in monomer solution in Figure 6 seems to mean the decreased concentration of AA. Therefore, the degree of grafting decreases with the concentration of PEGDA. In this case, the grafting reaction is thought to be initiated only from the radical $R^-$ in equation (8). When the grafted PE is treated with NaOH aqueous solution, it was detected by infrared spectroscopy that $-\text{COOH}$ in the grafted chain was converted to $-\text{COONa}$. When the sample was immersed in water, $-\text{COONa}$ or $-\text{COOH}$ dissociate to $-\text{COO}^-$ and $\text{Na}^+$. $-\text{COO}^-$ ions are thought to repulse each other and make the space to accept water molecules. The dissociation constant of $-\text{COONa}$ seems to be higher than that of $-\text{COOH}$ and the degree of swelling of the sample treated with NaOH seems to become higher as shown in Figure 7. The swelling rate is thought to increase with temperature. Therefore, the peak temperature thought to become higher when the immersing time was short as shown in Figure 9. It is not clear why the degree of swelling is best at 30 °C. The temperature dependence of the dissociation constant is thought to be related to this phenomena.

CONCLUSION

1. PP films and PE films can be modified by preirradiation method using LEEB and adhesive strength was improved.
2. The differences of grafting reactions among films and between $\gamma$-ray and LEEB were explained by the combination of crystallinities, dose rate and the diffusion of oxygen molecule.
3. The swelling of AA grafted PE films treated with NaOH aqueous solution exhibited temperature dependence in which the best value was at 30 °C.

REFERENCES

THE APPLICATION OF FIRE RETARDANT IN UV CURING SYSTEM

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ABSTRACT

Certain specialized applications of UV curable coatings require significant levels of fire retardancy. The photoreactive fire retardants are suitable for this purpose. The enhancement effect of the combining used the fire retardants remarkably increase the fire retardancy. The best result would be obtained by using organic halogen contained systems, phosphours contained systems as well as some inorganic compounds. Above mentioned fire retardants suits for UV curable material systems too. In this paper the monoallyl tetrachlorophthalate and the bis(β — hydroxylethyl methacrylate) phosphate and inorganic compound, e. g. Sb$_2$O$_3$ are investigated. The study of the fire retardancy of the UV curable systems was investigated through comparison of single and combined prescription of several fire retardants. The evaluation and discussion are carried out for applied result of photoreactive fire retardants in UV curable material systems, in accordance whith the UL94 burning test method V—0 grade standard.

INTRODUCTION

Recently, the conflagration losses was aroused by the electric cable and the electrical equipments are even more an immeasurable. The photocurable materials are without exception. In most current applications of UV curable materials, fire retardancy is not required. But certain special applications, such as insulating coatings on flexible circuitry and cable coatings require excellent fire retardancy$^{[1]}$. Although the additive fire retardants are more convenient for applications, but it generally would change the characteristic of basic materials, such as colour, strength and electric properties and so on. Specially the high concentration of the additive fire retardants leads to difficult photocuring and severe degradation of photocuring properties. Thus the traditional additive fire retardants are not suited for the photocurable materials. And for the reactive fire retardants, their raw materials contained the fire retardantive elements, which have taken part in the chemical reaction combining the fire retardantive element into the main—chain or side—chain of the photocuring materials at the photochemical reaction. The characteristic of the reactive fire retardants is quite stable and not easy to be disappeared$^{[2]}$. Specially, the influence of them on the
curing speed and the characteristic of basic materials is smaller. Therefore, the photoreactive fire retardants are much suitable for the photocurable materi.

In this paper the photoreactive fire retardants are monoallyl tetrachlorophthalate (MATCP) and bis(β-hydroxyethyl methacrylate) phosphate (DHEMAP). The used photocurable coating systems consist of the prepolymer, the photoactivemonomers, the photoinitiators, other additives and the photoreactive fire retardants. Because of (MATCP) and (DHEMAP) contain respectively the photoactive groups, e.g. allyl and acrylic groups. For the photocurable coating systems, they are both a fire retardant and a photoactivemonomer. They could take part in the photochemical reaction during UV-light irradiation, thus to combine the fire retardative elements into the UV photocurable material systems and to play a fire retardantive role. As a composition of UV photocurable material systems, they have not got any harmful effect to the properties of the basic materials and the curing speed. The fire retardantive function of the photoreactive fire retardants have been examined and discussed in accordance with the UL94 the burning test methods V-0 grade standard.

EXPERIMENT

Materials; terachlorophthalic anhydride (TCPA) and propylene alcohol (PPA) were purchased from Shanghai chemical reagent Procurement station. β-hydroxyethyl methacrylate (HEMA) were supplied by Beijing medical Co. Beijing Dong Fang Chemical plant. KAYAMER PM-2 from Nippon Kayaku Co., Ltd. of Japan.

Instruments: infrared spectrometer (IR-420) made in Japan. NMR (EM-3601) spectrometer from U.S.A. High pressure mercury lamp 1000W (> 80W/cm) home-made.

Preparation of MATCP (1): the four mouth flask is equipped with stirrer, reflux condensor thermometer and dropping funnel. The TCPA, CTC, TEA and propylene alcohol are put into the flask. The flask was heated to raise the temperature till reflux, the reaction was stopped after 3~4 hours then the rude product was separated from the reactant solution, it was washed and treated with CaCl2 and active carbon. The crystal masses was obtained, and was recrystalized with petroleum ether.

Preparation of DHEMAP (1); the (1) were synthesized by the known method. The raw material are phosphoric anhydride and HEMA.

Fire retardantive experiments: to prepare the standard samples, the samples were prepared and pretreated in accordance with UL94 V-0 standard (Size: Length 127mm, width 12.7mm, thickness 2.3mm, PVC plate), to apply a standard Bunson burner, gas source is butane gas. The experiment should be carried out in the ventilating cabinet without ventilation. The testing samples were coated by UV curable coating, which should be irradiated 10 seconds under the high pressure mercury lamp. Each group
have five samples, the data is repeated over three times.

RESULT AND DISCUSSION

1. Analysis and identification
MATCP (1)
IR spectra: Fig. 1 is IR spectra of the synthesized compound (1). The stretching modes of C=O of the Aryl ester carbonyl is observed at the 1740 cm\(^{-1}\) and the stretching modes of C—O—C is observed at 1262 cm\(^{-1}\), there is the stretching mode of C=O of the carboxylic acid at 1710 cm\(^{-1}\); the stretching mode of —CH=CH\(_2\) is observed at 1641 cm\(^{-1}\), the out plane of bending of —CH=CH\(_2\) is observed at 1118 cm\(^{-1}\) and 928 cm\(^{-1}\), the stretching mode of OH in the COOH group is observed at 3280 cm\(^{-1}\). So that the analysis results above mentioned indicate that Ar—C—O—, —CH=CH\(_2\) and —COOH exist in the synthesized compounds (1).

\[\text{Fig. 1: IR spectra of MATCP}\]

\(^1\)H—NMR spectra: Fig. 2 is \(^1\)H—NMR spectra of the synthesized compounds (1). Three set of absorption peaks corresponded to three kinds of hydrogen (a, b and c) in the molecule (1). The ratio of these peak area is 1:3:2, which in accordance with number of the hydrogen proton in the molecule (1). It was shown that the chemical sheft of hydrogen proton in Ar—COOH were considered \(\delta_a\) at 11.4, and the chemical sheft of the hydrogen proton of —CH =CH\(_2\) is \(\delta_b\) at 5.2—5.7, which is very complicated due to three hydrogen constituted a ABC systems and to be cracked by adjacent a hydrogen proton. There is \(\delta_c\) that is the chemical sheft of the hydrogen in —CH\(_2\)— of esteric carbonyl group at 4.8—4.9, which are splitted up double peak. Above mentioned analysis of \(^1\)H—NMR spectra further appraise the molecule structure of (1).

Element analysis: The data of element analysis of the (1) is as follows; the measuring value is C = 38.51%, H = 1.7 3%, C/H = 22.26 and theoretical value is C = 38.37% H = 1.74% C/H = 22.05.
DHEMAPC (1)
IR spectra: Fig. 3 is IR spectra of synthesized (I). Fig. 4 is IR spectra of KAYAMER PM-2. The IR spectra of synthesized (I) is equal to that of KAYAMER PM-2 by comparison with the peak position, peak shape and strength of characteristic absorption of IR spectra. (Fig. 3 and Fig. 4 were be omitted)

2. Fire retardative experiments

The experiments were completed in accordance with the UL94 V-0 grade plastic burning test method, the measuring items are given in Table 1.

Table 1 UL94 V-0 grade measuring items

<table>
<thead>
<tr>
<th>UL94 Vertical burning</th>
<th>A burning length with flame after to provide fire</th>
<th>A burning time with flame of the 10 times of five samples</th>
<th>A burning length with flame (test sample)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UL94 V-0</td>
<td>&gt;10 Sec</td>
<td>&gt;50 Sec</td>
<td>not burn to the fixture</td>
</tr>
</tbody>
</table>

(1) The chloro and phosphorus series photoreactive fire retardant (I) and (II):

Table 2 Test results of the fire retardants (I) and (II)

<table>
<thead>
<tr>
<th>Testing group</th>
<th>Number of sample</th>
<th>First burning time with flame (sec)</th>
<th>Second burning time with flame (sec)</th>
<th>Total Burning time with flame of five samples (sec)</th>
<th>Burning length with flame of sample (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1* blank</td>
<td>1</td>
<td>1.7</td>
<td>8.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2.8</td>
<td>10.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.6</td>
<td>9.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>2.6</td>
<td>10.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1.8</td>
<td>8.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2*</td>
<td>1</td>
<td>1.2</td>
<td>4.5</td>
<td>55.5</td>
<td>Not to burn to the fixture</td>
</tr>
<tr>
<td>(1)</td>
<td>2</td>
<td>2.5</td>
<td>5.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(10%)</td>
<td>3</td>
<td>1.5</td>
<td>4.0</td>
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<td></td>
<td>4</td>
<td>1.5</td>
<td>3.5</td>
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</tr>
<tr>
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<td>5</td>
<td>2.3</td>
<td>3.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3*</td>
<td>1</td>
<td>1.5</td>
<td>5.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1)</td>
<td>2</td>
<td>2.5</td>
<td>6.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(10%)</td>
<td>3</td>
<td>1.6</td>
<td>4.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>2.0</td>
<td>4.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1.6</td>
<td>5.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The results of fire retardantive test of (I) and (II) are provided in the table 2. 1* is
the blank samples, 2* is samples contained ( I ) and 3* is samples contained ( II ). It is shown that second burning time with flame of the each sample of 1* is all over or near 10 Sec.. Total burning time with flame of five samples is over 50 Sec.. 1* can not met with the UL94 V—0 grade standand, while other samples e. g. 2* and 3* all reached. It indicated that the reactive fire retardantants MATCP and DHEMAP have good fire retardative effect. The fire retardacy of the 2* and the 3* is different, while the content of the fire retardants 2* and 3* both is 10% Wt.. Because the contents of fire retardative elements in the 3* and 2* are different. The choro—element content in MATCP is 41.3% weight and the phosphorus element content in DHEMAP is 9.6% weight total molecule. Therefor total burning time with flame of five samples is all shorter (29.5 Sec.) for 2* and first or second burning time with flame are all less than 7that of 3*.

It is well know that the fire resistantive mechanism of them are difference. When the polymer is burned, the fire retardants contained choro elements could be decomposed into large non—combustible gases, e.g. HCl gas, which play a fire retardative role by the dilution effect, the cover effect and the inhibiting action of the elimination of free radical. So that the fire retardantive efficacy are remarkable. The fire retardants contained phosphorus elements could be decomposed into non—combustible liquid phosphoric acid and the polymetaphosphoric acid, that can cut off from air and heat by the cover effect of liquid membranes and the protecting carbon membranes[2].

(2) The combined fire retardants MATCP( I ), DHEMAP( I ) and Sb2O3( II )

<table>
<thead>
<tr>
<th>Testing groups</th>
<th>Number of samples</th>
<th>First burning time with flame( sec )</th>
<th>Second burning time with flame( sec )</th>
<th>Total burning time with flame of five samples( sec )</th>
<th>Burning length with flame of sample( sec )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4*</td>
<td>1</td>
<td>1.0</td>
<td>2.0</td>
<td>Not to burn to</td>
<td>13.5</td>
</tr>
<tr>
<td>( 1 )+( I )</td>
<td>2</td>
<td>1.0</td>
<td>4.0</td>
<td>21.0</td>
<td></td>
</tr>
<tr>
<td>6% 4%</td>
<td>3</td>
<td>0.5</td>
<td>4.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4% 4%</td>
<td>4</td>
<td>1.0</td>
<td>2.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5%</td>
<td>5</td>
<td>1.0</td>
<td>4.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5*</td>
<td>1</td>
<td>0.5</td>
<td>1.5</td>
<td>Not to burn to</td>
<td>13.5</td>
</tr>
<tr>
<td>( 1 )+( II )</td>
<td>2</td>
<td>1.0</td>
<td>2.0</td>
<td>13.5</td>
<td></td>
</tr>
<tr>
<td>6% 3%</td>
<td>3</td>
<td>0.5</td>
<td>2.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3%</td>
<td>5</td>
<td>0.5</td>
<td>2.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The 4* samples are consist of ( I )+ ( I ), 5* samples are consist of ( I )+( II ) in table 3. It can show clearly that the first and second burning time with flame of every sample of the 4* is below 10 Sec. in table 3. Total burning time with flame of five samples of 4* could be reduced to 21 Sec.. It is because DHEMAP containing phosphorus element can play a fire retardative role on the surface of the burning object by liquid and solid phase, and MATCP containing choro elements, that can play a fire retarda-
tive role by gas phase. Obviously, the enhancement effect of combining (I) and (II) lead to the strengthener fire retardancy of 4° samples. Also it is observed that the burning time with flame of every sample of 5° is shorter than that of 4°. Total burning time with flame of five samples was only 13. 5 Sec., because the specific density of the produced SbCl₃ gas on surface of the burning object is much bigger than that of HCl. The stable cover layer, which can not be disappeared and volatilized during the burning and play to cut off from air and heat a role. And the gas state SbCl₃ is able to catch the free radical during the burning, which inhibit the chain reaction and cause the burning speed to reduce. Therefore, the 5° samples combined (I) and (II) demonstrated excellent function in this test. Also it is shown that above mentioned the photoreactive fire retardants on the UV curing speed and the property of UV curable materials fire retardantive have not got any harmful effect. This is exactly the advantage of the photoreactive fire retardants or so called the photoreactive fire retardative monomer.

CONCLUSIONS

2° and 3° testing samples reached all UL94 V-0 garde test standard in this test. It is indicated that the fire retardancy of the photoreactive fire retardants (I) and (II) are very nice and quite satisfied with this photocurable material systems. And the 4° and 5° testing samples express a remarkable combination action of the fire retardants. Specifically, the 5° testing samples combined (I) and (II) manifest excellent fire retardancy.

It is shown that, the photoreactive fire retardants are the best selection to enhance the fire retardancy of UV photocurable materials, and obviously the photoreactive fire retardants are one of best product which has a bright future of development.

REFERENCES

FURANYLSILICONE:
NEW PREPOLYMERS IN CATIONIC CHEMISTRY

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ABSTRACT

Furfuryl alcohol and its ethoxylated analogs are reacted into their allyl ethers in high yield. Hydrosilylation of the allyloxy double bond with various hydrosiloxanes generates novel silicocene compounds with the furan ring attached to the silicone backbone by ether spacers.

The furan ring provides the reactive site for the oligomeric siloxanes by which they can be crosslinked by cationic mechanisms. In combination with iodonium salts furanylsiloxanes can be cured within seconds to tack-free coatings after irradiation with short-wave UV-light.

INTRODUCTION

Cationic chemistry designed for UV-curing is very much dominated by epoxy compounds. This is also true for prepolymer with siloxane backbones. Silicone epoxies are well established by now [1, 2, 3] and new and effective combinations of materials are presented every year [4].

Alternatives to epoxies in UV-curing cationic silicone chemistry have rarely been seen [5]. In the early 1990's novel propenyloxy functionalized siloxanes were published in the patent literature [6, 7]. Silicone oxetane monomers showed up about the same time [8]. Just recently we introduced a new class of very reactive UV-curing materials: Vinyl ether silicone copolymers in combination with onium salts were shown to cure at much faster speed than other known cationic curing silicones [9]. Despite the fact that enoxy groups provide very high cure speed they also have a serious drawback. The enoxy group itself is subject to hydrolyzation under certain conditions. To rule out this problem we looked into the furan chemistry to utilize the furan ring as kind of vinyl ether with a very low tendency to hydrolyze. This paper is focused on approaches towards the synthesis of furanylsiloxanes as well as on their analytical evaluation.

EXPERIMENTS AND DISCUSSION

1. Background

Furans are well known to yield polymeric resins upon treatment with strong acid. An old fashioned analytical method is based on this reaction: A piece of pinewood treated with a drop of hydrochloric acid turns dark green after exposure to fumes of furan. The furan ring is basically of heteroaromatic nature with a resonance energy of 96 kJ/mole. So far it is certainly not
the best candidate for being polymerized. On the other hand the furan ring exhibits aliphatic features like reactions typical for a diene or a vinyl ether. Furanylsiloxanes were not supposed to set records in cure speed, but the question was: Will they, as another class of chemical compounds, join the very limited selection of cationic UV-curing siloxanes?

Only few publications about furanylsiloxanes exist. In the mid 1960's Hammann [10] and coworkers synthesized cyclic siloxanes with the furan ring in 2-position directly bonded to the silicon atom. Expensive lithium techniques were involved and it turned out that the furanyl-silicon-bond is easily cleaved by acids. Ten years earlier two Japanese patents appeared covering syntheses of furfuryloxysilanes [11] and their application for making coatings by thermal treatment [12]. Recently a method for making siloxane-urethane oligomers was published with furfuryl alcohol providing the terminal groups of a linear siloxane chain [13].

2. Syntheses of Materials

Based on several drawbacks involved with the published techniques the strategy to synthesize furanylsiloxanes became quite obvious: An attractive path should utilize a cheap furanyl compound which can be converted into a derivative with an additional terminal C=C-double bond in a simple process. The final reaction step should be the hydrosilylation of such a derivative at this terminal unsaturation with an oligomeric hydrosiloxane under usual conditions. Furfuryl alcohol therefore was the starting material of choice to screen methods for the synthesis of furanylsiloxanes. The origin of this compound are renewable agricultural resources such as fibrous residues of food crops. From pentosan polysaccharids furfuryl aldehyde is produced in large scale. More than 100,000 tons/year are converted to furfuryl alcohol. It can be reacted with allyl chloride to the corresponding ether (I) in high yield without attacking the furan ring.

In a glass vessel 10 moles of aqueous sodium hydroxyde (50% w/w) is mixed with 14 g of trimethylbenzylammonium chloride and 5 moles of furfuryl alcohol at 45°C. A ten percent excess of allyl chloride is added dropwise over a period of about one hour. The reaction mixture is heating up slowly, later boiling under reflux. 100 ml of cyclohexane and 700 ml of water are added. After phase separation and washing with water the crude allyl furfuryl ether is fractionated over a short column which yields 548 g of the 96% pure product (I) (69-70°C/13 hPa).

It is well known from literature that allyl ethers add SiH-compounds across the C=C-double bond. To fix allyl furfuryl ether onto a siloxane backbone a simple linear α,ω-dihydopolydimethylsiloxane was chosen: HMe₂SiO(Me₂SiO)ₙMe₂SiH (II). The chain ends are far enough apart from each other to study the functional groups of the resulting oligomer independently.

Figure 1: Synthesis of 3-furfuryloxypropylsiloxanes

![Synthesis of 3-furfuryloxypropylsiloxanes](image_url)
237 g of this siloxane oligomer (II) is homogeneously mixed with a 20% molar excess of allyl furfuryl ether (I) made by the procedure described above. 4 mg of platinum as a divinyl tetramethyl disiloxane complex is added and the batch is heated up slowly. At about 60°C an exothermic reaction heats up the mixture to about 135°C within a few minutes. After gradually cooling down to about 90°C within one hour volatiles are distilled off at 3 hPa. The resulting yellowish polymer (III) has a viscosity of 36 mm²/s. Further details will be published [14].

3. Analysis of Products

¹H-NMR analysis of the above linear furfurylsiloxane revealed that SiH-groups are no more present, but there was also evidence for side-reactions. The main product by far, however, is the expected α,ω- bis (3-furfuryloxypropyl) polydimethylsiloxane (III).

Figure 2: Linear α,ω- bis (3-furfuryloxypropyl)siloxane, 400 MHz ¹H-NMR

Signal pattern and chemical shift of minor peaks support the presence of dioxatricyclo-decyl-Si endgroups, as well as a trace of the β-adduct isomer of the main product:

<table>
<thead>
<tr>
<th>Normal Addition Product</th>
<th>Isomeric Addition Product</th>
<th>Unexpected Addition Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>-OMe₂Si</td>
<td>-OMe₂Si</td>
<td>-OMe₂Si</td>
</tr>
</tbody>
</table>
| 88                      | 1                         | 11                          | mole-%
Reason for the unexpected side-reaction is the instability of allyl furfuryl ether: An internal cycloaddition reaction slowly produces an unsaturated tricyclic diether compound (IV). The rate of formation in bulk is about 2% (rel.) per month at 25°C and increases at elevated temperatures. Similar results were found by a group in the former USSR [15].

Under reaction conditions for preparing furanylsiloxanes the dioxatricyclodecene (IV) is active enough to add SiH-groups across its double bond as part of the strained tricyclus to yield the silylated derivative. The same conditions (100-135°C) must also be responsible for creating more of this tricyclic ene than present at the beginning of the hydrosilylation reaction (4-6% in fresh allyl furfuryl ether), which results in a higher proportion of the silylated species according to the mix found in the final product.

The cyclization of allyl furfuryl ether does not represent a very typical situation for Diels-Alder reactions, and may be driven mainly by a very favourable stereochemistry. To check this statement the reactive groups were separated by ethylene oxide spacers. Such a precursor is readily available by PTC-allylation of ethoxylated furfuryl alcohol (about 3 EO per OH) with allyl chloride [14]. It does not show the proton NMR signals otherwise typical for the tricyclus (6.41 ppm and 6.37 ppm for the unsaturated protons, 5.08 ppm for the bridge-head proton). These peaks do not appear either in the spectrum after heat treatment of the ether. Therefore the allyl ether of ethoxylated furfuryl alcohol should yield close to quantitative endcapping of the siloxane with furan groups. The overall reaction scheme of a synthesis run with a 30% excess of allylic double bond over SiH from the polymer precursor is given below in figure 3:

**Figure 3: Synthesis of ethoxylated 3-furfuryloxypropylysiloxanes**
The 'H-NMR spectrum of the ethoxylated version (VII) of linear furanylsiloxane (III) does not even show a trace of a potential hydrosilylated ethoxylated tricyclus (VI). Endcapping of the siloxane with furane groups is better than 97%. However, the final polymer does contain small amounts of isomerized starting material which cannot be evaporated for boiling point reasons.

4. UV Cure Experiments

Before starting UV-studies we wanted to make sure that the furan ring in furfurylether compounds actually reacts under strong acidic conditions. To keep the furfuryl material from gelling the monomer V was chosen to be treated with a trace of aqueous HSbF6. Strong increase in viscosity indicates the onset of a polymerisation reaction. The 'H-NMR spectrum shows a decrease of the furane protons. The IR absorptions at 1503 cm\(^{-1}\) and 885 cm\(^{-1}\) typical for 2-substituted furans also decrease with resinification of V.

The furanylsiloxanes used for cure tests were prepared from different siloxane backbones by the method described above. Structural parameters are given in table 1. The experiments were run with 1% of bis (dodecylphenyl) iodoniumhexafluoroantimonate as cationic UV-active catalyst added to the prepolymer. The clear mixtures were applied on paper substrate in about 5 μm thickness. A medium pressure mercury lamp served as light source. The minimum dose to get tack-free coatings in air is given below.

<table>
<thead>
<tr>
<th>Prepolymer</th>
<th>Reactive Group</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>mequ./g</th>
<th>Tack-free Dose</th>
</tr>
</thead>
<tbody>
<tr>
<td>III</td>
<td>F</td>
<td>1</td>
<td>11</td>
<td>0</td>
<td>1.6</td>
<td>2000 mJ/cm(^2)</td>
</tr>
<tr>
<td>VII</td>
<td>F'</td>
<td>1</td>
<td>11</td>
<td>0</td>
<td>1.4</td>
<td>2000 mJ/cm(^2)</td>
</tr>
<tr>
<td>VIII</td>
<td>F</td>
<td>0</td>
<td>48</td>
<td>12</td>
<td>1.8</td>
<td>800 mJ/cm(^2)</td>
</tr>
<tr>
<td>IX</td>
<td>F</td>
<td>1</td>
<td>80</td>
<td>6</td>
<td>1.0</td>
<td>300 mJ/cm(^2)</td>
</tr>
</tbody>
</table>

\(F = -\text{C}_3\text{H}_6\text{OCH}_2 - \text{C}_4\text{H}_8\text{O}\) \(F' = -\text{C}_3\text{H}_6\text{O(C}_2\text{H}_4\text{O})_2\text{CH}_2 - \text{C}_4\text{H}_8\text{O}\)

Special feature of all tested furanylsiloxanes is a discolourization of the coating layer during irradiation, which renders these prepolymers not suitable for thick coatings. UV/VIS spectra of fresh versus acid-treated ethoxylated allyl furfuryl ether (V) clearly show a considerable bathochromic shift of the absorption bands. The untreated ether (V) with its maximum at 216 nm and almost no absorption above 250 nm turns into products with quite high absorption between 240 and 350 nm and on into the visible region. These structural elements therefore are in competition for sharing UV light from the mercury lamp with the iodonium catalyst. The consequences on acid production after decay of the irradiated iodonium salt in the formulation and furthermore on UV-cure are presently investigated.
CONCLUSIONS

It could be demonstrated that furanyl rings bonded to siloxane backbones by Si-C linkages can serve as reactive groups to cure silicone prepolymer in a cationic reaction triggered by UV light. Compared to vinyl ether silicone chemistry it is necessary to get a tack-free coating. On the other hand furanylsiloxanes get their reactive groups from a cheap and almost unlimited supply of agricultural residues. The prepolymer mixtures with onium initiators exhibit good stability for several months. UV curing can be achieved without inertisation in ambient atmosphere. Furanylsiloxanes may be an option for formulating thin-film coatings.

ACKNOWLEDGEMENTS

The authors would like to express their thanks to Wacker-Chemie GmbH for permission to present these findings. We also thank Dr. Jochen Dauth and Dr. Bernward Deubzer for numerous contributions as well as Martina Blöchl, Elfriede Rieger and Inge Seeger-Feichtinger for synthetic expertise in the preparation of the prepolymer.

REFERENCES

THE SENSITIZATION ON PHOTOPOLYMERIZATION OF SOME THIOPHENOL COMPOUNDS
XiaoXiu Ren, Wei Wang, Lei Shao, HuaBin Yin
(Beijing University of Chemical Technology, China)

ABSTRACT
The influence of thiophenol compounds on the rate of photopolymerization (Rp) was studied in the MMA/BIP system (BIP = benzoin isopropyl ether) by using an automatic recording dilatometer. Comparison of Rp indicated that thiophenol compounds could improve the photoinitiation activity and anti-oxygen power of the benzoin alkyl ether initiator, also thiophenol compounds containing donor group (Hammett's constant < 0) raise Rp more than those containing acceptor group (Hammett's constant > 0).

INTRODUCTION
Sulfur-containing compounds were investigated actively recently for its excellent antioxidability. Although there were many reports on photoinitiator system containing those compounds, photoinitiator system containing benzoin alkyl ether/thiophenols has not been known so far.

For this reason, we selected five thiophenols whose Hammett's constant are between -0.27 to +0.23 to constitute the photoinitiator systems in which benzoin alkyl ether acts as photoinitiator; studied the kinetic behavior of these systems and UV absorption spectrum in an attempt to seek ways to improve the initiation and antioxidation ability of the benzoin alkyl ether.

EXPERIMENT

A. Synthesis, Purification and Characterization of Thiophenols

Thiophenol was commercially available. The other substituted thiophenol compounds were prepared by the following method. First the corresponding aromatic hydrocarbon compounds were chlorosulfonlated by chlorosulfonic acid. The products were then reduced to thiophenol compounds by Sn/HCl.

The general formula of the obtained thiophenol compounds is

\[ R\text{-C}=\text{O} \rightarrow \text{SH} \]

Wherein R represents CH₃, Cl, CH(CH₃)₂, OCH₃.
The crude liquid products obtained were purified by vacuum distillation. The fraction collecting range of the products, such as \((\text{CH}_3)_2\text{CH}\underline{\text{S}}\text{H}\) and \(\text{CH}_3\underline{\text{O}}\text{S}\text{H}\), were 109-21\text{mmHg} and 108-110 \text{°C}/15\text{mmHg} respectively. The crude solid products obtained were purified three times by recrystallization from anhydrous ethanol.

The synthesized compounds were characterized by IR spectrometry, NMR spectrometry, elementary analysis, melting point test etc. The results showed that products purity met the requirement of kinetic determination.

**B. Kinetic Experiment**

The kinetic experiment was performed using an apparatus as described before\(^5\).

**C. UV absorption spectrum**

The UV absorption spectrum of the sample was metered by Nippon Shimazu Model UV-260 Ultraviolet-visible spectrometer. The sample concentration is \(1 \times 10^{-4}\text{mol/l}\).

**RESULTS AND DISCUSSION**

**1. EFFECT OF THIOPHENOLS CONCENTRATION ON MMA PHOTOPOLYMERIZATION RATE**

A number of criteria of the effect of BIP concentration on MMA Rp have been suggested\(^5\). So by fixing the BIP concentration at 0.01848M, and varying the thiophenols concentration, we studied the photo polymerization kinetics of MMA/BIP/thiophenols system. The similar results were obtained (shown in Fig. 1).

As will be seen from Fig. 1, photopolymerization rate is influenced without exception by thiophenols concentration. The variation tendency with different thiophenols is similar. When thiophenols concentration is in a certain range, the Rp of MMA/BIP/thiophenols is higher than those of MMA/BIP in same conditions. The results indicate an important role of thiophenols on photopolymerization, whose effect may exist as following:
(i) Reaction of thiophenols with O₂

In the presence of O₂, thiophenol compounds are easily photooxidized into disulfide which may further photodecompose into radicals. The general mechanism is shown as follows.\(^\text{[6]}\)

\[
hv \quad hv
\]

\[
\text{RSH} \xrightarrow{hv} \text{RSSR} \xrightarrow{hv} 2\text{RS}^\cdot \quad \text{O}_2 \quad \text{(A)}
\]

(A) is an active free radical which can initiate MMA photopolymerization. In addition, thiophenols itself can also photodecompose into free radicals—RS' and H'—for decreasing of the bond energy of S-H from the conjugated system formed by S and benzene ring.

(ii) Reaction of thiophenols with BIP

Because the α-hydrogen of BIP's ether group is very active, radical RS' can easily abstract α-hydrogen from BIP, therefore another radical is produced which can form hydroperoxide in the presence of O₂ and then decomposed to active free radicals. This process is shown as follows:

\[
\begin{align*}
\text{C=O} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
\text{H} & \quad \text{Pr} \\
\end{align*}
\]

\[
\xrightarrow{\text{SAR}} \quad \begin{align*}
\text{O} & \quad \text{O} \\
\text{Pr} & \quad \text{Pr} \\
\end{align*}
\]

\[
\text{(1)}
\]

\[
\begin{align*}
\text{C} & \quad \text{C} \\
\text{O} & \quad \text{O} \\
\text{H} & \quad \text{Pr} \\
\end{align*}
\]

\[
\xrightarrow{\text{SA}+\text{R}} \quad \begin{align*}
\text{O} & \quad \text{O} \\
\text{Pr} & \quad \text{Pr} \\
\end{align*}
\]

\[
\text{(2)}
\]

Fig 1 Rp at different thiophenols concentration

BIP's concentration: 0.01848M
As seen from (i) and (ii), with the range of said thiophenol compounds concentration, the reaction of thiophenols with BIP and O₂ may multiply the primary free radicals in the system. Furthermore, the polymerization inhibition of O₂ is also restrained. The overall result lead Rp to increase and induced period (tᵢ) to decrease.

When the thiophenol compounds concentration exceeds certain critical value, the decrease tendency of Rp occurs. This will probably be the results of recombination among active radicals.

2. EFFECT OF DIFFERENT THIOPHENOLS ON MMA PHOTOPOLYMERIZATION RATE

The effect of different thiophenols on MMA photopolymerization rate under the same condition is variant. The substituent effect has been assessed using Hammett's constant as shown in Tab. 1.

<table>
<thead>
<tr>
<th>R</th>
<th>-OCH₃</th>
<th>-CH(CH₃)₂</th>
<th>-CH₃</th>
<th>-H</th>
<th>-Cl</th>
<th>control</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hammett's constant</td>
<td>-0.268</td>
<td>-0.2</td>
<td>-0.17</td>
<td>0</td>
<td>0.227</td>
<td>/</td>
</tr>
<tr>
<td>Rp \text{*10}^{4} mol/l \cdot s</td>
<td>5.504</td>
<td>5.307</td>
<td>5.406</td>
<td>5.137</td>
<td>5.182</td>
<td>4.757</td>
</tr>
</tbody>
</table>
* control: BIP/MMA

It can be seen from Tab. 1, thiophenols whose substituent's Hammett's constant is below zero raise Rp more than those whose substituent's Hammett's constant is above zero.

On the point of structure, the substituent scarcely influences the activity of the hydrogen of SH group because of the conjugated system. However, the substituent has an obvious effect on the disulfide as mentioned above. Tab. 2 shows The S-S bond energy of different disulfide[^6]
Tab.2 The S-S Bond Energy Of Different Disulfide

<table>
<thead>
<tr>
<th>disulfide</th>
<th>(P-MeOPhS)$_2$</th>
<th>(P-MePhS)$_2$</th>
<th>(P-PhS)$_2$</th>
<th>(P-NO$_2$PhS)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-S/bond-energy (Kcal/mol)</td>
<td>29- 35</td>
<td>26- 32</td>
<td>20- 26</td>
<td>46- 52</td>
</tr>
</tbody>
</table>

It can be seen from Tab2, the S-S bond energy of the disulfides whose substituent is donor group (Hammett's constant < 0) is lower. In the condition of same lumina, the disulfide containing donor group will decomposed more easily than those containing acceptor group, therefore more free radicals formed lead to higher $R_P$.

As for unsubstituted thiophenol, the least light absorbility (UV absorption spectrum shown in Fig2.) leads to its poor sensitization effect, though the S-S bond energy of its disulfide is the lowest.

3. EFFECT OF O$_2$ ON PHOTOPOLYMERIZATION

Though O$_2$ is as a quencher of active radicals, it exhibits complex effect on $R_P$. Tab.3 shows kinetic results of BIP/MMA system and BIP/MMA/CH$_3$SH system in the presence of O$_2$ and N$_2$ respectively.
It can be seen from Tab.3, the presence of O₂ not only increase $t_i$ of the BIP/MMA system but also decrease $R_p$ of it. As for BIP/MMA/CH₃-SH system, the presence of O₂ don't exhibit obvious effect on $t_i$, however, it increases $R_p$ greatly. The results indicate that the reaction occurring between thiophenols and O₂, just as mentioned above.

CONCLUSION

1. In MMA/BIP photopolymerization system, the addition of the following thiophenol compounds have an obvious sensitization effect.

   \[
   \text{CH}_3\text{SH}, \quad \text{(CH)}_3\text{CH}\text{SH}, \quad \text{CH}_2\text{O}\text{SH}, \quad \text{H}\text{SH}, \quad \text{ClH}
   \]

   Furthermore, thiophenol compounds containing donor substituent (Hammett's constant<0) can raise $R_p$ more than those containing acceptor substituent (Hammett's constant>0).

2. Only within definite concentration range and under appropriate compounding ratio with photoinitiator can the sensitization effect of thiophenols on BIP/MMA system be completely embodied.

3. The presence of O₂ has good effect on the photopolymerization of BIP/MMA/thiophenols system.

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SYNTHESIS AND PROPERTIES OF BENZOINETHERS

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ABSTRACT

Benzoinethers are used widely as photoinitiator of photopolymers. Eight benzoinethers were prepared using benzoin and corresponding alcohols (methyl, ethyl, propyl, isopropyl, butyl, isobutyl, octyl, 2-butoxylethanol). Phase transfer catalysts were used in this synthetic method. The spectral data and physical constants of these compounds were given. Photosensitivities of eight benzoinethers were compared.

INTRODUCTION

Benzoin and benzoinethers are used widely for photoreactions. In general, synthesis of benzoinether is by reaction of benzoin and corresponding alcohol in the presence of dry hydrochloric. Some acid catalysts such as PCl₃, AlCl₃, POCl₃, SOCl₂⁻, are used in this reaction. But none of them is satisfactory in the reaction conditions.

In this reaction the product is benzoinether and water. Aqueous phase and organic phase are formed. In our synthetic method some quaternary ammonium salts are used as phase transfer catalyst. The synthetic reaction is much improved. Eight benzoinethers are prepared.

\[ \text{C}_6\text{H}_5\text{COCH(OH)}\text{C}_6\text{H}_5 + \text{ROH} \rightarrow \text{C}_6\text{H}_5\text{COCH(OR)}\text{C}_6\text{H}_5 + \text{H}_2\text{O} \]

R: CH₃, C₂H₅, C₃H₇, CH(CH₃)₂, C₄H₉, CH₃CH(CH₃)₂, C₆H₁₇, CH₂CH₂OC₄H₉

The spectroscopy data and physical constants of eight compounds are given. The photosensitivities of these benzoinethers have been compared to each other.

EXPERIMENTS
1. Preparation of Benzoinethers

Added 1g of benzoin, 0.01g of UA and 10g of n-butyl alcohol which abstrated 0.5g of dry HCl to a 100ml of reactor. Heated and refluxed for 0.5 hour. Then destilled out alcohol to get crude product. Dissolved the crude product with chloroform and abstracted TEBA from the solution using water for three times. Fine benzoin butylether was obtained after chloroform was destilled out. Other benzoinethers are prepared in similar procedure.

2. Evidence of Chemical Structure

Benzoin methylether (BME): White crystalline powder; M.P. 49-50 °C; IR(cm⁻¹) 1685 (ν c=o), 1213 (ν c-o-c); ¹HNMR(TMS,CDCl₃), δ (ppm) 7.25-8.05(m,10H,C₆H₅), 5.45(s,1H,CH), 3.42(s,3H,OCH₃).

Benzoin ethylether (BEE): White crystalline powder; M.P. 54.5-60.5 °C; IR(cm⁻¹) 1686(ν c=o), 1109 (ν c-o-c); ¹HNMR(TMS,CDCl₃), δ (ppm) 7.20-8.10 (m,10H,C₆H₅), 5.55(s,1H,CH), 3.60(q,2H,OCH₂), 1.25(t,3H,CH₃).

Benzoin n-propylether (BPE): light yellow liquid; B.P. 278-280 °C; n²₁ 1.5610; IR(cm⁻¹) 1678(ν c=o), 1110 (ν c-o-c); ¹HNMR(TMS,CDCl₃), δ (ppm) 7.25-8.10(m,10H,C₆H₅), 5.50(s,1H,CH), 3.55(t,2H,OCH₂), 1.67(m,4H,CH₂CH₂), 0.90(t,3H,CH₃).

Benzoin iso-propylether (BIPE): White crystalline powder; M.P. 76-77 °C; IR(cm⁻¹) 1681(ν c=o), 1096 (ν c-o-c); ¹HNMR(TMS,CDCl₃), δ (ppm) 7.25-8.10 (m,10H,C₆H₅), 5.60(s,1H,CH), 3.75(m,1H,OCH), 1.30(d,3H,CH₃), 1.20(d,3H,CH₃).

Benzoin n-butylether (BBE): yellow liquid; B.P. 284-286 °C; n²₁ 1.5530; IR(cm⁻¹) 1679(ν c=o), 1110 (ν c-o-c); ¹HNMR(TMS,CDCl₃), δ (ppm) 7.30-8.10 (m,10H,C₆H₅), 5.50(s,1H,CH), 3.55(t,2H,OCH₂), 1.50(m,4H,CH₂CH₂), 0.85(t,3H,CH₃).

Benzoin iso-butylether (BIBE): light yellow liquid; B.P. 238-240 °C; n²₁ 1.5538; IR(cm⁻¹) 1680(ν c=o), 1109 (ν c-o-c); ¹HNMR(TMS,CDCl₃), δ (ppm) 7.20-8.10(m,10H,C₆H₅), 5.50(s,1H,CH), 3.35(d,2H,OCH₂), 1.90(m,1H,CH), 0.90(d,6H,CH₃,CH₃).

Benzoin n-octylether (BOE): light yellow liquid; B.P. 256-258 °C; n²₁ 1.6118; IR(cm⁻¹) 1680(ν c=o), 1115 (ν c-o-c); ¹HNMR(TMS,CDCl₃), δ (ppm) 7.20-8.10(m,10H,C₆H₅), 5.55(s,1H,CH), 3.50(t,2H,OCH₂), 1.30-1.60(m,12H, (CH₂)₆), 0.85(t,3H,CH₃).
Benzoin 2-butoxyether (BBXE): light yellow liquid; B.P. 218-220 °C; n\textsubscript{D} 1.6210; IR (cm\textsuperscript{-1}) 1694 (ν C=O), 1116 (ν C–O–C); \textsuperscript{1}H NMR (TMS, CDCl\textsubscript{3}), δ (ppm) 7.25–8.10 (m, 10H, C\textsubscript{6}H\textsubscript{5}), 5.27 (s, 1H, CH), 3.35–3.80 (m, 6H, OCH\textsubscript{2}CH\textsubscript{2}OCH\textsubscript{2}), 1.2–1.5 (m, 4H, (CH\textsubscript{2})\textsubscript{2}), 0.90 (t, 3H, CH\textsubscript{3}).

3. Photosensitivity

Table 1 Photosensitivity *

<table>
<thead>
<tr>
<th>Benzoinether</th>
<th>BME</th>
<th>BEE</th>
<th>BIPE</th>
<th>BIBE</th>
<th>BPE</th>
<th>BBE</th>
<th>BOE</th>
<th>BBXE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (sec.)**</td>
<td>60</td>
<td>66</td>
<td>70</td>
<td>72</td>
<td>75</td>
<td>80</td>
<td>200</td>
<td>310</td>
</tr>
</tbody>
</table>

* Curing system: unsaturated polyester/styrene, 5g of polyester, 5g of styrene, 0.1g of benzoin ethylether; 400W UV light. ** Time required for curing.

RESULTS AND DISCUSSION

1. Alcohol

Table 2 Yield of Benzoinethers

<table>
<thead>
<tr>
<th>Product</th>
<th>BME</th>
<th>BEE</th>
<th>BPE</th>
<th>BIPE</th>
<th>BBE</th>
<th>BIBE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature °C</td>
<td>65</td>
<td>80</td>
<td>95</td>
<td>83</td>
<td>98</td>
<td>105</td>
</tr>
<tr>
<td>Yield %</td>
<td>44.5</td>
<td>90.0</td>
<td>98.5</td>
<td>84.3</td>
<td>95.0</td>
<td>90.4</td>
</tr>
</tbody>
</table>

* Time of reaction: 0.5 h, PTC: 0.1% of TEBA, Benzoin/alcohol=1/10 (wt). The procedure see experiment.

2. Phase Transfer Catalyst

Table 3 Comparison of PTC

<table>
<thead>
<tr>
<th>PTC</th>
<th>TEBA</th>
<th>TPBP</th>
<th>TBAB</th>
<th>PEG-400</th>
<th>no PTC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield %</td>
<td>95.0</td>
<td>93.2</td>
<td>90.3</td>
<td>67.1</td>
<td>34.0</td>
</tr>
</tbody>
</table>
• TEBA: Triethyl benzalammonium chloride;  
TPBP: Triphenyl benzalphosphonium chloride;  
TBAB: Tetrobutylammonium bromide;  
PEG-400: Polyethylene glycol 400;  
Reaction product is BTE; Reaction temperature: 80°C;  
The procedure see experiment.

3. Time of Reaction

<table>
<thead>
<tr>
<th>Time (hour)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>93.0</td>
</tr>
<tr>
<td>0.5</td>
<td>95.0</td>
</tr>
<tr>
<td>1.0</td>
<td>95.3</td>
</tr>
<tr>
<td>5.0**</td>
<td>95.2</td>
</tr>
</tbody>
</table>

* Reaction product is BTE. ** Without phase transfer catalyst. 
The procedure see experiment.

4. Amount of dry HCl in alcohol

<table>
<thead>
<tr>
<th>HCl (g)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>93.0</td>
</tr>
<tr>
<td>0.5</td>
<td>95.0</td>
</tr>
<tr>
<td>1.0</td>
<td>97.0</td>
</tr>
</tbody>
</table>

* Reaction product is BTE. The procedure see experiment.

CONCLUSIONS

It is a useful method for synthesis benzoinethers that in reaction of benzoin and corresponding alcohol using a little of TEBA or other quaternary ammonium salts.

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4. US, 4101584
Study of Oxygen Inhibition Effect on Radiation Curing

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Abstract  Michael addition reaction product was used in the research of oxygen inhibition effect of radiation curing. The experimental results was measured by the content of gel and percentage of double bonds. It was proved that 9% of Michael addition product could speed up 1.2 times of the radiation curing rate at 30 kGy of EB irradiation. This kind of formulation can withstand oxygen inhibition effect obviously, so it was the foundation of application for radiation curing in atmospheric condition.

Keywords  Radiation Curing  Oxygen inhibition  Michael addition reaction

1. Introduction

In radiation curing research, oxygen inhibition effect is an important topic, and its aim is to develop a coating formulation which could be withstood the oxygen inhibition effect and realized in atmospheric condition. If the coating research could be successful, radiation curing might be promoted with improved properties and lower investment.

In this work, we tried to search for the possibility of withstanding oxygen inhibition effect and its corresponding kinetics by using Michael reaction product in radiation curing technology. It is a foundation to develop the formulation of radiation curing under atmospheric condition.

2. Experiment

The product was synthesized by using Michael addition reaction and the urethane acrylates was also synthesized as in reference. The main component of
paint included urethane acrylate, Michael reaction product and some active diluent. Four samples, with number of $A_1, A_2, A_3, A_4$, were prepared. In order to compare with above samples, sample B was prepared without Michael reaction product. The irradiation facility used was a set of 600 Kev Electron Accelerator of China Sichuan University. After irradiation, the gel content was measured, and the double bonds percentage was determined by a set of Nicolet 20 BxS infrared spectrometry (IR). And assuming the double bonds percentage of non-irradiated sample is 100% (standard example).

3. Results and Discussion

The gel content, double bonds percentage and its experimental conditions are listed in Table 1.

Table 1: Gel Content and Double Bonds Percentage of Different Sample*

<table>
<thead>
<tr>
<th>Samples</th>
<th>Content of Michael Reaction Product (%)</th>
<th>Irradiation Dose (kGy)</th>
<th>Gel Content (%)</th>
<th>Double Bonds Percentage (%)</th>
<th>Double Bonds Transfer Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard example</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td>0</td>
<td>30</td>
<td>60.1</td>
<td>87.3</td>
<td>10.7</td>
</tr>
<tr>
<td>$A_1$</td>
<td>9</td>
<td>10</td>
<td>58.7</td>
<td>89.9</td>
<td>10.1</td>
</tr>
<tr>
<td>$A_2$</td>
<td>9</td>
<td>20</td>
<td>70.9</td>
<td>78.7</td>
<td>21.3</td>
</tr>
<tr>
<td>$A_3$</td>
<td>9</td>
<td>30</td>
<td>75.8</td>
<td>67.2</td>
<td>32.8</td>
</tr>
<tr>
<td>$A_4$</td>
<td>9</td>
<td>40</td>
<td>78.5</td>
<td>51.9</td>
<td>48.1</td>
</tr>
</tbody>
</table>

* The irradiation dose rate was $1 \text{kGy} \cdot \text{s}^{-1}$

From Table 1, the irradiation dose of sample B and sample $A_3$ were 30 kGy for both, however the gel content of $A_3$ was 75.8% and double bonds transfer percentage was 32.8% respectively, all of the results were higher than sample B without Michael reaction product. The gel content of sample B was 60.1% and double bonds transfer percentage was 12.7% respectively. It is obvious that the Michael reaction product can withstand oxygen inhibition effect in radiation curing process. To assume curing rate as $R^{(2)}$, then

$$R = \frac{d\gamma}{dt} = kM(1 + \gamma)(1 - \gamma)D$$

(1)

Where $\gamma$ is the gel content, $t$ is the time, $D$ is the irradiation dose, $k$ is the
rate constant and $M$ is regarded as the percentage of double bonds. Then the rate constant of $A$ and $B$ can be expressed as

$$\frac{k_A}{k_B} = \frac{M_B(1+\epsilon_B)(1-\epsilon_B)}{M_A(1+\epsilon_A)(1-\epsilon_A)} \cdot \frac{R_A}{R_B} = 2.2$$  \hspace{1cm} (2)

From (2), we can know that the radiation curing rate of sample $A_3$ is 2.2 times as big as sample $B$. According to Decker et al., the mechanism of oxygen inhibition effect can be expressed as

Chain initiated \[ \begin{array}{c}
\text{R} \\
\text{EB or hv}
\end{array} \rightarrow \begin{array}{c}
\dot{\text{R}} \\
M
\end{array} \rightarrow \begin{array}{c}
\dot{\text{P}} \\
\text{Chain propagated}
\end{array} \rightarrow \begin{array}{c}
\text{O}_2 \\
\text{RO}_2
\end{array}
\]

So that, the radiation curing process can be continued in air, it must obey the following prerequisite conditions that the eliminating rate of resolved oxygen in coating must be as fast as possible than the oxygen diffusing into coating from air, then the chain propagating can be maintained.

4. Conclusion

From this work, it is proved that the Michael addition reaction product can promote the radiation curing reaction under atmospheric condition and its effects are:

- a) to speed up the radiation curing rate.
- b) to play as a scavenger to eliminate oxygen resolved in coating.

Reference

(1) U.S. Patent 3,479,185.
(2) U.S. Patent 4,822,841.
RADIATION CURING OF OLIGOMER-MONOMER SYSTEMS IN THE PRESENCE OF ADDITIVES.

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ABSTRACT

The inhibiting action of oxygen on radiation initiated polymerization of oligomer-monomer mixtures in thin films is one of the important problems for curing technology of coatings via irradiation procedure. To lower the inhibiting effect of oxygen, several options can be suggested, i.e. variation of chemical composition of oligomer-monomer mixture, incorporation of additives affecting the rate and mechanism of polymerization, inert atmosphere in irradiation zone. Radiation-sensitive comonomer of N-vinyl pyrrolidone and ferrocene additives have been investigated to show an efficient lowering option of oxygen inhibition.

INTRODUCTION

Considerable attention is paid to inhibiting effect of oxygen on thin layer polymerization of unsaturated oligomers. Several methods are known to make polyester systems inhibition resistant, e.g. modification of oligomer or monomer, incorporation of additives, film protection, inert atmosphere. The most suitable way is to select a comonomer that makes unsaturated polyester curable in the presence of oxygen.

Earlier (1) the authors investigated vinyl esters as comonomers in radiation-cured compositions. They were shown to decrease a little oxygen inhibition. Further research dealt with possible variation of the oligomer structure via incorpo-
ration of chlorine-containing fragments (2), that enable change a radical route of polymerization for ion type. When used as accelerating additives, the salts of varying valence metals (acetyl acetonates of Co, Mn, Zn) affected insignificantly the rate of polymerization in the air. However, surface hardness increased drastically as a result of post-polymerization.

This paper presents the investigated effect of radiation sensitive monomer of N-vinyl pyrrolidone (N-VP) and dicyclopentadiene of iron (ferrocene) on thin-layer radiation polymerization of unsaturated oligomers in the presence of oxygen.

**EXPERIMENTAL**

The investigated compositions are based on oligoethylene glycol fumarate phthalate modified with diallyl ester of trimethylolpropane (TMP). Lacquer PE-284 is a solution of this composition in triethylene glycol methacrylate (TGM-3) in ratio 50:50 %wt. Lacquer PE-2120 is oligoethylene glycol fumarate phthalate modified with TMP and monomethacrylate of ethylene glycol, solution in TGM-3 and MG-9 (α,ω-methacryl-bis-triethylene glycol fumarate) in ratio 50:40:10%wt.

The oligomer compositions were polymerized under the action of accelerated electrons 300-700 keV at a dose rate 3.0-20.0 kGy/s. Total absorbed dose was determined by a chemical dosemeter with regard to varying optical density of triacetate cellulose film. Comparative assessment of the cured coatings was based on the surface hardness H measured on a pendulum device (time ratio of dying oscillations of pendulum on the film surface and on a glass plate); sticky layer 3% (washing off the noncured polymer with acetone or visual method). The ESR spectra were recorded on PE-1301 radiospectrometer at 77K. To register the ESR spectra, the films were subject to accelerated ageing through UV-light irradiation of PRK-4 mercury-quartz lamp at 77K. The intensity of 365nm mercury line at sample location was 3.13 × 10^12 quanta/cm²·s.
RESULTS AND DISCUSSION

The research focused on interaction of unsaturated oligomers with N-vinylpyrrolidone (N-VP) comonomer in the course of polymerization initiated by accelerated electrons. A double bond N-VP is known as very active. Tertiary amine group N-VP can accelerate degradation of peroxides formed in the process of polyester composition curing in the air.

As follows from investigated effect of N-VP concentration on the curing PE-284 oligomer composition in the air (Fig.1), substitution N-VP for TGM-3 and high concentration of N-VP increases the surface hardness. Comparison of curves 1 and 5 shows that composition curing in the presence of N-VP is less inhibited by oxygen and polymerization completes at 150 kGy.

The data in Fig.2 enables to conclude that curing of PE-284 + N-VP(70:30) composition in the air is independent of the dose rate in the range ~3-10 kGy/s in contrast to

![Graph](image)

Fig.1. The dependence of the surface layer hardness on the amount of N-VP in the composition:
1 -PE-284+TGM-3(50:50), 2 -PE-284+TGM-3+N-VP(60:30:10)
3 -PE-284+TGM-3+N-VP(70:10:20), 4 -PE-284+N-VP(70:30)
Fig. 2. The influence of the dose rate (kGy/s) on the radiation curing of PE-284+N-VP(70:30)/1,2/ and PE-284+TGMI-3(50:50)/3,4/; 1 - O 3kGy/s; 2 - 10kGy/s; 3 - 3kGy/s; 4 - 10kGy/s.

PE-284+TGMI-3(50:50) that shows lower hardness at the same doses with increasing dose rate. Independence of the dose rate proves monomolecular mechanism of chain termination in N-VP containing composition, while TGMI-3 containing composition has a bimolecular mechanism of chain termination at the initial stage of polymerization. The results suggest that a rigid network should be immediately formed in N-VP containing composition even at low radiation doses that is only possible with high radiation-sensitive compositions.

Thus, curing in the air of PE-284+N-VP proves evident efficiency of N-vinylpyrrolidone comonomer as compared with TGMI-3.

Application of dicyclopentadiene of iron (C5H5)2Fe (ferrocene) are extremely wide. To this contribute the advantages of ferrocene to inhibit light ageing of the cured coatings and to protect from radiation(3), to accelerate efficiently curing
process of unsaturated compounds in the presence of peroxides (4). With regard to such a behaviour, it seemed reasonable to incorporate ferrocene into unsaturated oligomer compositions for subsequent radiation curing. Ferrocene was expected a beneficial additive both at the stage of oligomer composition curing and in further practical applications.

When cured in the air with 0.1 - 2.5%wt. ferrocene addition, unsaturated oligomers produce higher surface hardness of as coatings and lower stickiness of the surface layer. Figure 3 shows dose dependence of uncured monomer S for PE-2120 lacquer and PE-2120 + 1%ferrocene. The additive-containing sample is less sticky than without ferrocene.

Curing in the air probably causes an initiating system "organic peroxide - ferrocene" in the surface layer of the coating. This is proved by gradually increasing surface hardness of ferrocene-containing films after irradiation (Fig. 4). Presumably ferrocene can insignificantly affect polymerization initiated by accelerated electrons. Major contribution is made into post-effect when additional curing of the surface layer after irradiation takes place at the expense of initiating system "organic peroxide - ferrocene".

Photooxidation destruction was investigated on the samples of radiation-cured oligomer systems in the presence of ferrocene. Figure 5 presents the accumulation kinetics of free radicals which are formed in PE-284 lacquer film under UV-light accelerated ageing. (Preliminary decay of polymerization radicals was ensured). The concentration of UV-light initiated radicals in ferrocene-containing films is much lower than in the pure lacquer that proves high light stabilizing efficiency of ferrocene due to intensive absorption in 200-500 nm region.

Ferrocene-containing coatings are much more resistant to overirradiation. Besides, the applied concentrations of the additive do not produce any negative effect on physical and mechanical properties of the films.
Fig. 3. The dependence of the amount of uncured part of the polymer (S,%) on the dose for PE-2120/1/ and PE-2120+ +1% ferrocene/2/.

Fig. 4. Postradiation additional curing of PE-2120 films:
1 - without additives, 2 - 0.1% ferrocene, 3 - 1.0% ferrocene, 4 - 1.5% ferrocene
CONCLUSION

As follows from the results, N-vinylpyrrolidone used as a comonomer in radiation cured compositions enables to produce hard non-sticky coating in the air at relatively low radiation doses. Low concentration of ferrocene can be surely added to radiation cured oligomer systems as antioxidant and efficient stabilizer of light ageing with no influence on the cross-linked polymer formation. The additives of ferrocene decrease the dose of sticky surface hardening and ensure reliable performance characteristics of the cured coatings in various practical applications.

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PHOTOINDUCED COPOLYMERIZATION CONSISTING OF N-SUBSTITUTED MALEIMIDES AND ELECTRON DONOR OLEFINS.

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3) Nippon Steel Chemical Co., Ltd., Chiba, Japan
4) Univ. of Southern Miss., Polymer Sci. Dept., Hattiesburg, Miss., USA.

ABSTRACT

The free radical induced copolymerization or alternating copolymerization from a photoexcited state acceptor and / or acceptor / donor complex are a new field of growing interest in the radiation curing industry. This is mainly due to the potential possibilities of formulating a UV curable system without the presence of a free radical producing photoinitiator. Photoinitiator free nonacrylate based compositions will attain an enhanced interest and importance. This is due to a number of additional attractive properties, such as potential outdoor use, lower costs of formulations, improved odour, no formation of benzaldehyde, no formation of low molecular weight fragments from the photolysis of the photoinitiator, less extractables and so on. Some of the basic and fundamental aspects of a direct photolysis of the acceptor and the D/A complexes, and their potential use in practical "UV curing" will be outlined.

INTRODUCTION

Copolymerization reactions via charge transfer complexes is still a field of considerable interest and numerous publications are available in the literature¹-⁶. The main part are dealing with thermally or photo induced copolymerization by the use of free radical producing initiators. Hall et.al. have studied the direct photoinduced copolymerization of CT complexes of various monofunctional acceptors and donors⁷. The overall conclusion from these studies is that a direct photolysis of a CT complex can indeed lead to polymerization via a free radical process. This causes us to speculate that a reasonable efficient radiation curable system might be developed by finding the "right" combinations of acceptor and donors together with an irradiation source generating high intensity light and the possibility of changing the spectral distribution.

Formation of excited state CT complexes:

The possibilities of formation of an excited state AD complex are outlined in Scheme 1 and 2.

\[ \text{A} + \text{D} \xrightarrow{\text{hv}} \text{A}^* + \text{D} \xrightarrow{\text{hv}} [\text{A} \cdots \text{D}]^* \]

SCHEME 1. Formation of an exciplex type AD*.

\[ \text{A} + \text{D} \xrightarrow{\text{hv}} [\text{A} \cdots \text{D}] \xrightarrow{\text{hv}} [\text{A} \cdots \text{D}]^* \]

SCHEME 2. Formation of an AD* from a ground state CT.
The formation of an AD* can take place from an excited state donor or acceptor, whereby the D* or A* associates with a ground state A or D. The other route is a direct excitation of the ground state CT complex. It is suggested in the literature that in some cases these two different mechanisms generate photochemically identical excited state "species"8-12. In many cases, especially by the use of a broad bandwidth distribution profile from the irradiator both of these excitation mechanisms might occur simultaneously.

**Decay reactions of the excited state CT complex:**
The decomposition of an excited state CT complex can potentially be any of a variety of all intermediate types from a pure ionic Zwitterion nature to a 1,4 biradical nature. The possibilities have been elegantly and thoroughly described by Hall and Padias in reference 13. Depending on the polarity of the medium, e.g. the polarity of the A and D monomers, a strong influence of the ionic / biradical ratio of the shortlived excited CT complex will be noticeable. Besides the direct decay back to the ground state, a photochemically allowed 2+2 cycloaddition formation can take place. This cycloaddition reaction generates a thermodynamically stable cylobutane ring as a linkage between the two A and D monomers, as well as between an excited state A* and a ground state A13. For multifunctional structured A and D oligomers, this could be operable to a certain extent in the formation of crosslinks. Depending on the "strength" of the CT complex, which can be controlled by the choice of the A and D monomers, one can favour the existence of the free radical polymerization process. In order to promote the formation of the 1,4 biradical intermediate and the following free radical induced copolymerization, it is important to generate an excited state complex having as low ionic character as possible.

**Ground state CT complexes:**
The Mulliken theory predicts a maximum charge-transfer stabilization for the case where an maximum overlap exists between the HOMO of the donor and the LUMO of the acceptor. This situation will, however, produce complexes of high ionic character, normally "strongly coloured". In Scheme 3 are outlined the relative energy differences between some typical donors and acceptors compared to the relative energy level of an acrylate. Also UV-Vis spectroscopy shows a strong red shifted absorbance for those examples where the LUMO and HOMO levels are close together. In extreme cases, the shift in absorbance may be more than 100 nm at a total concentration of 0.25 M. If the the HOMO-LUMO overlap is too strong, a thermodynamicallyfavoured separated radical ion pair might be formed already upon mixing of the two monomers. In cases like this the thermal stability and the photo latency are lost completely and a spontaneous polymerization occurs. This can be a cationic or a combination of cationically and free radical induced homo and / or copolymerization.

On the other hand, excited state complexes exhibiting a "low" degree of ionic character normally show very weak absorbance and no red shifting19. In most cases this absorbance is not detectable by UV-Vis spectroscopy, since the weak absorbance is overlapped by the A or D monomer itself. Lee and Hall17 have clearly explained the concept of "weak" donor / "strong" acceptor or "strong" donor / "weak" acceptor combinations in order to obtain suitable combinations for promotion of free radical induced copolymerizations. As a consequence, the concentration of ground state CT complexes is fairly low, due to the very small equilibrium constant. The molar absorptivity is small and even a high intensity irradiation source might not be capable of producing a sufficient amount of 1,4 biradicals.

**Exciplex type of excited state CTC:**
This situation appears to be interesting, due to the fact that either the donor or the acceptor or both can to a certain extent be selected to absorb at a specific wavelength. Furthermore, even if the charge-transfer interaction in the ground state is weak for donor/acceptor pairs, photoexcitation of the donor or acceptor into an excited state enhances the donating or the accepting power. The stabilization ability of a complex between an excited state donor or acceptor with a ground state acceptor or donor will also prolong the lifetime of the collision exciplex16 formed.
Spin multiplicity:
Usually the exciplexes are considered to be singlets. Interestingly, in the case of exciplexes triplet states have also been found\(^1\). The importance of spin multiplicity is connected to the great differences in lifetimes between singlets and triplets, which can easily be three or four orders of magnitude longer for triplets, thereby allowing for a diffusion controlled initiation of the copolymerization to take place. Moreover, the triplet promotes the photoefficiency of initiation, since the recombination, giving a cyclobutane ring, from a triplet is a “forbidden” process.

Hydrogen Abstraction:
As will be discussed in the results and discussion section, fluorescence studies and triplet quenching of N-alkylmaleimides and styryloxy/vinylether combinations show the existence of a triplet state N-alkylmaleimide. Certain N-substituted maleimides will also undergo homopolymerization in the absence of a photoinitiator, although the efficiency of this polymerization is fairly low. However, in the presence of strong H-donors, the H-abstraction process will be quite efficient. In Scheme 4 is outlined the mechanisms of H-abstraction that can take place. Especially interesting is the fact that mixtures of N-alkylmaleimides and acrylates do polymerize rapidly provided that the mixture contains easily abstractable hydrogens, either as added hydrogen donors (tertiary amines, sec. alcohols, etc.) or as ethyleneglycol/propyleneglycol backbones in the acrylate monomer/oligomer.
Hydrogen Abstraction from Excited State N-Alkylmaleimide

Intramolecular H - Abstraction :

\[
\text{O} \quad \text{N-H} \quad \text{R} \quad \stackrel{\text{hv}}{\rightarrow} \quad \text{O} \quad \text{N-OH} \quad \text{R}
\]

Intermolecular H - Abstraction :

\[
\text{O} \quad \text{N-R} \quad \stackrel{\text{hv}}{\rightarrow} \quad \text{O} \quad \text{N-OH} \quad \text{R}
\]

Radical Rearrangement :

\[
\text{O} \quad \text{N-R} \quad \leftrightarrow \quad \text{O} \quad \text{N-OH} \quad \text{R} \quad \leftrightarrow \quad \text{O} \quad \text{N-R}
\]

**EXPERIMENTAL**

**Materials**

Triethylene glycol divinyl ether, TEGDVE; 1,2 - Cyclohexane dimethanol divinylether, CHVE; Dodecylmonovinyl ether, DDVE; 2-Ethyl-1-hexylvinylether, EHVE, and 4-Hydroxybutylvinyl ether were obtained from International Specialty Products and used as received. Bis (4-vinylxobutyl) isophthalate, iPDBDVE; Bis (4-viniloxy) - adipate, ADBDVE were obtained from Allied-Signal and used as received. Phenyl-4-viniloxybutylcarbonate, PCVE was prepared from HBVE and phenylchloroformate. Maleic anhydride, MAN; Maleimide, MI; Ethyl maleimide, EMI; Phenylmaleimide, PMI; Cyclohexylmaleimide, CHMI; Diethyl fumarate, DEF; Diethylmaleinate, DEM; Diallyl maleinate, DAM; Paramethoxystyrene, p-MOS and 4,4'dimaleimidobisphenolF, BPPBMI were obtained from Aldrich and used without further purification. Hexyl maleimide, HMI, and all para-substituted phenylmaleimides, were synthesized according to standard procedures described in the literature. See Synthetic Com., 20 (11), 1607 - 1610 (1990). Para-Glycidyloxystyrene, p-GOS, was a gift from J.S.Ericsson, Pharmacia Biotechnology, Uppsala, Sweden. Hexyl acrylate, HA; Hexanediol diacrylate, HDDA; Triethyleneglycoldiacrylate, TEGDA and Tripropyleneglycoldiacrylate, TPGDA were obtained from Scientific Polymer Products and passed through a column of Al₂O₃ before being used. 2,2-Dimethoxy -2-phenylacetophenone, Irg. 651, ( Ciba - Geigy ) was recrystallized twice from n- hexane.

**Procedures**

**Fluorescence Spectroscopy**

Fluorescence spectra were recorded on a Spex Fluorolog-2 spectrofluorometer. 0.1 M acceptor type monomer solutions were prepared in dichloromethane or benzene, and the electron donor olefin quenchers were added at increasing concentrations.
Polymerization was studied by using a modified Perkin Elmer DSC 2B. Monomer mixtures were placed in crimped aluminium DSC pans, using a calibrated microsyringe, 3 mL and degassed in the DSC for three minutes before irradiation. Polymerizations were carried out at 40 °C. Light from a 450 W medium pressure mercury lamp (Canrad Hanovia) was filtered through pyrex before reaching the sample and the reference cells. The resulting exotherms were fed into a stripchart recorder, from which polymerization data could be calculated. The light intensity was determined by placing a black DSC pan in the sample cell. The light intensity was measured after the pyrex filter. Typical values are 13 to 20 mW/cm².

RESULTS AND DISCUSSION

1. Absorption characteristics of donors and acceptors
The UV-Vis absorptions of the donors and acceptors were recorded and the data was published in our previous study. An additional comparison between vinyl ethers and propenyl ethers was investigated by Lapin et al. The vinyl ethers all show a very weak absorption at 300 nm, A < 0.1, and at 250 nm it is still smaller than 0.2. The maleic and the corresponding fumaroic diesters all show strong absorptions between 300 and 350 nm, whereas maleic anhydride itself has the broadest absorption due to its "weak aromatic" nature. The maleimides also exhibit a "weak aromaticity" and the N-alkyl and the N-aryl substituents will enhance absorptivity at longer wavelengths.

2. Formation and Existence of ground state CT complexes
From the UV-Vis spectroscopy studies it is evident that the combinations of vinyl ethers and maleimides do not exhibit any red shift due to strong ground state CT complexes. However, the existence can not be neglected, because the absorptivity might be fairly small and covered by the absorption from the maleimides. At higher concentrations (neat) we would probably expect to see weak CT absorption and of course the formation of an exciplex between an excited state maleimide and a ground state alkenyl ether is also a distinct possibility. All combinations of styryloxyderivatives with maleimides, show fairly weak ground state CT complexes, although they are quite noticeable at 0.25 M mixtures. Some of these mixtures also appear as coloured solutions at 0.25 M.

The differences in photoreactivity, as it relates to the strength of the CT complexes has been examined for the acceptor and donor combinations above. In this specification, mainly the vinyl ether and the maleimide combinations are compiled. Exotherms for HA and HDDA / HA containing 1 wt % photoinitiator are also added as practical references from the standard "state of the art" conditions. The heats of polymerization, ΔH_pol, are calculated from lit. ref. 21 to be approximately 90 kJ / mol for the alternating copolymerizations. From the same lit. ref. we used 78 kJ / mol for the acrylate based system.

4. Kinetics and Degree of conversion

4.1 Monofunctional Donor / Monofunctional Acceptor
Maleimides / Vinylethers versus Maleates / Fumarates / Vinylethers.
In Figure 1 are shown the reactivity differences between hexylacrylate and maleimide / vinylether versus combinations of maleates and fumarates / vinylethers. All combinations are monofunctional with respect to the double bond present. 1% α,α-dimethoxydeoxybenzoin (BDK) was used as photoinitiator and the photoreactions were all carried out in a nitrogen atmosphere. The most reactive combination is the 4-Vinylxoxyphenylcarbonate (PCVE) / hexylmaleimide (HMI), showing an exotherm as high as 11.5 mcal/sec. Also the 2-Ethylhexylvinylether (EHVE) / hexylmaleimide is very reactive. The somewhat low reactivity of hexylacrylate is more or less expected as notified from a previous study.
The maleate, fumarate / vinylether combinations show extremely low photoresponse even with an initiator present. However, difunctional systems based on these combinations are today well accepted as potential candidates for acrylate replacements in the UV curing industry despite the low reactivity. In a recent study by Decker et al., the participation of a ground state CT in these systems was elegantly shown from interpretation of kinetic data. Interestingly, in Figure 2 are shown the comparative reactivity of the hexylacrylate + 1% initiator to the initiator free PCVE/HMI and EHVE/HMI combinations. Although the acrylate / initiator system is more reactive, the maleimide / vinylether mixtures do perform quite well. It is well worth mentioning, as will be shown later, that the degree of conversion under the 4 minutes of exposure is higher for the maleimide / vinylether mixtures.

4.2 Difunctional Donor / Monofunctional Acceptor
Mono maleimides / Divinylethers
A 'time - conversion' plot is shown in Figure 3, for the CHVE / HMI system and a comparison with an acrylate system is also included. The most interesting performance in the graph is the high reactivity of the CHVE / HMI mixture, where a fairly high conversion is obtained even in air. The corresponding photoinitiator containing acrylate system does not show any exotherm within the time frame of 150 seconds of exposure. Especially noteworthy is the high reactivity of the CHVE / HMI mixture in the presence of a photoinitiator, giving polymerization rates as high as for the acrylate system. Furthermore it is worth noticing that the reactivity of CHVE / HMI is higher in a N₂ atmosphere than the corresponding CHVE / HMI / Irg. 651 / Air combination. Even more exiting is the high reactivity in air for the IPDBDV / HMI combination. Remember though that the light intensity in obtaining these these plots are only 13.6 mW / cm². Nevertheless this difference will be present even for "practical" UV curing, where the light intensities are 100 to 1000 times higher. The surprisingly high reactivity for the IPDBDV / HMI combination in air is also illustrated in Figure 4. Only the induction period (t₈₅) was affected by the presence of O₂, whilst the rate of polymerization at tₙ and the final conversion was hardly affected at all.

4.3 Difunctional Donor / Difunctional Acceptor
Di maleimides / Divinylethers
In Figure 5 is shown the increased reactivity for a difunctional maleimide (DEGBMI) and CHVE under nitrogen inerting. As usual in all multifunctional systems an early microgelation, often followed by some vitrification, will decrease the total degree of conversion due to reduced mobility of the radical species. On the other hand, a higher functionality will of course increase the reactivity under the initial phase of the polymerization. This is also the fact in these systems. As can be seen in Figure 5, the area under the difunctional exotherm is smaller than under the corresponding mono / di combination. Evidently, the initial reactivity is increased quite dramatically. The inherently different reactivities in air of the examined divinylethers in combination with DEGBMI are illustrated in Figure 5. The sensitivity towards oxygen inhibition varies at lot depending on the backbone structure of the divinylether. In nitrogen all these combinations do polymerize almost at equal rates. The importance of oxygen solubility, diffusion coefficients and polarity of the divinylether backbone will of course strongly influence the inhibition period. Added to that, a high concentration of ethyleneglycol groups, which is the case for the DEGBMI / TEGDVE combination, will promote an enhanced chain transfer by a hydrogen abstraction mechanism, which will if it is present strongly reduce the kinetics of the system due to the enhanced effect of oxygen quenching by formation of peroxyradicals. Perhaps the most astonishing feature of these systems is shown in Figure 7, where the reactivity and degree of conversion between hexandioldiacrylate (HDDA) +1% photoinitiator and a dimaleimide / divinylether mixture are compared. As expected the initial rate of polymerization for the diacrylate is much higher, but the degree of conversion after 3 minutes of exposure at this low light intensity is 80% for the dimaleimide / divinylether mixture, whereas the diacrylate reaches 61%.
5. Mechanisms of initiation

5.1 Maleimide Fluorescence Quenching

In view of the electron donor / acceptor character of vinylether / maleimide systems, photoinitiated polymerization via either an electron transfer quenching process, such as excited state maleimide plus ground state vinylether (exciplex formation) or a direct excitation of a ground state maleimide / vinylether charge transfer complex can occur. Figure 8 shows the quenching effect of EHVE on the fluorescence of HMI in dichloromethane. Although no direct evidence for a singlet exciplex is seen from the presence of a new emission at longer wavelengths, the fact that the fluorescence of HMI is effectively quenched by a vinylether with high singlet energy suggests quenching via some type of electron transfer process which might involve a non-emissive exciplex. Similar results are found when paramethoxystyrene (pMOS) is used as a quencher. This is shown in Figure 9. For this combination a new emission band from the excited singlet state of the exciplex is detectable at 560 to 570 nm. Since the photoinduced polymerization of styrylethers and maleimides do produce an alternating copolymer, which is most probably initiated from the 1,4 biradical, outlined in the introduction session, formed by the decay reaction from the triplet state exciplex.

5.2 Free Radical Generation - Hydrogen Abstraction by Excited state Maleimides.

It is also plausible to assume, that under proper circumstances, maleimides will generate initiating radicals from hydrogen abstraction from the triplet state\(^{24}\). This mechanism can, provided it can take place, origin from two main pathways. As shown earlier in Scheme 4, the possible intra and intermolecular hydrogen abstraction pathways are outlined. If free radicals are generated by any of the hydrogen abstraction mechanisms, then N-aliphatic maleimides should be effective in initiating radical polymerization in cases where readily available hydrogens are present. In order to determine if maleimides can generate radicals capable of initiating radical polymerization in the absence of electron donors comonomers such as vinylethers or styrylethers, maleimide / acrylate mixtures were exposed to UV irradiation. Acrylates will not form either charge transfer complexes or exciplexes with maleimides, since they are typical weak acceptors themselves. In the presence of free radicals, generated from hydrogen abstraction from excited state maleimides, acrylates will rapidly and very efficiently polymerize. The experimental verification of these proposals are illustrated in Figures 10, 11 and 12. In Figure 10 are shown the relative efficiencies in hydrogen abstractability depending on the N-alkyl substituent on the maleimide for the photoinduced polymerization of HDDA. In this investigation, the hydrogen abstraction will predominantly take place by the intramolecular abstraction within the maleimide itself, since the only abstracable hydrogens in the HDDA molecule are \(\alpha\)-ester type and these are hard to abstract. The results indicate that the N-cyclohexylmaleimide indeed undergo an efficient intramolecular H-abstraction and the resulting biradical initiates the polymerization of acrylates. It is also obvious that the other N-alkylmaleimide analogs do perform less efficient due to the fact the the available abstracable hydrogens are becoming harder and harder to be abstracted. This is even more clear for the N-Methylmaleimide and the N-Tert.butylmaleimide, where an extremely small or almost no exotherm is present. The corresponding photoextherms for the intermolecular abstractions are presented in Figures 11 and 12. As expected, a formation of a separated radical pair, the initiation efficiency would be higher. This is also the fact, as can be seen in Figure 11, where typical H-donors are added to the N-Methylmaleimide / HDDA mixture. In Figure 12, the H-abstraction takes place from the ethylene or propyleneglycol chain now present in the diacrylate backbone. These data suggest that the efficiency in photoinitiation of acrylate polymerization is higher for the intermolecular H-abstraction than for the intramolecular, since the exotherms for the inter are all higher than for the intra. It should also be clearly mentioned that the overall efficiency of the Maleimide / Diacrylate systems are lower compared to the Maleimide / Vinylether systems described above.
CONCLUSIONS

Some viable CT photocurable systems have been described. Mechanistic information will be forthcoming in a future work, but as of now we simply note systems which are potentially rapid curing. From Photo - DSC studies, proper selections of donors and acceptors has enabled us to develop UV curable systems, without the need for a photoinitiator. From a commercial point of view, this will for the future introduce an attractive way for formulating UV curable coatings. Especially, since there is a strong interest in developing alternatives for acrylates. In cases where either inter or intramolecular hydrogen abstraction by excited state maleimides is possible, relatively rapid rates of polymerization of acrylates are achieved without the addition of an external photoinitiator. We expect that the films produced from maleimide based systems will have excellent long-term photostability, therby making them candidates for a number of applications.

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Photo-DSC Exotherms

Monoacrylate versus:
Monofumarate / MonoVE
Monomaleate / MonoVE
MonoMI / MonoVE

1% Irgacure 651, $N_2, I_0 = 19 \text{ mW/cm}^2$

Figure 1.

Photo-DSC Exotherms

Monoacrylate + 1% PI versus MonoVE / MonoMI
No Photoinitiator, $N_2, I_0 = 19 \text{ mW/cm}^2$
Reactivity of MI and VE Mixtures
Effect of Average Functionality

**Figure 5.**

**Photo-DSC Exotherms**
HDDA + 1% PI versus DiMI / DIVE
Air, \( I_0 = 19 \text{ mW/cm}^2 \)

**Figure 6.**

Exotherm from DEGBMI/Vinylether (Under Air)

**Figure 7.**

HDDA + 1% PI, conv. = 61 %

**Figure 8.**

Fluorescence Quenching of HMI in presence of EHVE
Figure 9. Fluorescence Quenching of HMI in presence of p-MoS
Exclusion at 377nm
[HMI] = 0.1 M Benzene
[p-MoS] = 0.2
[p-MoS] = 0.4
[p-MoS] = 0.6
[p-MoS] = 0.8

Fig. 11. Effect of Hydrogen Donor

Fig. 10. Effect of N-Substituent of Maleimide

Fig. 12. Effect of Acrylate Structure
Bis-Acylphosphine-Oxide/ α-Hydroxyacetophenone Blends

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THE APPLICATION OF SILICA POLYMER IN UV PHOTORESIST

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ABSTRACT

A series of silane dichlorodimethyl-dihydroxy alcohol polycondensate have been synthesized from dichlorodimethylsilane and some type of dihydroxy alcohol compound, such as 1,3-propanediol, 1,5-pentanediol, etc. In this paper, we studied the influence of the polymer on UV positive photoresist and found that the property of coating was improved in a high degree after adding the polymer to the resist.

INTRODUCTION

In the modern industrial production of large scale integrated circuits, photoresist plays more important role and the need to applied property of the resist becomes more severe. In the processing of coating of the photoresist, sometimes there will be stripe found on the surface of the coating layer. The stripe leads to a surface irregularity of the coating layer and decrease the productive efficiency seriously. For this reason, we discussed the preparation of the polymer silica and the possibility that through adding this polymer into resist to erase the stripe and improve the coating property.

The following scheme displays the synthetic route for the polycondensation in this study:

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{Cl}-\text{Si}-\text{Cl} + \text{OH}-\text{(CH}_2\text{)}_n-\text{OH} & \rightarrow \{-\text{O-Si-O-(CH}_2\text{)}_m-\}_n \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

scheme 1
EXPERIMENTS

1. Preparation of the polymer

A solution of 50g (0.39 mol) of dichlorodimethylsilane in 70 ml chloroform was added to a mixture of 30g 1,3-propanediol (0.38 mol), 60g pyridine (0.76 mol) and 200 ml chloroform through a dropping funnel with stirring and under cooling with ice over 1 hour. Thereafter, the stirring was further continued at 50°C for 6 hours. Then the resulting white salt (pyridine hydrochloride) was filtered out and temperature was raised to 80°C and the chloroform and the residual monomer were evaporated out. After that the resulting liquid was dried at 90°C under vacuum for about 10 hours. Thus 47.3 g colorless transparent liquid was obtained (1st polymer).

Repeat above experiments except that 1,5-pentanediol and 1,8-octanediol were used in place of the 1,3-propanediol and 2nd polymer and 3rd polymer were obtained.

2. Measurement of the polymer

The structure of above polymers were identified by IR spectra. In addition, the molecular weight of the polymers were measured by 150°C ALC/GPC apparatus (WATERS Company).

3. Preparation of photoresist

The resist solution was prepared by following composition:
- cresol-formaldehyde resin
- PAC (photo active compound)
- ethylcellosolve acetate

The PAC was synthesized from 2,3,4-trihydroxybenzophenone and 1,2-naphthoquinonediazide-5-sulfonyl chloride

4. Adding the polymers to resist

A series of different quantity of each polymers were adding to above photoresist.

RESULTS AND DISCUSSION
Table 1  Molecular Weight of the Polymers

<table>
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<th>( M_n )</th>
<th>( M_w )</th>
<th>DISPERsITY</th>
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<tr>
<td>1&quot;</td>
<td>1267</td>
<td>2145</td>
<td>1.69</td>
</tr>
<tr>
<td>2&quot;</td>
<td>1740</td>
<td>3196</td>
<td>1.84</td>
</tr>
<tr>
<td>3&quot;</td>
<td>1289</td>
<td>1832</td>
<td>1.42</td>
</tr>
</tbody>
</table>

Figure 1 shows the IR spectrum of 1" polymer. Peaks at 1261 and 1080cm\(^{-1}\) shows the existence of Si-O groups. The peak at 3370cm\(^{-1}\) is very little and proves there is very few O-H groups exists in the polymer. Therefore the structure of the polymer has been proved as scheme 1.

Figure 1 IR spectrum of polymer 1"
Table 2 shows the influence of the polymers on some of the applied property of resist.

Table 2 influence on applied property of resist

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>surface detail</td>
<td>✔</td>
<td>✗</td>
<td>✗</td>
<td>✗</td>
</tr>
<tr>
<td>surface tension (dyne/cm)</td>
<td>52.8</td>
<td>24.6</td>
<td>28.8</td>
<td>30.2</td>
</tr>
<tr>
<td>film thickness retention</td>
<td>98.5</td>
<td>96.0</td>
<td>96.7</td>
<td>95.5</td>
</tr>
</tbody>
</table>

0": pure resist solution without adding polymers

✔: surface detail found  ✗: surface detail erased

Through the studying of effect of polymers on photoresist performance, we found that the polymers didn’t affect some of the applied property of resist obviously, such as sensitivity, resolution rates. There was no difference after adding the polymers. In another way, the polymer can decrease the surface tension and erase the stripe on the surface coating layer effectively. We also found that action of decreasing the surface tension become less with the increasing of the number of CH₂ groups on the polymer. The action varied in small extent with different quantity of the polymers adding to the resist. In the same time, it was found that the film thickness retention (ratio of film thickness after development to that of before development in exposed area) decreased in some degree.
CONCLUSIONS

The polycondensation of dichlorodimethylsilane and dihydroxyalcohol can improve the coating property of the photoresist by decreasing surface tension and erasing stripe on the coating layer of photoresist and make the layer more even. But the polymer can also decrease the film thickness retention. More studies about application of polymer of dichlorodimethylsilane and other compound such as diamine compound in UV positive photoresist will be continued.

ACKNOWLEDGEMENTS

The author would like to acknowledge the support of many colleagues in our institute.

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STRUCTURAL EFFECT OF DNQ-ESTERIFIED PAC ON POSITIVE PHOTORESIST PERFORMANCE

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ABSTRACT

Several poly-functional photoactive compounds (PAC), which are 1,2-diazonaphthoquinone (DNQ)-5-sulfonyl ester of poly-phenol compounds (Ballast molecules), are synthesized. Relation between photoresists performance and number of DNQ, degree of esterification and distribution of DNQs across ballast molecule have been investigated. These PACs give photoresists higher sensitivities, r-values and resolutions than those fully esterified PACs. Comparison of dissolution properties of several novel selectively DNQ-esterified PACs with those of fully esterified PACs suggests that the presence of -OH enhances dissolution rates and resist performance. Experimental results show novel PACs give good solubility and good stability in storage in photoresist solvent.

INTRODUCTION

Recently, particularly in the production of integrated circuits, miniaturization has proceeded as the integration level has increased, which results in demands for formation of patterns of submicron order and improved resolution. In submicron photolithography, still the novolac-based positive resists are conventionally used and the basis of the resist systems is on the dissolution inhibition of standard diazonaphthoquinones. The lithographic performance of novolac-diazonaphthoquinone (DNQ) positive photoresists is dramatically affected by the molecular structure of the photoactive compound (PAC) and the resin. Some papers have delineated structural factors of the PAC most affecting the resist performance, namely, DNQ group proximity [1, 2], hydrophobicity [2], and number of the DNQ groups in one PAC molecule [3]. Recently, relation between photoresists performance and number of DNQs, degree of esterification and distribution of DNQs across ballast molecule have been investigated intensively by dissolution rate measurements [1-6].

Improvement of resolution and focus latitude of positive photoresist are important requirements for the fabrication of half- and sub-half micron devices. Therefore, design of PACs are significant.

PAC is characterized by number of DNQs (n) and -OH groups (n) per ballast molecule, and
their orientations on a ballast molecule[7].

In this paper, we will report some partially DNQ-esterified PACs and their properties. By the light of these findings, this paper will also discuss the structure parameters on the PAC design for reaching a high performance of practical positive resists.

**EXPERIMENTAL**

1. Synthesis

Fully DNQ-esterified PACs were prepared by condensation reaction of the polyhydroxy compounds with an excess amount of 1,2-naphthoquinonediazide sulfonyl chloride followed with isolation by precipitation. Purity was higher than 97% for the most of all PACs, when TMG(1,1,3,3-Tetramethylglidine) was used as a esterification reaction catalyst.

Partially DNQ-esterified PACs having -OH groups were isolated from the isomers mixture of different esterification degrees obtainable by the condensation reaction with a less equivalence in the DNQ feed. A 4cmx80cm silica-gel column chromatography was used for the isolation. The PAC structure were determined by mass and NMR spectra.

PACs having hindered -OH groups were synthesized by controlling reactant ratio and reaction condition. The selective esterification process requires, (1) a backbone molecular design which isolates one OH from the other OHs in terms of steric crowding nearby, (2) reduced esterification rate on the isolated OH group (Fig.2).

**Synthetic Example 1:**

Into a 500 ml flask equipped with a stirrer, a condenser, a water separator and a thermometer, 2,5-xylenol (122.0g, 1mol), salicylaldehyde (30.5g, 0.25mol), p-toluenesulfonic acid (0.75g) and toluene (250g) were added and stirred on an oil bath at 115°C for 15 hours while removing condensed water. The resulting mixture was filtered at a temperature of 50°C to obtain a crude cake. The cake was dissolved in ethanol (500g) at a room temperature and charged into ion-exchanged water (1400g). Thereafter, the resulting solution was filtered and dried to obtain the compound (ballast molecule of PAC-67) 75g, MS: m/e 348(M+), M.P.: 276-278°C. The structure is confirmed by NMR, IR and element analysis.

The other hydroxyl compounds were synthesized by some known procedures.

**Synthetic Example 2:**

DNQ-PACs (Fig.1) were synthesized by condensation of 1,2-diazonaphthoquinone-5-sulfonyl chloride (DC) with various polyhydroxy compounds. 25 - 35 grams of the polyhydroxy compounds and 30-70 grams of DC were dissolved in 180-400 ml of 1.4-dioxane. TEA or TMG dissolved in 100 ml of acetone was added dropwise over 30 min, at 25°C. The molar ratio of the reactants were: DC/total number of the hydroxy groups = 0.5 - 1.05 catalyst.
organic base) / DC = 1.10. After completion of the addition, the reaction mixture was stirred for 30 min. at room temperature and then was poured into 2-4 L of water to precipitate PAC. The reaction product was isolated by filtration and washed with 2-4 L of cold methanol. The purity of the products was determined by using a HPLC.

2. Resist solution preparation

Resist solutions with the following composition were used both for dissolution rate study and for lithography.

- PAC: 3.25x10^{-3} eq. (in terms of DNQ groups)
- Novolac*: 5 g
- Solvent**: 15 g

* Cresol novolac resin, m/p=7:3 in feed ratio, Mw=9000 (GPC, PS standard)
** ECA PGMEA, or EL

The composition maintains the same DNQ group concentration per solid for varying PACs, and gave approximately the same DNQ absorbance per unit dry film thickness, 0.32 μm (at 436 nm).

3. Lithographic evaluation

The resist samples were spun on the bare silicon wafers and evaluated for their resolution, pattern profile and photospeed under the following conditions. (Table 1)

4. Experimental methods of dissolution properties

Resist sample was spin-coated on a silicon wafer and softbaked on a hot plate at 90 °C for 1 min. to give a 1.6 μm thick film. The film was exposed on SUSS MJB 3 MASK ALIGNER, and the dissolution rates of the unexposed and exposed area of the film were measured on Alpha-Step, TENCOR, with a 2.5% TMAH (Tetramethylammonium hydroxide) aqueous solution as a developer. Three indices, dissolution inhibition (Di), dissolution promotion (Dp), and dissolution contrast (Dc), were defined as follows:

\[ Di = \frac{R_r}{R_u} \]
\[ Dp = \frac{R_e}{R_r} \]
\[ Dc = \tan \theta \]

Rr: dissolution rate of the novolac resin
Ru: dissolution rate of the unexposed area
Re: dissolution rate of the fully exposed area

Fig 3 shows the definition of the three indices with a typical behavior of the dissolution rate vs exposure dose curve.
RESULTS AND DISCUSSIONS

1. PAC structures

Fig. 1 shows the structures of the PACs used in this paper with the general expressions for the isomers with varying DNQ esterifications.

2. Dissolution properties

In the exposed area, $R_{\text{max}}$ of PACs are considered to be a dissolution rate of indenecarboxylic acid. As all the samples were adjusted to have similar initial concentration of DNQ, their final concentrations of indenecarboxylic acid are also considered to be same. Polyphotolysis of PAC is described as follows.

\[
\begin{array}{c}
PAC-1 \\
PAC-2 \\
PAC-6
\end{array}
\begin{array}{c}
\cdot DD \\
\cdot DDA \\
\cdot DDH
\end{array}
\begin{array}{c}
\cdot DA \\
\cdot DAA \\
\cdot DAH
\end{array}
\begin{array}{c}
\cdot AA \\
\cdot AAA \\
\cdot AAh
\end{array}
\]

Here, $a$ is a concentration of each photolysis product, and suffix indicates the number of DNQ on a ballast molecule.

In the unexposed area, significance of thermal cross-linking at bake was emphasized as an effective process which provide a high contrast. Thermally induced reaction between $p$-cresol and DNQ compound provides three types of product as shown in Fig. 8. It can be assumed that DNQ compounds in resist film react with hydroxy group in novolac resin or ortho (or para) sites of hydroxy group.

Fig. 2 shows the substantial contribution of the DNQ moiety to the inhibition through the chemical reaction. The dissolution inhibition by the DNQ-PAC is apparently not only due to hydrophobicity of the PAC. Although several interactions between a novolac resin and a DNQ-PAC have been reported, for example, hydrogen bond at the DNQ moiety, hydrogen at the sulfonyl ester group, electrostatic interaction and the alkaline catalyzed coupling reaction, it is still controversial which is dominant.

Fig. 4 shows the temperature dependence of the dissolution rate for a novolac resin and some samples containing an DNQ-PAC with the resin. For the DNQ-PAC sample, the dissolution rate of the fully exposed area increases as the temperature goes up, while that of the unexposed area exhibits the reverse tendency. This tendency has been observed by Ito et al. and H. Nemoto et al., and the dissolution process of the film has been considered as a diffusion limited process or a reaction limited process. In either case, dissolution rate should increase with an increase in temperature. Thus the opposite temperature dependence in the unexposed area strongly suggests the contribution of the DNQ-PAC to the dissolution kinetics. Although most of the proposed interactions are generally considered to be weak at higher temperature, the rate of the...
chemical coupling reaction should increase with an increase in temperature, so that it is concluded that the observed temperature dependence suggests the participation of the alkaline catalyzed coupling reaction in the dissolution process. The behavior of the exposed area in the DNQ-PAC sample (indenecarboxylic acid), which could not cause the coupling reaction because of the lack of DNQ moiety, supported the importance of the coupling reaction. Thus the dissolution rates of the samples containing them increase with an increase in temperature as expected.

3. Solubility in resist coating solvents

It is desirable to use PACs of esterification level as high as possible for achieving high discrimination in general. This is, however, not practical in reality because of the PAC solubility problems that generally arise on going to high DNQ esterification level. Although there could be some exceptions, fully esterified PACs mostly lack sufficient solubility in resist coating solvents, e.g., ECA, PGMEA, EL etc.

The partially esterified PACs provide an apparent advantage in this view. Fig. 5 gives an example of the solubility comparison for PACs. The significant differences between the partially esterified PACs and their fully esters are to be noted. Fig. 4 also demonstrates the advantage of the partially esterified PAC over the equivalent isomer mixture, PAC-6-2D. Fig. 6 shows partially esterified PAC have better stability than fully esterified PAC. Solvent and esterification level of PAC could also dramatically affect the stability of resist.

4. Lithographic imaging potential

Fig. 7 actually examines several typical PAC isomers including the partially esterified PAC for their resolution. The resolution of each PAC, measured by mask linearity, was plotted against its respective OH/(OH+DNQ) value. The best resolution was demonstrated along with good correlation between the resolution and OH group.

CONCLUSIONS

1. Partially DNQ-esterified PACs having one or two unesterified -OH groups can be synthesized with high selectivity by using steric hindrance on a ballast molecule and by controlling reaction condition.
2. Those novel partially esterified PACs show higher sensitivity, r-value and resolution.
3. Novel partially esterified PACs having a hindered -OH are important compounds to improve resists performance.
4. Novel partially esterified PACs can enhance dissolution rate.
5. Novel partially esterified PACs give good solubility and good stability in storage in resist solvent.
ACKNOWLEDGEMENT

The author would like to thank C.S.N.A for his encouragement. The author would also like to thank Z.Q.HUANG for helpful discussions, and H.X.MA, X.M.JIAO, H.L.ZHANG for experimental works. The author also thank to Beijing Chemical Reagent Institute for supporting this study.

REFERENCES

2. K. Uenishi et al., ibid., 1466, 102-116 (1991)
Table 1 Experimental Conditions

<table>
<thead>
<tr>
<th>Lithographic Evaluation</th>
<th>Dissolution Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>4 inch Si wafer</td>
</tr>
<tr>
<td>Prebake</td>
<td>85°C, 60s</td>
</tr>
<tr>
<td>Film Thickness</td>
<td>1.05 μm, 1.59 μm</td>
</tr>
<tr>
<td>Exposure</td>
<td>50–150 mJ/cm²</td>
</tr>
<tr>
<td>Development</td>
<td>2.5 wt% TMAH</td>
</tr>
<tr>
<td></td>
<td>25°C, 60s</td>
</tr>
</tbody>
</table>

Fig. 1 Several PACs Structure

Fig. 2 Reaction Scheme of synthesis of PAC-6 and PAC-2

Fig. 8 Thermal induced reaction between cresol and PAC
Fig 3. Definition of the dissolution characteristics

Fig 5. Solubility of PAC

Fig 4. Temperature dependence of dissolution rate.
Developer: 2.5% TMAH aqueous solution. Resin m/p=7/3

Fig 9. Exposure time vs. film thickness retention in exposed area

Fig 6. Stability in storage in resist solvent

Fig 7. OH/(OH+DNQ) vs. resolution
PHOTOCROSSLINKING OF MULTIFUNCTIONAL
OLEFINE CONTAINING SPIROCYCLIC STRUCTURE

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(Institute of Photographic Chemistry Academia Sinica,
Beijing 100101, P.R.China)

ABSTRACT

To modify and/or eliminate the shrinkage of adhesives and
coatings during photocuring process, a multifunctional olefine
with spirocycle structure 3,9-dipropenyl-2,4,8,10-
tetraoxaspiro(5,5)undecane (DPTU), was used for the photocurable
formulation, when the photocrosslinking system composed of DPTU
and pentaerythritol tetrakis(thioglycolate) (PTTG) is irradiated
by UV light in the present of radical photoinitiator,
photopolymerization easily occurs through ene/thiol radical
transfer addition and simultaneously spirocyclic ring of DPTU
opens, leading to formation of an anomalous structure. The
kinetics of photocrosslinking was studied by measuring the change
in IR spectra of double bond at 1680 cm\(^{-1}\) and thiol group at
2570cm\(^{-1}\), as well as with determination of the gelation fraction
and hardness of cured film with irradiation time. The result
obtained indicate that the rate of photopolymerization is
strongly dependent on the nature and concentration of
photoinitiators and ratio of DPTU/PTTG. A variety of radical
photoinitiators, such as benzoin alkyl ether, benzil,
acetophenone derivative, aromatic ketone/amine combinations and
aryl disulfides were examined. The initiation efficiencies are
closely related with the compatibility of initiators with
prepolymer mixes and mobility of radical species formed, along
with the primary radical photogeneration. Among the commercial
products used the initiators of a-cleavage type appear more
effective than these of H-abstraction type, the gelation and
hardness of cured film were also determined with varing ratio of
DPTU/PTTG under same conditions. The optimum values were obtained
in the scale of ratio of 2:1--3:1. The kinetics and mechanism of
photopolymerization were also discussed.

In the vinyl addition polymerization the shrinkage in volume
frequently and substantially diminishes the performance and
durability of polymeric materials. In the case of coatings and
adhesives, especially when used on deformable substrates such as
metal sheets and foils, polymer shrinkage during curing causes
distortion of substrates. Thus in order to modify or eliminate
the shrinkage, novel monomers which polymerize with no change in
volume were first developed by Bailey in 1972[1]. These compounds
contain two or more heterocyclic rings in which each pair of
rings shares a single spiro carbon atom, and shrinkage diminishes
profoundly as the ring, which is opened, becomes larger.
Therefore this type of monomers have become known by the trival
name "expanding monomers". A number of bicyclic and spirocyclic
monomers have now been designed for use in different addition
polymerization, cationic, anionic and free radical
polymerization. The unsturated spirocyclic monomers are more of interest to commercial application because they can undergo a faster and more controllable photocrosslinking through radical addition polymerization and ring-opening reaction separately. For this purpose in this work we have prepared a unsaturated spirobicyclic compound DPTU and studied kinetically the copolymerization with multifunctional thiol through the ene/thiol radical transfer addition pathway by irradiation of UV light.

EXPERIMENTAL

DPTU was prepared by method as described in the literature[2], m.p, 57-58°C, HNMR IR UV spectra were indentified. PTTG was purchased from Tokoy Kasei Chemical Co.. Various photoinitiators were used as received. Photocrosslinking reaction was carried out in the film with 12-15μm thickness on glass plate at room temperature, using 300W high pressure mercury lamp as light source, the incident light intensity was measured to be 17.5mw/cm².

The curing rates were evaluated by measuring the change in IR spectra of double bond at 1680cm⁻¹ and thiol group at 2570cm⁻¹, as well as with determination of the gelation fraction and hardness of film after different irradiation time.

UV spectra were recorded on Hitach 300 spectrophotometer, IR spectra were recorded on Perkin-Elmer 983 spectrophotometer and hardness of film was measured with QBY pendulum hardnessmeter.

RESULT AND DISCUSSION

Addition of a thiol (RSH) to an olefine (CHₓ=CHR) is readily induced by photosensitizer (Sᵢ). The free radical mechanism proposed to account for this addition are illustrated in equs. 1-6[3].

\[
\begin{align*}
Sᵢ & \xrightarrow{hν} Sᵢ^* \quad 1 \\
Sᵢ^* + RSH & \rightarrow RS^* + S1H \quad 2 \\
Sᵢ^* & \xrightarrow{hν} Rᵦ \quad 3 \\
Rᵦ + RSH & \rightarrow RS^* + SH \quad 4 \\
RS^* + CHₓ=CHR & \rightarrow RSCHₓCHR^* \quad 5 \\
RSCHₓCHR^* + RSH & \rightarrow RSCHₓCHₓ₂R' + RS⁻ \quad 6
\end{align*}
\]

The sensitizer (Sᵢ) is excited by the absorption of light, then abstracts a hydrogen atom from the thiol to form thiy radicals (eq. 1,2), or directly gives a free radical species, then occurs radical transfer with thiol to yield thiy radicals (eq. 3,4). Thiy radicals add to the ene by a chain mechanism (eq. 5,6). It can be seen from equations above that if multifunctional thiols and multifunctional olefines were used a crosslinked polymer would be formed via radical chain transfer addition processes.

In this paper multifunctional unsaturated spiro bicyclic oligomer (DPTU) and multifunctional thiol (PTTG) were chosen as components for the photocurable thiy/ene systems. The photocrosslinking efficiencies for different initiation system and various important influences on photocuring rates were investigated below.

I. INFLUENCE OF PHOTINITIATORS
The following four types of photoinitiators will be considered for DPTU/PTTG photocuring system.

1. Benzoin derivatives

\[
\begin{align*}
& \text{R}_1 \text{C-C-Ph} \\
& \text{R}_2 \text{H}
\end{align*}
\]

- Abbreviation: BH
- S1: 73.14 Kcal/mol
- \( \text{R}_1 \text{H} \text{OEt} \text{OME} \text{Me} \text{CN} \)

2. Acetophenone derivatives

\[
\begin{align*}
& \text{R}_1 \text{Ph-C-R}_2 \\
& \text{OH}
\end{align*}
\]

- Abbreviation: HMIP
- S1: 70.97 Kcal/mol
- \( \text{R}_1 \text{i-C}_3 \text{H}_7 \text{C-OH} \)

3. Aromatic Ketones

\[
\begin{align*}
& \text{R}_1 \text{Ph-C-Ph-R}_2 \\
& \text{N(Me)}_2 \text{N(Me)}_2
\end{align*}
\]

- Abbreviation: BP
- S1: 69.18 Kcal/mol

4. Aryl Disulfide

\[
\begin{align*}
& \text{Ph-S-S-Ph} \\
& \text{H}
\end{align*}
\]

- Abbreviation: DPDS
- S1: 68.92 Kcal/mol

In order to evaluate the photocuring efficiency of various initiators the comparative studies for DPTU/PTTG photocrosslinking were performed under the same conditions. Fig.1 and Fig.2 show the conversion plots of the thiol group and double bond in curable formulation respectively. It can be seen that the crosslinking polymerization process appears to develop quite extensively and the majority of functional group, double bond and thiol group were consumed at the beginning of the irradiation, then reaction decreases progressively, with increasing time. The rate and extent polymerization differ largely with varying initiator used.

Fig.1 plot of SH conversion vs. irradiation time

DPTU/PTTG=2/1, [initiator]=4Wt%,
1.HCHP, 2.DEAP, 3.HMIP, 4.BZ, 5.BEPN,
6.DMPA, 7.TX, 8.BEE, 9.DPDS
Quantum yields (Qp), rates (Rp) and extents (Dp) of polymerization of DPTU/PTTG system with different initiators were listed in table 1. It can be found that the initiators which undergo intramolecular C-C bond cleavage upon photolysis (I and II type) appear to be substantially more efficient than the initiators undergoing hydrogen abstraction (III type). Among the initiators of a-cleavage type, the larger rates of polymerization (Rp) can be obtained when HCHP, DMPA and BEPN were used, but the polymerization quantum yield (Qp) is somewhat higher with HCHP than with DMPA and BEPN, because DMPA and BEPN absorb about two to four times as much of the 365nm UV radiation.

Table 1. Photopolymerization of DPTU/PTTG with various initiators

<table>
<thead>
<tr>
<th>initiator</th>
<th>A (%)</th>
<th>Rp (mol/l.s)</th>
<th>Qp (mol/einstan)</th>
<th>Dp* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BH</td>
<td>0.112</td>
<td>0.344</td>
<td>62.5</td>
<td>70</td>
</tr>
<tr>
<td>BEE</td>
<td>0.582</td>
<td>0.173</td>
<td>6.2</td>
<td>55</td>
</tr>
<tr>
<td>DMPA</td>
<td>0.413</td>
<td>1.75</td>
<td>85.8</td>
<td>70</td>
</tr>
<tr>
<td>BEPN</td>
<td>0.172</td>
<td>0.76</td>
<td>89.7</td>
<td>87</td>
</tr>
<tr>
<td>BZ</td>
<td>0.163</td>
<td>0.269</td>
<td>33.5</td>
<td>74</td>
</tr>
<tr>
<td>HMIP</td>
<td>0.675</td>
<td>0.372</td>
<td>11.2</td>
<td>70</td>
</tr>
<tr>
<td>DEAP</td>
<td>0.216</td>
<td>0.516</td>
<td>48.3</td>
<td>65</td>
</tr>
<tr>
<td>HCHP</td>
<td>0.111</td>
<td>0.599</td>
<td>109.8</td>
<td>93</td>
</tr>
<tr>
<td>BP</td>
<td>0.047</td>
<td>0.054</td>
<td>11.3</td>
<td>31</td>
</tr>
<tr>
<td>TX</td>
<td>1.69</td>
<td>0.217</td>
<td>2.61</td>
<td>55</td>
</tr>
<tr>
<td>MK</td>
<td>4.14</td>
<td>0.073</td>
<td>0.36</td>
<td>21</td>
</tr>
<tr>
<td>DPDS</td>
<td>1.61</td>
<td>0.061</td>
<td>0.77</td>
<td>35</td>
</tr>
</tbody>
</table>

Obviously, these results are related to the nature of initiators used. Table 2 shows primary photodecomposition of several initiators of a-cleavage type in the curing process of DPTU/PTTG film. It appears that the photochemical reaction of these compounds proceed rapidly with similar reaction rates and their half of concentration have been consumed after irradiation of 20 seconds. These observations demonstrat an important fact,

Table 2. Photodecomposition rates of some initiators

<table>
<thead>
<tr>
<th>initiator</th>
<th>irradiation time (s)</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>90</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>residual concentration Wt%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCHP</td>
<td>4</td>
<td>3.9</td>
<td>3.5</td>
<td>3.0</td>
<td>2.2</td>
<td>1.7</td>
<td>1.1</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>HMIP</td>
<td>4</td>
<td>3.5</td>
<td>3.2</td>
<td>2.5</td>
<td>1.8</td>
<td>1.4</td>
<td>1.1</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>DMPA</td>
<td>4</td>
<td>3.9</td>
<td>3.5</td>
<td>2.9</td>
<td>1.8</td>
<td>1.2</td>
<td>0.8</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>BEE</td>
<td>4</td>
<td>3.5</td>
<td>3.2</td>
<td>2.6</td>
<td>1.8</td>
<td>1.4</td>
<td>0.9</td>
<td>0.6</td>
<td></td>
</tr>
</tbody>
</table>

that the mobility of initiating radical species formed in rigid medium of film plays a significant role in the photocuring process of multifunction curable system, which considerably affects the rate and extent polymerization as show in table 1. Finally, in the case of disulfides as initiator the poor reaction efficiency may be explained by the side reaction with spirocyclic unite of PTTG. Another important effect on the photocrosslinking
of DPTU/PTTG system is the concentration of initiator. The relationship between functional conversion and concentration of initiator (HMIP) at fixed irradiation time is given in table 3.

<table>
<thead>
<tr>
<th>HMIP concentration Wt%</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion* (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-SH</td>
<td>48</td>
<td>60</td>
<td>72</td>
<td>75</td>
<td>76</td>
<td>76</td>
</tr>
<tr>
<td>&gt;C=C&lt;</td>
<td>33</td>
<td>45</td>
<td>57</td>
<td>60</td>
<td>63</td>
<td>64</td>
</tr>
</tbody>
</table>

DPTU/PTTG=3/1

From the data above, it can be seen that the polymerization rate is strongly dependent on the concentration of initiator. Paralle reaction tendencies were obtained by measuring -SH and >C=C< consumption. Rp grow remarkably in the lower concentration range and become very slowly after concentration above 4Wt%.

II. INFLUENCE OF THE COMPOSITION

Interestingly, it was found that the crosslinking polymerization of DPTU/PTTG occurred directly by UV irradiation in the absence of photoinitiator. As shown in Fig.3. The conversion of -SH group and double bond grow progressively with radiation time, comparing with production of insoluble gel.

Fig.3 Photocrosslinking of DPTU/PTTG in the absence of photoinitiator
DPTU/PTTG=3/1

The spiro bicyclic pentaerythritol acetal compounds, as reported[5], are unstable photochemically and undergo C-O bond cleavage to form ester group and generate active radical, which results in the initiation of radical chain addition to produce crosslinked form in the case of DPTU/PTTG and leads to reduce shrinkage in volume of product. The photocleavage of spiro bicyclic unite of DPTU can be depicted as follow:
The relative composition is an important factor which significantly affects the photocrosslinking and properties of product. Table 4 shows the relationships between the ratio of DPTU/PTTG and properties of cured film using DMPA as initiator at air condition. It can be found that the gelation fraction and hardness raise sharply at beginning of irradiation, except the case of high ratio of 4:1, after that photocuring processes become slow. The optimum ratio value of DPTU/PTTG can be obtained at the scale of 2:1--3:1 Wt/Wt, which is near their equimolecular value.

Table 4. Dependence of properties of product on the ratio of DPTU/PTTG

<table>
<thead>
<tr>
<th>property</th>
<th>irradiation time (s)</th>
<th>ratio of DPTU/PTTG</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1:1</td>
<td>2:1</td>
</tr>
<tr>
<td>gelation</td>
<td>5</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>62</td>
</tr>
</tbody>
</table>

|        | 10   | 58   | 75   | 43   | 30   |
|        | 20   | 70   | 80   | 65   | 48   |
|        | 40   | 79   | 85   | 85   | 60   |
|        | 60   | 81   | 91   | 89   | 72   |
|        | 120  | 92   | 99   | 98   | 86   |

In the work described above, we have shown the photocrosslinking processes of several curable formulation composed of multifunctional DPTU/PTTG system having spirocyclic unite, using different photocuring initiators. The notable advantage of this photocurable system, in contrast to the majority of radiation curable system, is that air inhibition dose not occur to any extent and inert blanketing gas system are not necessary. Therefore we can consider that utilizing spirocyclic monomer or oligomer as component, which reduce the shrinkage in the photocuring process, would be highly desirable for practical applications.

REFERENCES

SYNTHESIS AND APPLICATION
OF 1,6-HEXANDIOL GLYCEROL ETHER

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ABSTRACT
1,6-Hexandiol glycerol ether is an excellent modifier for UV curable epoxy—acrylates coatings for optical fibres. This paper describes the synthesis of 1,6-hexandiol glycerol ether from 1,6-hexandiol and epoxy chloropropane and its application to said coating.

INTRODUCTION
More often than not, the mechanical performance of UV curable epoxy—based coating for optical fibres is not so good. Therefore, some measures must be taken to modify the coating. As part of our program regarding the study of such kind of modification, we report here the preparation and application of 1,6-hexandiol glycerol ether.

EXPERIMENTAL
1. Ring—Opening Reaction

\[
\begin{align*}
&\text{Cl—CH—CH—CH—CH—CH—Cl} \\
&\uparrow \\
&\text{OH—(CH₂)₅—OH} \\
&\downarrow \\
&\text{Cl—CH—CH—CH—CH—OH}
\end{align*}
\]

(a)

1,6-Hexandiol (7.3 mol), epoxy chloropropane (18.5 mol) were added into a 5 dm³ reactor, and then 98% sulfuric acid (50 cm³) was added in drops with stirring and cooling. After 1,6-hexandiol was completely dissolved, the ring—opening reaction was carried out at 138—140°C for 3 hours.

2. Ring—Closure Reaction

\[
\begin{align*}
&\text{Cl—CH—CH—CH—CH—Cl} \\
&\text{OH—(CH₂)₅—OH} \\
&\text{Cl—CH—CH—CH—CH—Cl}
\end{align*}
\]

(b)

Potassium hydroxide (560 g) dissolved in absolute ethyl alcohol (2.0 dm³) was slowly added...
into said reactor. The mixture was stirred at 50—60°C for an hour, cooled, and vacuum filtered. The filtrate obtained was evaporated until 138°C under ordinary pressure to leave (b), of which refraction index (1.4686, 25°C), mean molecular weight (325, VPO Method) and epoxide number (0.25, hydrochloric acid /acetone Method) were analyzed respectively.

RESULTS AND DISCUSSION

1. Ratio of Reactants

When the molar ratio of the epoxy chloropropane and 1,6—hexandiol is 2 : 1, theoretically compound (b) of n=1 can be obtained. But the yield is not so good (less than 60%). In order to make full use of expensive 1,6—hexandiol, 30% more epoxy chloropropane was used, of which advantages are that: (i) The yield of (b) is increased (more than 90%); (ii) Epoxy chloropropane here is used as solvent as well as reactant, and extra epoxy chloropropane can be recovered after reaction, therefore no other solvent is needed.

2. Reaction Temperature

Because the primary stage of ring—opening reaction is an exothermic reaction, it is necessary that primary temperature be controlled below 140°C. Otherwise, it is difficult to obtain (a) because of the accelerated polymerization by released heat.

3. The Components of the Products

For the product obtained, molecular weight is 325 which is close to that of (b) (330, n=2). However practical analyzed epoxide number (0.25) differs greatly from that of (b) (0.60, n=2). This shows that the product is a mixture of glycerol ethers of different n and, as shown by Ritter,[1] with condensation, for example

\[
\text{CH}_2—\text{CH—CH}_2—\text{O—[(CH}_2)_n—\text{O]}_n—\text{H}
\]

leads to the decrease in epoxy groups and epoxide number. As a modifier for UV curable coatings for optical fibres, the presence of this type of compounds is useful, because the presence of hydroxyl group in polyethers from polybasic alcohols prevents the forming of over—crossed structure during the preparation of prepolymer from bisphenol A epoxide resins, and therefore, the low—temperature performances of the coating are improved.

4. Applications of the Compound (b)

In the process of developing UV curable coatings for optical glass fibres, the most difficult thing is to conduct curing at a high rate with perfect low—temperature properties. The product from esterification of bisphenol A epoxide resins with acrylic acid used as prepolymer, together with proper combined active diluents and photosensitizers, makes it easy to obtain high curing rate and good mechanical performances. Unfortunately its glass transition temperature Tg is high, which may lead to such consequence that the low—temperature additional loss of the optical fibres will increase sharply at low temperature because of the difference of thermal expansion coefficients between the cured film in glass state and quartz glass (Table 1,a). To solve this problem, it seems reasonable that, hexane diacid and castor oil acid could be partly substituted for acrylic acid to both increase molecular weight of the prepolymer, with less shrinking during UV curing and decrease Tg of the cured films. However, it turns out to be the case that the viscosity
of the liquid coating becomes higher and the UV curing rate is sharply decreased although the low-temperature properties are improved (Table 1, b). Both theoretical analysis and literature indicate that the introduction of ether bonds into macromolecular chains and decrease of the density of benzene rings to some extent are favourable to the internal spin of the chains resulting in the decrease of Tg and the forming of hydrogen bonding action which is an additional adhesion between the cured film and the quartz fibre. Therefore, a combined-type epoxide containing both aromatic and aliphatic groups was prepared from the substitution of 1,6—hexandiol glycerol ether for bisphenol A epoxide. The reaction product of combined—type epoxide and combined—type acid composed of acrylic acid, hexane acid and castor oil acid was used as a prepolymer. The prepolymer, together with properly combined active diluents and combined photoinitiators, gives the UV curable coating for optical fibres with satisfactory curing rate and low—temperature properties (Table 1, c).

Table 1 The Properties of the Coatings and the Optical Fibres.

<table>
<thead>
<tr>
<th>Curing rate (m/min)</th>
<th>additional loss at $-40^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>a 80</td>
<td>$&gt;1.0$</td>
</tr>
<tr>
<td>b 30</td>
<td>$0.05~0.2$</td>
</tr>
<tr>
<td>c $&gt;100$</td>
<td>$0.01~0.05$</td>
</tr>
</tbody>
</table>

Note: exposed to the air in the light of high or middle pressure mercury lamps.

CONCLUSIONS

The synthesis and application of 1,6—hexandiol glycerol ether plays a decisive role in the development of high—quality UV curable coatings for optical fibres.

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THE REACTION KINETICS ON
DIAZO RESIN UNDER UV IRRADIATION
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ABSTRACT

The photochemistry reaction kinetics of diazo resin was investigated by dynamic UV and Infrared spectra.
When diazo resin was photodegraded in aqueous solution by UV irradiation, the Control step was the absorption process of absorption light; the rate equation is \( r = 1.0 \times 10^{-6} (1 - \frac{c_{\text{mol}}}{e^{-c_{\text{mol}}}}, \text{mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}) \); the kinetic equation is \( \ln(e^{2.84 - 0.25t} - 1) = 2.84 - 0.25t \); the quantum efficiency \( \Phi = 0.311 \).

When diazo resin was photodegraded in acrylic polymer film by UV irradiation, it is the first order reaction; the rate constant \( k = 1.72 \times 10^{-5} \text{S}^{-1} \).

INTRODUCTION

Photodegradation is an important photochemistry property of diazo compound. Diazoo resin is formed by reaction of diazo compound and the compound containing active carbonyl group so it has somewhat larger molecular weight and more diazo groups, which can be used as photosensitizer of UV-cured system, such as screen printing material. Diazoo resin photodegradation finally makes linear acrylic resin cross linking cured. The above-mentioned photodegradation reaction kinetics of diazo resin was less reported. This article has investigated the reaction kinetics of photodegradation for diazo resin in aqueous solution and acrylic resin film by ultraviolet and infrared spectra.

EXPERIMENT

1. Chemicals:
DP - 1: diazo resin of 4-diazo-diphenylamine doublesalt with zinc chloride produced by Wuxi Chemical Industry Research & Design Institute. recrystalized three times.

DP - 2: diazo resin of 4-diazo-diphenylamine doublesalt with toluene sulphonate prepared according reference[2].

Acrylic resin: is a copolymer which was prepared with MMA/AA/AN/FA - 1 by solution polymerization in acetone and methanol. The copolymer was precipitated in deion water to become white flocculate and was dried, with acid value of 109.1 mgKOH/g.

2. Determination
(1) Ultraviolet spectra were measured for diazo resin solution

The aqueous solution of DP—I diazo resin with concentration of \(1.2 \times 10^{-5}\) mol \(\cdot\) l\(^{-1}\) was accurately prepared, pour it into quartz sample cell of ultraviolet spectrograph to determine \(\lambda_{\text{max}}\) and absorbance \(D_0\). The instrument wave length was fixed at \(\lambda_{\text{max}}\), sample cell was exposed many times under mercury light until absorption peck at \(\lambda_{\text{max}}\) decaying to the minimum value. Tracked to measure ultraviolet spectra. Strength of irradiation for exposure face is 328 \(\mu\)w \(\cdot\) cm\(^{-2}\) which is measured by UV—A type ultraviolet radiation photometer.

(2) Infrared spectra was measured for diazo resin—acrylic resin photosensitive film:

Photosensitive solution was prepared in certain ratio with acrylic resin, DP—I diazo resin, ethylene glycol mono—methyl and was coated on a piece of glass of \(10 \times 10\) cm\(^2\) after full dissolution and filtration, drying then got a film. The Infrared spectrograph track to measure the decay process of the characteristic absorbance peak of diazo group at 2160 cm\(^{-1}\) under different exposure time with the photosensitive film. Strength of irradiation for exposure face is 328 \(\mu\)m \(\cdot\) cm\(^{-2}\).

3. Data Analysis and kinetic definition

(1) To measure the quantum efficiency of photodegradation reaction for diazo resin:

Quantum efficiency of photochemistry reaction is in the ratio of reacted number of molecules to absorbed number of photons in system.

Photodegradation process of diazo resin can be shown simply:

\[
\text{A} \xrightarrow{\text{hv}} \text{A}^* \rightarrow \text{P} \tag{1}
\]

ground state \(\rightarrow\) excite state \(\rightarrow\) product

Its photodegradation speed can be expressed as:

\[
-V \frac{d[A]}{dt} = R(t) \Phi \tag{2}
\]

\(R(t)\) is the absorbed light mass by reactant A at an unit time, \(\Phi\) is quantum efficiency of reaction. If the exciting light was single colour light and the product did not absorb it, we got an equation according to the law of Berr—Lambert:

\[
R(t) = I_o (1 - e^{-2.303d_0[A]}) \cdot S \tag{3}
\]

Substitute (2) equation by (3) equation, we got:

\[
-V \cdot \frac{d[A]}{dt} = I_o \cdot (1 - e^{-2.303d_0[A]}) \cdot S \cdot \Phi \tag{4}
\]

\(V\) — volume of solution for reaction \(\cdot\) cm\(^3\);
\(I_o\) — The light strenght of irradiation \(\mu\)w \(\cdot\) dm\(^{-2}\);
\(I\) — The transmitted light strenght at \(t\) time \(\mu\)w \(\cdot\) dm\(^{-2}\);
\(S\) — The irradiated area of solution \(\cdot\) cm\(^2\);
\(\varepsilon\) — The molecular extinction coefficient when the reactant is at the wave length of exciting light \(\cdot\) mol\(^{-1}\) \(\cdot\) dm\(^{-1}\) \(\cdot\) cm\(^{-1}\); 
\(l\) — The light distance length in solution \(\cdot\) cm.

Handle equation (4) with transposition of term and integration (suppose \(I_o\) does not change with time):

\[
\ln \left( e^{2.303d_0[A]}/ -1 \right) - \ln \left( e^{2.303d_0[A]/ -1} \right) = 2.303I_o \cdot \varepsilon \cdot l \cdot S \cdot \Phi \cdot V \tag{5}
\]

\(\varepsilon\) — The molecular extinction coefficient when the reactant is at the wave length of exciting light \(\cdot\) mol\(^{-1}\) \(\cdot\) dm\(^{-1}\) \(\cdot\) cm\(^{-1}\); 
\(l\) — The light distance length in solution \(\cdot\) cm.
The solution in glass cuvette was exposed by mercury lamp. Mercury output spectrum range of the mercury lamp was around 370 nm. Filtered out the UV—light before 320 nm and after 400 nm by filter glass then it was regarded as single colour light. I₀ equals 328 mw • dm⁻² at the exposed face of 370 nm wave band. \( V = s \cdot l \), substitute it into equation (5), got:

\[
\ln (e^{2.303I_0} - 1) - \ln (e^{2.303I_0}) = 23.03I_0 \cdot \Phi \cdot t
\]

At selected wave length \( \lambda_w = 370 \text{ nm} \) we can measure \([A]_0\) from \( D_0\). According to the law of Beer—Lambert, equation (6) can be expressed as:

\[
\ln (e^{2.303D_0} - 1) - \ln (e^{2.303D_0}) = 23.03I_0 \cdot \Phi \cdot t
\]

Measured \( D_0 \) at different irradiation time \( t \) and made drawing of \( t \) with \( \ln (e^{2.303D_0} - 1) \), we can got quantum efficiency \( \Phi \) of photodegradation through the slope.

(2) Rate and kinetic equations of photodegradation for diazo resin in aqueous solution.

Photodegradation reaction rate is \( R = -\frac{d[A]}{dt} \). Suppose \( I_0 \) is the light quantum (mole) absorbed by \( A \) in an unit time and volume of reactive system. According to the law of photochemical equivalent, we got:\(^{[4]}\):

\[
r = I' = k \cdot I_0
\]

The irradiation energy absorbed by reactive system of unit volume at unit time is \( (I_0 - I) / V \), while energy of molar photon is \( N_0 \cdot h \nu \) and \( V = S \cdot L \), the equation (8) can be shown:

\[
r = I' = \frac{(I_0 - I)}{N_0 \cdot h \nu \times l \times S} = \frac{I_0 - I}{N_0 \cdot h \nu}
\]

We can got \( I_0 = I_0 (1 - e^{-2.303[A]}) \) from the law of Beer—Lambert, so that

\[
r = \frac{I_0}{N_0 \cdot h \nu} (1 - e^{-2.303[A]})
\]

we can got equation (11) from equation (10)

\[
\frac{d[A]}{dt} = \frac{I_0}{N_0 \cdot h \nu} (1 - e^{-2.303[A]})
\]

Handle equation (11) with transposition of term and integration:

\[
\int_{[A]_0}^{[A]_t} \frac{d[A]}{1 - e^{-2.303[A]}} = -\frac{1}{N_0 \cdot h \nu} \int_0^t I_0 \, dt
\]

Suppose \( I_0 \) did not change with the time:

\[
\ln (e^{2.303I_0} - 1) - \ln (e^{2.303I_0}) = 2.303 \cdot \epsilon \cdot I_0 \cdot t
\]

After the datas \((N_0 \cdot h \nu, I_0, \epsilon, [A]_0) \) was known, substituted them into equation (11), we can got the rate equation of photodegradation for diazo resin in aqueous solution, substitute them to equation (12), we can obtained the reaction kinetic equation of photodegradation for diazo resin.

(3) The kinetic data of photodegradation for diazo resin in acrylic resin film.

For the research of photodegradation of diazo resin in acrylic resin film, infrared spectra were used to track measuring the disappearance of characteristic absorption peak of diazo group. \( D_0 \) the quantitative analysis according to the law of Beer—Lambert, intensity of infrared absorption peak is measured by base-line method. Absorbance \( D = \ln I_0 / I \).
By making drawing of t with InD, we obtained the straight lines. The slope was constant of reactive rate.

RESULTS AND DISCUSSION

1. The reaction kinetic of photodegradation reaction for diazo resin in aqueous solution.

The ultraviolet absorption spectra of diazo resin DP—I in aqueous solution.

Fig. 1.
The ultraviolet absorption spectra of diazo resin DP—I in aqueous solution.

Footnote:
(1) Concentration of aqueous solution is $1.2 \times 10^{-5}$ mol/dm$^3$;
(2) Irradiation time (from above to below): 0, 20, 25, 30, 40, 45, 50, 55, 60, 70, 80 sec.

The results showed that the intensity of the absorption band of diazo group decreases by photoradiation. DP—I absorpt band is at $\lambda_{max} = 370$nm. Absorbance $D$, of different irradiation time were measured by base-line method and the obtained datas are listed at Table 1. Made the figure for t with $ln(e^{2.303D} - 1)$ according to the data of Table 1, we got Fig. 2.

Table 1. $ln(e^{2.303D} - 1) \sim t$ data table

<table>
<thead>
<tr>
<th>t/s</th>
<th>0</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_r$</td>
<td>2.36</td>
<td>0.67</td>
<td>0.46</td>
<td>0.26</td>
<td>0.13</td>
<td>0.07</td>
</tr>
<tr>
<td>$lnD_r$</td>
<td>0.23</td>
<td>-0.40</td>
<td>-0.84</td>
<td>-1.35</td>
<td>-2.04</td>
<td>-2.69</td>
</tr>
<tr>
<td>$e^{2.303D}$</td>
<td>18.29</td>
<td>4.68</td>
<td>2.69</td>
<td>1.82</td>
<td>1.35</td>
<td>1.18</td>
</tr>
<tr>
<td>$ln(e^{2.303D} - 1)$</td>
<td>2.85</td>
<td>1.30</td>
<td>0.53</td>
<td>-0.20</td>
<td>-1.05</td>
<td>-1.72</td>
</tr>
</tbody>
</table>
From Fig. 2 we got a straight line, linear correlation coefficient $\gamma = 0.9997$. \(\text{Slope} = -7.6 \times 10^{-2} \text{s}^{-1}\).

(1) Quantum efficiency

Based on equation (7), we can get:

\[
\ln(e^{2.303l}) - 1 = -23.03I_0 \cdot e \cdot \Phi \cdot t + \ln(e^{2.303s} - 1)
\]

\[
I_0 = \frac{32.8 \text{mW} \cdot \text{dm}^{-2}}{1 \text{Einstein}} = \frac{32.8 \text{mW} \cdot \text{dm}^{-2}}{0.1196/\lambda} = \frac{32.3 \times 10^3 \text{mW} \cdot s \cdot \text{mol}^{-1}}{1.01 \times 10^{-7} \text{mol} \cdot s^{-1} \cdot \text{dm}^{-2}} = 0.311
\]

This result is smaller than the quantum efficiency 0.36 of single diazo compound — diazonium reported by reference \[^{15}\].

(2) Rate and kinetic Equations:

After determination of \(N_{\text{e}}\), \(I_0\), \(\Phi\), and \([A]_0\) according to equation (11), we can obtained rate equation of photodegradation reaction for diazo resin DP-I in aqueous solution.

\[
r = -\frac{d[A]}{dt} = \frac{32.8 \text{mW} \cdot s^{-1} \cdot \text{dm}^{-2}}{3.28 \times 10^6 \text{mJ} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1} \cdot 1.01 \times 10^{-7} \text{mol} \cdot s^{-1} \cdot \text{dm}^{-2}} (1 - e^{-2.303s} 0.05 \times 10^6 [A]_0 S_{mol})
\]

\[
= 1.0 \times 10^{-6} (1 - e^{-2.42} 0.05 [A]_0 S_{mol}) \text{mole} \cdot \text{dm}^{-1} \cdot \text{s}^{-1}
\]

Similarly, when the constant is substituted into equation (12), we can get the kinetic equation of photodegradation reaction for diazo DP-I in aqueous solution.

\[
\ln(e^{2.303l}) - 1 = -\ln(e^{2.412 \times 10^6 [A]_0 S_{mol}}) - 1)
\]

\[
= \frac{2.303 \times 10^3 \text{mW} \cdot \text{dm}^{-1} \cdot \text{cm}^{-1} \times 32.8 \text{mW} \cdot \text{dm}^{-2} \cdot s^{-1}}{3.28 \times 10^6 \text{mJ} \cdot \text{mol}^{-1}} \cdot t
\]

\[
\ln(e^{2.412 \times 10^6 [A]_0 S_{mol}}) - 1) = 2.84 - 0.25t
\]

The result of Fig. 2 shown that the control step of the photodegradation for diazo resin DP-I in aqueous solution is a process of absorption light.

Infrared spectra were measured for photosensitive film of diazo resin DP—I/ acrylic resin after UV irradiation.

The result showed that the intensity of the absorption peak of diazo group at 2160cm⁻¹, 1580cm⁻¹ decreases with UV irradiation (Fig. 3).

Fig. 3 Infrared spectra for photosensitive film of DP—I/ acrylic resin after UV irradiation; Irradiation time from below to above: 0, 100, 210, 450, 800, 1130 sec.

Measured I₀ and I by base—line method at 2160cm⁻¹ (Fig. 3) and listed the data into table 2. we can got Fig. 4 about lnDₓ= t according to table 2.

<table>
<thead>
<tr>
<th>t/s</th>
<th>0</th>
<th>100</th>
<th>210</th>
<th>450</th>
<th>800</th>
<th>1130</th>
</tr>
</thead>
<tbody>
<tr>
<td>I₀</td>
<td>0.781</td>
<td>0.784</td>
<td>0.804</td>
<td>0.815</td>
<td>0.820</td>
<td>0.823</td>
</tr>
<tr>
<td>I</td>
<td>0.536</td>
<td>0.570</td>
<td>0.605</td>
<td>0.675</td>
<td>0.739</td>
<td>0.774</td>
</tr>
<tr>
<td>Dₓ</td>
<td>0.376</td>
<td>0.319</td>
<td>0.284</td>
<td>0.188</td>
<td>0.104</td>
<td>0.061</td>
</tr>
<tr>
<td>lnDₓ</td>
<td>−0.978</td>
<td>−1.143</td>
<td>−1.259</td>
<td>−1.671</td>
<td>−2.263</td>
<td>−2.797</td>
</tr>
</tbody>
</table>
Based on Fig. 4, there was good linear relation between lnD, and t. Linear correlation coefficient γ = 0.998. This meant that ultraviolet photodegradation was first order reaction when diazo resin DP—I was in acrylic resin photosensitive film. Slope = $-1.7 \times 10^{-3} \text{S}^{-1}$ in Fig 4, so $k = 1.7 \times 10^{-3} \text{S}^{-1}$, this was the rate constant of photodegradation for diazo resin DP—I in film.

CONCLUSIONS

Based on the results obtained from ultraviolet and Infrared Spectra for DP—I and DP—I diphenylamine—4—diazo resin system after UV irradiation, we calculate:
1. Quantum efficiency of photodegradation for DP—I in aqueous solution, $\Phi = 0.311$.
2. The rate equation and the kinetic equation of photodegradation for DP—I in aqueous solution.
   $$r = 1.0 \times 10^{-4} \left(1 - e^{-2.412 \times 10^5 A} \right) \text{mol \cdot dm}^{-3} \cdot \text{S}^{-1}; \quad \ln(e^{2.412 \times 10^5 A} - 1) = 2.84 - 0.25t$$
3. The control step of photodegradation for DP—I in aqueous solution was a process of absorption light.
4. The photodegradation of DP—I in acrylic photosensitivity film was first order reaction. Its rate constant of photodegradation $k = 1.72 \times 10^{-3} \text{S}^{-1}$.

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SWELLING BEHAVIOR OF PHOTOSENSITIVE POLY(VINYL ALCOHOL) GELS
BY PHOTOGENERATED CROSSELINKS

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ABSTRACT

Poly (vinyl alcohol) with pendent styrylpyridinium groups (SbQ) is insolubilized on photoirradiation. Swelling behavior of PVA-SbQ gels prepared by the photocrosslinks was investigated by the experiments of swelling in water or acetone and the water diffusion coefficient in the gel, the dynamic modulus, and DSC measurements. The proportion of the free water to the bound water in PVA-SbQ gels was 3.3-2.9 despite the large change in conversion, x=0.27-0.58, of SbQ groups. The values of the water uptake after swelling of the gels in water increased 6-27 times compared to the original weight at pH=7. The higher the degree of photocrosslinks, the lower was the degree of swelling. The water diffusion coefficients, D, were (2.2-5.8)x10^-6 cm^2 s^-1 for 88% saponified PVA with 1.3 mol% SbQ groups. The volume of a gel increases discontinuously about 10-fold for the 99% saponified PVA with 0.096 mol% SbQ in a polymer chain at 51% water (49% acetone). The acetone concentration at the transition shifts higher with increasing the degree of saponification of the PVA.

INTRODUCTION

Gels are known to undergo reversible and discontinuous volume changes in response to the changes in solvent composition, temperature, pH, salt concentration, etc. In recent years, hydrogels have become one of polymer materials that can absorb a significant amount of water while maintaining its structural integrity. Hydrogels have received attention for soft contact lenses, for medical therapeutics and diagnostics, and for drug-delivery devices. In particular, it is known that an aqueous poly(vinyl alcohol) (PVA) gel is essentially stable at
Photodimerization or PVA-SbQ. It has been well-known that PVA with pendent styrylpyridinium (SbQ) group is insolubilized on photocrosslinking by cyclodimerization (Fig. 1). This water-soluble polymer exhibits extremely high photosensitivity, even though the content of SbQ groups attached to the PVA chain is very low. The systematic investigation of PVA-SbQ has been performed by Ichimura et al.\(^5\-7\). In the present work, swelling behavior of PVA or PVA-SbQ gels was investigated by the changes in the environment conditions such as pH and solvent composition, the water diffusion coefficient in the gel, and the analysis of water in the gel.

**EXPERIMENTAL**

Photosensitive poly(vinyl alcohol) (PVA-SbQ) by acetalization with formylstyrylpyridinium (FSbQ) (0.096-1.75 mol% in polymers) were prepared to the according to the known method\(^5\). 99% and 88% saponified PVA's (M: 16,000, 86,000) were purchased from Scientific Polymer Products, Inc. and used without further purification. Partially saponified PVA (DP: 1,700, hydrolysis of 88%) with FSbQ 1.3 mol% in polymer was supplied from Toyo Gosei Kogyo Co., Ltd. and used as received. The sample solution was irradiated by a 450 W high-pressure Hg lamp (Ushio UM-452) or a 2 kW Xe lamp (JASCO CRM-MA Type) for 1-7 hours at 13-15 wt% polymer concentration. The disk-shaped gels having 40 mm in diameter and 3 mm in thickness were produced, and also they were prepared by the freezing(-20°C)-thawing (25°C) process. The disk-shaped gels cut in some specimens were swollen to the equilibrium condition on standing in water. Then the weight or dimension changes of gels was measured.

The content of SbQ groups in a polymer and the extent of cyclodimer formation of SbQ groups were evaluated from the change in the optical density at 342 nm in U.V. spectra (Hitachi 200-10 Type spectrophotometer), and by the disappearance of the 1635 cm\(^{-1}\) C=C absorption in I.R. spectra taken with a JASCO FT/IR-5300 Type spectrometer. The mechanical properties of gels were evaluated by dynamic viscoelasticity measurements (Rheology
MR-500 Type) at 1 Hz frequency. The differential scanning calorimetry (DSC) measurement on the gels was performed using Mac Science Thermal Analyzer System 001. The gel samples were sealed between two pans using a pancriper, and heated at a rate of 5.0 deg min⁻¹ in N₂ gas.

RESULTS AND DISCUSSION

1) Swelling and Shrinking of Gels

In the photocrosslinking reaction of PVA-SbQ (99% saponified, M : 86,000) in the aqueous solution. Fig. 2 shows the effects of the initial polymer concentration and the amount of SbQ groups in a polymer on the formation of gels. For the experiment of some highly concentrated aqueous solutions ([C] = 25-200 g dm⁻³) of PVA-SbQ (0.1-1.75 mol%), the resulting stable gels have several intermolecular crosslinks, and are transparent and homogeneous in appearance.

For the 13 wt% aqueous solution of partially saponified PVA with SbQ (1.3 mol%), the gels produced after five freezing(-20°C×24h)-thawing(25°C×24h) cycles can not hold their own weight. However, the stable gel is formed even when polymer solution is irradiated for 2h, i.e., the number of SbQ groups for crosslinks per polymer chain is about 6 units. Fig. 3 shows the pH dependence of the swelling of gels after immersing in water at an equilibrium state. The pH is controlled by adding the appropriate amount of aqueous NaOH or HCl. The weight of swelling gels, W, has been normalized with respect to the weight of gels, W₀, before immersing in water. The value of the water
uptake after swelling of gels in water has the maximum in the vicinity of pH 7. It was found that the higher the degree of photocrosslinks, the lower was the degree of swelling. Fig. 4 shows the dependence of the values of $W/W_0$ on the extent, $x$, of photodimerization of SbQ groups. The extent of swelling decreases linearly with increasing the conversion of SbQ groups, and eventually it approaches one point at $x = 0.56$, that is, at 12 units whose the number of SbQ groups for photocrosslinks per polymer chain.

The gel immersed in acetone-water mixtures exhibits a volume-phase transition which can be characterized by the effective SbQ groups in a polymer chain. Fig. 5 shows the relationship of acetone concentration to the swelling ratio, $V/V_0$. The quantity $V/V_0$ represents the ratio of the final network volume to initial network volume for the gels. For swollen gels $V/V_0 > 1$, whereas for shrunken gels $V/V_0 < 1$. For the photocrosslinked gel (88% saponified PVA with 1.3 mol% SbQ), a curve with a zero-slope inflection point first appears, and then the discrete transition are observed as the swelling of gels comes to equilibrium. The behavior of swelling and shrinking of gels differs from one another in the kinds of gels prepared by...
the photocrosslinking (R) or the freezing-thawing (F) or both (R/F). As shown in Fig. 6, photocrosslinked gel (R) in acetone-water mixtures shows a continuous change in equilibrium volume when the acetone concentration is changed. The volume change at the transition decreases gradually with the conversion of SbQ groups due to photocrosslinking. The acetone concentration at the transition shifts higher with increasing the degree of saponification of the PVA.

2) Water in Gels

It is widely accepted that the presence of the free and the intermediate and the non-freezing bound water exists in the hydrogel, respectively. But the presence of the non-freezing bound water cannot be recognized in the DSC curve because of its non-freezability or non-fusibility. The presence of a peak correspond to the intermediate water could not be recognized in the DSC curve for this experiment. The content of the non-freezing bound water was calculated by subtracting the content of the frozen water from the total content of water. For the freezing-thawing PVA gels, the content of free water increases as the low-temperature crystallization proceeds, the proportion of the free water to the bound water changes from 2.1 to 5.6. However, for the PVA-SbQ gels prepared by photocrosslinking, the values are 3.3-2.9, and is almost unchanged despite the large change in the extent of photocrosslinks of SbQ groups in a polymer as shown in Fig. 7. Fig. 8 represents the characteristic time, $\tau$, of the swelling gels as a function of the final diameter, $a(\tau=a^2/D)$. From the slope of the straight line we obtained the water diffusion coefficient, $D$, in the gels. The
results are listed in Table I. It is interesting to note that
the values of $D$ differ from one another in the process of
gelation or the extent of saponification of PVA. The value of $D$
decreases with increasing the number of freezing-thawing cycles.
This suggests that the gel has a more densified structure as the
low-temperature crystallization proceeds. As can be seen from
Fig. 9, the value of $D$ is a significant difference in 88% and
99% saponification. It was found that higher the degree of
saponification, the lower was the degree of the water diffusion
coefficient in the gel. For the photocrosslinked gels having 99%
saponification of PVA, the value of $D$ is almost dependent on the
conversion of SbQ groups due to photocrosslinking, however, for
88% saponified PVA-SbQ gels, it increases remarkably as the
conversion of SbQ groups proceeds. It is evident that the water
diffusion coefficients differ from one another in the network
structure of gels.

Fig. 10 shows the results of torque testing as a function of
the content of free water in the gels. For the PVA gel prepared
by the freezing-thawing or the PVA-SbQ gel by the photocross-
linking methods, the ratio of twisting moment to strain
decreases linearly with increasing the concentration of free water in the
gels at a similar total water content. On the contrary, the
ratio increases as the concentration of free water increases for
the PVA-SbQ gel prepared by the freezing-thawing process.
In conclusion, the resulting transparent and homogeneous macrogels in appearance consist of several intermolecular crosslinks per polymer chain. In spite of the large conversion, $x=0.27-0.58$, of SbQ groups, the ratio of the free water to the bound water in PVA-SbQ gels was $3.3-2.9$. It was found that higher the degree of saponification of PVA, the lower was the degree of the water diffusion coefficient in the gels. The PVA-SbQ gels undergo discrete, reversible transition in equilibrium volume with changes in solvent composition (acetone-water mixtures). The higher the degree of photocrosslinks, the lower was the degree of swelling in water, and stability and strength of the gels, on the contrary, increased with the extent of photocrosslinks.

REFERENCES
ABSTRACT

The production process of GMA includes the following five steps: 1. the neutralization of acrylic acid by alkaline solution; 2. the spray drying of sodium methacrylate (MANa); 3. the reaction between MANa and epichlorohydrin (EPC) by using phase transfer catalyst; 4. the washing process of obtained product with water in order to eliminate NaCl formed during the reaction; 5. the refinery distillation of GMA for separating EPC and sludge remained in the tower bottom; 6. the treatment of sodium chloride solution by using method of dilution with water and the sludge eliminated by burning. The productive capacity of GMA in above-mentioned Company is about 200-300 t/a.

INTRODUCTION

Glycidyl methacrylate (GMA) is an important difunctional monomer used in different domains of organic synthesis as well as in science and technology of macromolecular materials, in particular, for photochemical research and development. The molecular formula of above-mentioned monomer can be expressed as follows:

\[
\text{CH}_2 = \text{C} - \text{O} - \text{CH}_2 - \text{CH} - \text{CH}_3
\]

This monomer has been first commercialized in China recently by us. The productive capacity of GMA in above-mentioned Company is in the range of 200-300 t/a. The purity of GMA is about 97%.

EXPERIMENTAL

1. Materials

The materials involved in this process are methacrylic acid (MAA), epichlorohydrin (EPC), NaOH, PTC-LH (phase transfer catalyst), inhibitor-LH etc.
3. Industrial Process

3.1 The Production of Sodium Methacrylate

In a 1000L reactor with a stirrer was placed acrylic acid which was neutralized by alkaline solution of caustic soda. The reaction system was controlled between 6~8. After spray drying powdered sodium methacrylate MANa could be obtained. The moisture content of MANa was controlled within 1%.

3.2 Synthesis of GMA

The mixture of above described materials such as MANa, EPC, PTC-LH and inhibitor-LH, was placed respectively in 2000 L reactor equipped with a stirrer and reflux condenser. Then the mixture was heated under stirring at adjusted temperature. After several hours, when the reaction was completed, NaCl formed during the reaction was dissolved in added water and washed out from the reaction system.
3.3 The Treatment of Waste Water and Sludge.

The treatment of sodium chloride solution was used by method of dilution with water, and the sludge resulted in the bottom of the tower was eliminated by burning.

4. Analysis and Identification of GMA

The detecimation of GMA content in the end product was investigated by a SH-102g gas chromatography. The quantitative determination of epoxy group was carried out by hydrochloric acid-acetone method.

RESULTS AND DISCUSSION

1. Some Factors Affecting the Production of GMA

1.1 Formulation of Raw Materials.

The effect of the formulation of raw materials on GMA conversion is shown in Table 1.

<table>
<thead>
<tr>
<th>NO.</th>
<th>MANa/EPC</th>
<th>Conversion, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1/3</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>1/4</td>
<td>75</td>
</tr>
<tr>
<td>3</td>
<td>1/5</td>
<td>75</td>
</tr>
</tbody>
</table>

Therefore, No. 2 is the best formulation of raw materials to produce GMA.

1.2. Neutralization System

The neutralization of MAA using alkaline solution was completed in 1000 L enamel still with anchor agitator, the stirring speed of which is about 100 r/min, the temperature was controlled at 60°C by cooling water.

1.3. Spraying Siccity System of MANa

The spray dryer power was mainly determined by the input speed, input temperature as well as exit temperature of MANa solution. If 30% MANa solution is given to the siccity system, then the input speed is equivalent to 60 kg / h, the input temperature may be maintained at 300~320°C, and the exit temperature can be controlled at 100°C. The experimental results showed that the moisture content of MANa is less than 2%, the yield of MANa was more than 99%.

The spray dryer's capacity of the siccity system was about 100kgH₂O / h.

1.4. Reaction and Water-Washing System.

The resulted mixture was washed with water in order to eliminate NaCl formed in the reaction system.
The reaction and water-washing processes were completed in 2000L enamel still with blade-paddle mixer and reflux condenser, the cooling surface of which is equal to 6m². The stirring speed is about 130 r/min.

The duration of the reaction time between MANa and EPC in the presence of PTC-LH was about 3h, and the reaction temperature was maintained at 80°C.

1.5. Distillation System

All of the installation in this process are made of 1G 18Ni 9Ti. The capacity of this installation is 500 kg/h. The volume of distillation still is 1500L. The diameter of distillation tower is 500mm, the altitude of which is 10m. The column tray is large-hole screen plates, and the number of the plates is equal to 10.

1.6. Vacuum System.

In order to meet the requirements in production, we selected Type ZPB-3-II steam ejector vacuum pump, which consists of three stage ejectors and two inter-connected condensers. The ejectors of all stages are the same construction consisting of ejector nozzle, nozzle chamber, contraction and expansion pipes. This inter-connected condensers are surface type. The appropriate height of the steam ejector vacuum pump must be longer than 11m. The column top temperature is dependent on the degree of vacuum pressure.

The specification of the type ZPB-3-II steam ejector vacuum pump may be expressed as follows:

- Suction pressure: 0.67 Kpa
- Capacity: 15 kg/h
- Steam pressure: 0.6 MPa
- Cooling water temperature: <35°C
- Cooling water consumption: 15 m³/h
- Steam consumption: 400 kg/h

2. Purity and Epoxide Value of GMA

The purity and epoxide value are also important characteristics of GMA. Several samples of GMA obtained by us were analyzed and listed in Tab. 2

<table>
<thead>
<tr>
<th>No</th>
<th>Purity %</th>
<th>Epoxide Value (N/100g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>99.20</td>
<td>69.85</td>
</tr>
<tr>
<td>2</td>
<td>99.00</td>
<td>69.70</td>
</tr>
<tr>
<td>3</td>
<td>98.95</td>
<td>69.68</td>
</tr>
<tr>
<td>4</td>
<td>99.09</td>
<td>69.76</td>
</tr>
<tr>
<td>5</td>
<td>98.98</td>
<td>69.70</td>
</tr>
</tbody>
</table>
It's demonstrated through experiments that the content of GMA and its epoxide value are satisfied with the requirements of different users.

CONCLUSION

(1) Using MAA, EPC and NaOH as raw materials, GMA is commercialized in the presence of phase transfer catalyst-LH and inhibitor-LH. The process is relatively simpler with high yield of GMA. The quality level and the repetition rate of which is good enough.

(2) Through productive experiments the technological process of GMA is reasonable.

REFERENCES

THE SYNTHESIS OF BIS
[ 5—ALKYL—4—PHENYL—1,2,4—TRIAZOLE—3—YL ]
DISULPHIDE

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Department of Chemistry, Harbin Normal University,
Harbin 150080, P.R. China

ABSTRACT

The synthesis of Bis [ 5—alkyl—4—phenyl—1,2,4—triazole—3—yl ] disulphide was discussed in this paper. Two kinds of new disulphides have been synthesized by means of research and experiment:

1. Bis [ 5—butyl—4—phenyl—1,2,4—triazole—3—yl ] disulphide
2. Bis [ 5—amyl—4—phenyl—1,2,4—triazole—3—yl ] disulphide

The structure of these two new disulphides has been determined by Ultimate analysis, mass spectrographic analysis and infra—red analysis. Before now, we already synthesized three kinds of new series of disulphides which have good functions to prevent fog, fading and inhibit surface development, and can be used as additives of photographic materials. Thus we infer that these two new disulphides should have the functions as mentioned above. 

INTRODUCTION

Up to the present , there are about six oxidation methods to synthesize Bis [ 1,2,4—triazole—3—yl ] disulphide. they are: I₂, HNO₂, Br₂, HNO₃, Pb(oAc)₄, and electrolytic oxidation method. But every one has no strong oxidation regularity and the applications are also limited. With the development of the science and technology, the functions of Bis [ 1,2,4—triazole—3—yl ] disulphide are discovered continuously. Therefore we should take further steps to study the new synthesis methods, to enlarge the application range and to find out some oxidation methods that have strong regularity.

We have synthesized five new kinds of series Bis [ 5—alkyl—4—phenyl—1,2,4—tri—
azole-3-yl] disulphide and have had a tentative approach to their applications.

**EXPERIMENTAL**

1. **The synthesis of Bis [5-butyl-4-phenyl-1,2,4-triazole-3-yl] disulphide**

   Put 10g (0.06mol) 4-phenyl thiosemicarbazide and 80ml pyridine into three-mouth flask, stirred till dissolved and cooled to -9°C. 10.85g (0.09mol) amyl acyl chloride was dropped in for 1 hour. Kept the temperature at -7 - 9°C, Stirred for 3 hours. Added 300ml water, white crystal was deposited, filtered by Brinell funnel and dried it. m.p. 93.5°C - 95.5°C.

   Put the solid which you got into a flash added 70-80ml 10% NaOH, PH = 13 - 14, reflux for 2 hours, cooled, using HCL to acidify it to PH = 5 - 6. white crystal was deposited, filtered by Brinell funnel and recrystallized, output: 7.8g, yield: 55.8%, m.p. 132 - 134°C.

2. **The synthesis of Bis [5-butyl-4-phenyl-1,2,4-triazole-3-yl] disulphide**

   Put 0.466g (0.002mol) 5-butyl-4-phenyl-3-mercapto-1,2,4-triazole into a flask with 5ml alcohol, accommodated PH = 7.4 with NaOH, at 30°C, 0.8ml 20% H₂O₂ solution was dropped in for 5-10 min as stirring, kept the temperature for 0.5 hour, light yellow solution was obtained, added 4 - 5ml distilled water, the crystal was deposited, filtered by Brinell funnel, dried and recrystallized with 95% alcohol, output: 0.35g, yield: 75.4%, m.p. 98 - 100°C.

1. **The synthesis of Bis [5-amyl-4-phenyl-1,2,4-triazole-3-yl] disulphide**

   Put 10g (0.06mol) 4-phenyl thiosemicarbazide and 80ml pyridine into a flask and added 80ml pyridine, stirred and cooled to -3°C - -5°C, 12.1g (0.09mol) caprochloride was slowly dropped and at -3°C - -5°C reacted for 2 hours. then put the reactant into 350ml ice-water, the precipitate was separated out, filtered by Brinell funnel, moved it into 10% NaOH solution, accommodated the PH to 13 - 14, reflux for 2 hours, cooled, using HCL to acidify to PH = 6, white precipitate was obtained, filtered by Brinell funnel, recrystallized with alcohol, output: 4g, m.p. 136 - 137°C.

2. **The synthesis of Bis [5-amyl-4-phenyl-1,2,4-triazole-3-yl] disulphide**

   0.494g (0.002mol) 5-amyl-4-phenyl-3-mercapto-1,2,4-triazole was dissolved in 5ml alcohol, accommodated PH to 7 - 8. with base. At 30°C, 1ml 20% H₂O₂ was dropped, kept the temperature, reacted for 0.5 hour, stooded, yellow crystal was deposited, filtered by Brinell funnel, recrystallized with 95% alcohol, output: about 0.2g, yield: 40.7%.
RESULTS AND DISCUSSION

The oxidation method proposed from this research suits for direct oxidation of 5-alkyl-4-phenyl-3-mercapto-1,2,4-triazole. We oxidized 4-phenyl-5-phenyl-3-mercapto-1,2,4-triazole and 4-ethyl-5-ethyl-1,2,4-triazole, respectively, by H₂O₂ oxidation method. But the result was that the corresponding disulfide was not obtained.

The effect of the reaction conditions.

1. The effect of the concentration of oxidant

<p>| Table 1 | Bis [ 5-methyl-4-phenyl-1,2,4-triazole-3-yl ] disulfide |
| Condition: 25°C, reaction: 0.5 hour |</p>
<table>
<thead>
<tr>
<th>PH</th>
<th>Concentration %</th>
<th>H₂O₂ yield</th>
<th>6%</th>
<th>20%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
<td>31.6</td>
<td>23.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30.0</td>
<td>24.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.4</td>
<td>39.3</td>
<td>26.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>39.3</td>
<td>26.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.4</td>
<td>62.4</td>
<td>54.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>63.5</td>
<td>55.3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<p>| Table 2 | Bis [ 5-ethyl-4-phenyl-1,2,4-triazole-3-yl ] disulfide |
| Condition: 25°C, reaction: 0.5 hour |</p>
<table>
<thead>
<tr>
<th>PH</th>
<th>Concentration %</th>
<th>H₂O₂ yield</th>
<th>6%</th>
<th>20%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
<td>53.1</td>
<td>34.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>51.5</td>
<td>31.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.4</td>
<td>51.4</td>
<td>41.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>58.8</td>
<td>58.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.4</td>
<td>83.3</td>
<td>66.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>82.1</td>
<td>65.3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Table 3 | Bis [ 5-propyl-4-phenyl-1,2,4-triazole-3-yl ] disulfide |
| Condition: 30°C, reaction: 0.5 hour |

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Table 4 Bis [5—butyl—4—phenyl—1,2,4—triazole—3—yl] disulphide
condition: 30°C, reaction: 0.5 hour

<table>
<thead>
<tr>
<th>PH</th>
<th>Concentration</th>
<th>H₂O₂</th>
<th>6%</th>
<th>20%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
<td></td>
<td></td>
<td>48.2</td>
<td>55.0</td>
</tr>
<tr>
<td>6.4</td>
<td></td>
<td></td>
<td>52.8</td>
<td>82.6</td>
</tr>
<tr>
<td>7.4</td>
<td></td>
<td></td>
<td>69.0</td>
<td>89.4</td>
</tr>
</tbody>
</table>

The yield increased with increasing of H₂O₂ concentration. But when the concentration of H₂O₂ is high enough, you can't get the product you want. The suitable range of the concentration of H₂O₂ is 6%~20% (for oxidation).

2. The effect of the reaction temperature

Table 5 Bis [5—methyl—4—phenyl—1,2,4—triazole—3—yl] disulphide
Condition: 2.5ml, 6% H₂O₂
Reaction: 0.5 hour

<table>
<thead>
<tr>
<th>PH</th>
<th>Concentration</th>
<th>Temperature</th>
<th>25°C</th>
<th>30°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
<td></td>
<td></td>
<td>31.6</td>
<td>16.8</td>
</tr>
<tr>
<td>6.4</td>
<td></td>
<td></td>
<td>39.3</td>
<td>35.5</td>
</tr>
<tr>
<td>7.4</td>
<td></td>
<td></td>
<td>62.4</td>
<td>39.4</td>
</tr>
</tbody>
</table>
Table 6  Bis [ 5—ethyl—4—phenyl—1,2,4—triazole—3—yl ] disulphide
Condition: 2.5 ml, 6% H₂O₂
Reaction: 0.5 hour

<table>
<thead>
<tr>
<th>PH</th>
<th>Temperature</th>
<th>20°C</th>
<th>25°C</th>
<th>30°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
<td></td>
<td>4.9</td>
<td>53.1</td>
<td>24.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.3</td>
<td>51.5</td>
<td>32.3</td>
</tr>
<tr>
<td>6.4</td>
<td></td>
<td>14.7</td>
<td>51.5</td>
<td>42.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.8</td>
<td>58.8</td>
<td>43.1</td>
</tr>
<tr>
<td>7.4</td>
<td></td>
<td>17.2</td>
<td>83.3</td>
<td>45.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>22.1</td>
<td>82.1</td>
<td>44.8</td>
</tr>
</tbody>
</table>

Table 7  Bis [ 5—propyl—4—phenyl—1,2,4—triazole—3—yl ] disulphide
Condition: 2.5 ml, 6% H₂O₂
Reaction: 0.5 hour

<table>
<thead>
<tr>
<th>PH</th>
<th>Temperature</th>
<th>25°C</th>
<th>30°C</th>
<th>40°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
<td></td>
<td>18.3</td>
<td>48.2</td>
<td>25.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20.6</td>
<td>45.9</td>
<td>23.9</td>
</tr>
<tr>
<td>6.4</td>
<td></td>
<td>16.1</td>
<td>52.8</td>
<td>48.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>13.8</td>
<td>55.0</td>
<td>45.9</td>
</tr>
<tr>
<td>7.4</td>
<td></td>
<td>31.4</td>
<td>69.0</td>
<td>52.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>32.2</td>
<td>71.1</td>
<td>50.5</td>
</tr>
</tbody>
</table>

Table 8  Bis[ 5—butyl—4—phenyl—1,2,4—triazole—3—yl ] disulphide
Condition: 2.5 ml, 6% H₂O₂
Reaction: 0.5 hour

<table>
<thead>
<tr>
<th>PH</th>
<th>Temperature</th>
<th>30°C</th>
<th>35°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
<td></td>
<td>51.7</td>
<td>22.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50.6</td>
<td>19.5</td>
</tr>
<tr>
<td>6.4</td>
<td></td>
<td>60.3</td>
<td>23.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>62.5</td>
<td>23.7</td>
</tr>
<tr>
<td>7.4</td>
<td></td>
<td>71.1</td>
<td>39.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>64.7</td>
<td>40.9</td>
</tr>
</tbody>
</table>

The yield decreased with the increasing of the temperature. But you can't obtain the
product when it was under 25°C. The suitable reaction temperature is about 30°C.

三、A test for preventing fog of white—black photographic material

Prescription for developer solution: DK-50 film, Taihang brand 27 white—black constant high speed film. Per liter solution, add 6ml 2% benzotriazole and Bis [5—propyl—4—phenyl—1,2,4—triazole—3—yl ] disulphide in CH₃CH₂OH solution, respectively. Developing time: 15min under 30°C, 10min under 38°C. It's advantageous for sensitizing developer to use the high temperature development, It can increase photosensitivity 1.5~2 times and also increase contrast and density a lot.

### Photographic Property of Benzotriazole

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Photosen—sitivity</th>
<th>Fog</th>
<th>Contrast</th>
<th>Maxinus—density</th>
<th>Optical Wedge Value at all Levels density</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>29</td>
<td>0.6</td>
<td>1.36</td>
<td>3.44</td>
<td>0.66 0.72 0.84 1.0 1.24 1.38 1.61 1.77 2.03</td>
</tr>
<tr>
<td>38</td>
<td>31</td>
<td>0.8</td>
<td>1.52</td>
<td>3.78</td>
<td>0.84 0.88 0.93 1.0 1.12 1.27 1.52 1.75 2.0</td>
</tr>
</tbody>
</table>

### Photographic Property of Bis [5—Propyl—4—Phenyl—1,2,4—triazole—3—yl ] disulphide

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Photosen—sitivity</th>
<th>Fog</th>
<th>Contrast</th>
<th>Maxinus—density</th>
<th>Optical Wedge Value at all Levels density</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>30</td>
<td>0.51</td>
<td>1.43</td>
<td>3.51</td>
<td>0.52 0.52 0.54 0.55 0.61 0.67 0.79 0.93 1.13 1.34 1.61 1.81</td>
</tr>
<tr>
<td>38</td>
<td>33</td>
<td>0.71</td>
<td>1.52</td>
<td>3.87</td>
<td>0.72 0.75 0.81 0.92 1.0 1.17 1.25 1.31 1.45 1.88 2.15</td>
</tr>
</tbody>
</table>

四、A test for preventing white—black photographic material from yellowing and fading standard density after thorough water washing

<table>
<thead>
<tr>
<th>Density before stabilization</th>
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<td>1.9</td>
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<table>
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<th>Density after H₂O₂ Processing</th>
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<table>
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<tr>
<th>Density after Bis [5—propyl—4—phenyl—1,2,4—triazole—3—yl ] disulphide processing</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.8</td>
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</table>
The results indicate that the dissolving property of Bis [5—propyl—4—phenyl—1, 2,4—triazole—3—yl] disulphide is good and the effect of protecting from yellowing and fading is better.

CONCLUSIONS

The \( \text{H}_2\text{O}_2 \) oxidation method which we used in our study suits for synthesizing Bis [5—alkyl—4—phenyl—1,2,4—triazole—3—yl] disulphide. It has several advantages; easy to operate, strong regularity, less by-products and lower price of the reagents. It is a comparatively ideal synthesis method.

Because of the time, some data haven’t been finished. The work is still going on.

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MASS SPECTRUM
SAMPLE: BIS(5-methyl-4-phenyl-1,2,4-triazole-3-yl)disulphide
FILE: J205 -JMK (2) SCAN NO. 70 TO 78; TX 30; SP 190-933.7
PEAKS 250(1); RANGE 10 TO 450(10 TO 450); LEVEL 0(0)

MASS SPECTRUM
SAMPLE: BIS(5-ethyl-4-phenyl-1,2,4-triazole)disulphide
FILE: K37F0896-PML (4)
(3) 138.08/260.927 258(21.37); 240; TX 30; RP 132-990.8
PEAKS 254(4); RANGE 10 TO 800(10 TO 500); LEVEL 0(1)
**Mass Spectrum**

Sample: Bis(5-propyl-4-phenyl-1,2,4-triazole-3-yl) disulphide

**File:** T205, ABD (0...)

1115/64 1000 44 (1.00) TS 30, RP 219-51.5

Peaks: 112(0), RANGE 10 TO 600(10 TO 600), LEVEL 0(0)

![Mass Spectrum Graph]

**Mass Spectrum**

Sample: Bis[5-amy|1-4-phenyl-1,2,4-triazole-3-yl] disulphide

**File:** T205, ABD (0...)

1115/64 1000 44 (1.00) TS 30, RP 219-51.5

Peaks: 112(0), RANGE 10 TO 600(10 TO 600), LEVEL 0(0)

![Mass Spectrum Graph]
PHOTOPOLYMERIZATION OF LINEAR
AND HYPERBRANCHED POLYESTERS

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ABSTRACT

In a previous paper the preparation and modification with epoxy-methacrylate, methacrylic anhydride of
hyperbranched aromatic polyesters with structural symmetry, high degree of branching and high density of
terminal functionality have been described. The flow time of the hyperbranched methacrylated polyesters
was compared with epoxy acrylate-modified unsaturated polyester of linear type, and shown that the flow
time for the former is only a third of that for the latter. The resulting hyperbranched polyester resins have
high photocure rate than linear unsaturated polyester and form crosslinked polymers containing amounts
of residual unsaturation which are on an acceptable level compared with conventional linear acrylate
oligomers by addition of benzildimethylketal (Irgacure 651) as photoinitiator and trimethylolpropane
triacrylate (TMPTA) as comonomer. The addition of 10 to 40 wt% TMPTA had only small effects on the
mechanical properties of glass fiber-reinforced laminates except the tensile strength which decreased
about 15%.

Keywords: hyperbranched polyester, (meth)acrylated epoxy resin, unsaturated polyester, radiation
curing, photocrosslinking, glass fiber-reinforced plastic laminate.

INTRODUCTION

The principal components of a radiation-curable resin are oligomers (or prepolymers) and
comonomers. The oligomers constitute the backbone of the three-dimensional polymer network formed
by curing. Important types of oligomers commonly used for coatings are acrylated epoxies, acrylated
polyurethanes, unsaturated polyesters and acrylated polyesters (or polyethers) which give desired
properties of the final cured films. However, those oligomers usually consist of linear molecular chains.
The viscosity of the resin increases rapidly with increasing chain length of the oligomer. To obtain an
operational viscosity of the formula for coating, inks, adhesives and laminations, large amounts of
multifunctional comonomer are required for the primary function of viscosity-control. In addition, the
comonomers have important effects on the cure reaction and the properties of the final product. Some of
the comonomers have low cure rate, cause shrinkage of the film during curing, high cost or limited shelf
life. Multifunctional acrylates are the preferred comonomers in radiation-curable systems because of their
rapid curing rates and low prices. The common acrylate monomers are volatile and toxic, and have strong
odour. Therefore, the trend is to use radiation-curable oligomers with viscosity close to the required
application viscosity in order to reduce or eliminate the use of comonomers.

In a previous article we have synthesized hyperbranched methacrylated polyesters for radiation
curing. These modified hyperbranched polyesters containing about 8, 12 and 16 double bonds per
oligomer molecule, designated as D-1, D-2 and D-3, respectively, have low viscosity, high curing rate,
and high degree of curing containing amounts of residual unsaturation which are on an acceptable level
compared with conventional linear acrylate oligomers. Compared with conventional linear type the
hyperbranched polyesters have a three-dimensional molecular architecture and starburst topology, which
cannot form entanglement of the molecular chains. Each hyperbranched molecule carries a high number
of terminal functional groups.

This work describes the differences in molecular structure, viscosity and photopolymerization kinetics
between the linear and hyperbranched polyesters, and also compares the mechanical properties of UV
cured epoxy acrylate-modified and thermally cured styrene-containing unsaturated polyester laminates.

EXPERIMENTAL

Materials

Three hyperbranched methacrylated polyesters were prepared from pentaerythritol and 1,2,4-
benzenetricarboxylic anhydride, and end-capped by glycidyl methacrylate and methacrylic anhydride via
controlled stepwise divergent preparation, i.e., the synthesis started at the center of the hyperbranched
polyester. At least two steps were needed to obtain hyperbranched polyesters numbered D-1, D-2 and D-
3 with about 8, 12 or 16 terminal methacrylic double bonds, respectively, located at surface of the
oligomeric sphere, as shown in Figure 1. The idealized formula of the polyester with 16 double bonds is
shown in Figure 2.

![Fig. 1 Reaction scheme for the synthesis of the hyperbranched polyester (B: hydroxyl groups; C: carboxyl groups; D: unsaturated groups).](image)

![Fig. 2 Idealized formula of the hyperbranched polyester with 16 double bonds.](image)
The epoxy acrylate-modified unsaturated polyester (MUP) was synthesized from fumaric acid, phthalic anhydride, propylene glycol and neopentyl glycol by standard azeotropic polycondensation technique to a molecular mass of about 2200, with the formula as follows:  

\[
\begin{align*}
\text{H}_2\text{C}=\text{CH}-\text{C}=\text{O}-\text{H}_2\text{C}-\text{HC}-\text{H}_2\text{C} & \quad \text{Unsaturated} \\
\text{OH} & \quad \text{Polyester} \\
\text{CH}_2\text{CH}-\text{CH}_2\text{O}-\text{C}=\text{CH}=\text{CH}_2 \\
\text{OH}
\end{align*}
\]

The multifunctional comonomer added to the polyesters was trimethylolpropane triacrylate (TMPTA) (supplied by Aldrich, Germany). Benzilidimethylketal (BDK, Irgacure 651) from Ciba Geigy, Switzerland is used as photofragmenting initiator for curing the hyperbranched polyesters. The laminates in this investigation are made of modified hyperbranched polyesters and unsaturated polyesters (MUP) with multifunctional comonomer added and cured with mat of chopped E-glass fibers. The glass fiber mats were of randomly oriented chopped fibers bonded in mat form (450g/m²) (Scandinavian Glass Fiber AB). The polyester resins with 3% BDK and 15% TMPTA by weight were prepared as laminates with 35 wt% glass fiber mats.

**UV Curing**

A Fusion UV Curing Systems, Model F300 was used in this study. Unless otherwise stated, the curing was accomplished by passing the test samples under 300 W/in (120 W/cm) D bulb at variable conveyor speeds in air.

**Measurements**

**Flow Time**

Flow time of the resins with multifunctional comonomer TMPTA added was measured using a viscometric cup of number 68 for comparison of the viscosity of the hyperbranched polyesters with that of modified linear unsaturated polyester.

**Tack-free Time**

The coated test samples were irradiated in N₂ with a high-pressure mercury lamp (1 kW, HPM-15 from Philips, Holland) built into a UV-CURE device, constructed in our laboratory. The distance from lamp to sample was 100 mm. Tack-free time was evaluated as the irradiation time required to obtain completely tack-free state by lightly touching the surface with a cotton ball immediately after UV exposure.

**Conversion of Unsaturation**

The conversion of vinyl groups measured as residual unsaturation in the UV cured films were determined with a Perkin-Elmer 1725X FT-IR Spectrometer using the acrylic double bond (out of plane deformation vibration) at 810 cm⁻¹ by a base-line method. The spectra were normalized using the carbonyl peak at 1730 cm⁻¹ as internal standard to account for variations in sample thickness and instrument recording. The double bond content of the uncured formulation was defined as 100%.

**Mechanical Properties**

For tensile testing the specimen is clamped into a 100 KN INSTRON universal tester with a jaw separation of 50 mm. The specimen is extended at a rate of 0.5 mm/min to failure. For bending testing the specimen is loaded in a three-point holder with a 50 mm span and strained at a rate of crosshead motion of 0.2 mm/min. The Charpy impact strength is measured with a 1.67 Kg pendulum of 100 kgcm capacity to break unnotched specimens.
RESULTS AND DISCUSSION

 Structural Character and Viscosity

An important structural difference between linear oligomers and hyperbranched polyesters is that a linear oligomer of sufficient molecular weight contains an entanglement of flexible molecular chains, while a hyperbranched polyester is a compact molecule with many branches which carry a high number of terminal functional groups on each molecule. The generalized structures of conventional oligomers with acrylate functions at the end groups of the backbone which is mainly a polyester, epoxy resin, or a urethane polyester, and with vinylene double bonds at the middle chain, which is an unsaturated polyester are shown in Figure 3.

The principal difference of viscosity between the branched and linear polyester molecules lies in the smaller spatial extension of the branched molecule at a given molar mass (Figure 4). It can be considered from Figures 2 to 4 that the segment density within the volume occupied by a hyperbranched molecule in solution is higher than for a linear molecule with the same number of monomer units, as indicated in literature.

The viscosity of the resin is related to the dynamic extension in space and the segment density within the volume of the molecule. Therefore, the sphere-like starburst polyester has lower viscosity than a corresponding linear polyester. Flow time measurements are an evaluation of the relative viscosity of various coating and adhesives, using a viscometric cup which is common practice in industry. The viscosities of the hyperbranched methacrylated polyesters containing 15 wt% TMPTA with MUP
containing 35 wt% TMPTA at 21 °C are compared in Figure 5. It can be seen that the flow times through the viscometric cup for hyperbranched polyester resins are three times shorter than MUP resin. This means that the viscosity of MUP is three times higher than hyperbranched polyester. A practical consequence is that the processibility of hyperbranched polyester-containing resins is improved due to their lower viscosities.

**Residual Unsaturation**

It is well known that complete conversion of unsaturation is never obtained in UV curing of acrylate polyester systems, especially when multifunctional monomers are used.\(^5\)\(^6\) There are numerous reports showing that about 30% unreacted C=C double bonds remain in acrylate prepolymer films after UV curing. The residual unsaturated groups will further react, e.g., with oxygen which is a source of aging of the end products. In the case of the hyperbranched polyesters, there are more terminal acrylate double bonds on each molecule than in conventional linear polyesters. Therefore, the investigations of the rate and the final degree of polymerization for the hyperbranched polyester resins are very significant for the end uses.

The decrease of the IR absorption band (out of plane deformation vibration) at 810 cm\(^{-1}\) as a function of the irradiation time allows an evaluation of the number of methacrylic double bond in the resin during curing. The residual unsaturation in the cured resins of hyperbranched polyester D-1, D-3 and MUP containing 20% TMPTA and 4% photoinitiator, as a function of irradiation time with a 2 kW, HPM lamp in N\(_2\) is shown in Figure 6. The conversion of methacrylic double bonds in the cured films of hyperbranched polyester reaches the same level as the conventional linear acrylated polyester system. The lower conversion of the resin with D-3 can be interpreted as due to reduced mobility and accessibility of the reactive groups with increased functionality of the hyperbranched methacrylated polyester molecules, i.e., some residual methacrylate double bonds will be trapped in the three-dimensional polymer matrix formed and unable to react.\(^7\) A more compact network of crosslinked polymer is expected at higher crosslinking density of the cured resin. As a result, the conversion of double bonds in resin system with high functionality of the polyester molecules is lower.

![Fig. 5 Flow time of hyperbranched polyesters and MUP using viscometric cup.](image1)

![Fig. 6 Residual unsaturation in the cured films of D-1 and D-3 resins compared with film of MUP resin.](image2)

In order to compare the UV curing rate of hyperbranched polyesters with conventional linear polyesters, the tack free times for hyperbranched polyester resins with D-1, D-3, and MUP, all with 20% wt% TMPTA, were measured using the high-pressure mercury lamp (1 kW) (Figure 7). The curing time of
Hyperbranched polyesters is only a third of that of MUP. The hyperbranched polyesters have a high number of functional groups on each molecule, resulting in higher curing rate than resins of the linear polyester (MUP) which has only two acrylate double bonds per molecule. The maleate double bonds in the middle of the chains of the molecule are much less reactive than the vinyl groups, which explains the low curing rate.

![Tack-free time graph]

**Fig. 7** Tack-free time of the cured films of hyperbranched polyester resins with D-1 and D-3 compared with that of MUP.

**Mechanical Properties of Laminates**

The tensile strength of the UV cured hyperbranched polyester laminates and the MUP laminate (dotted line), as a function of the comonomer TMPTA added shows different behavior (Figure 8). The tensile strength of the laminates with the three hyperbranched polyesters decreases rapidly with increased amounts of comonomer added while the tensile strength of cured MUP laminate increases to an optimum at about 30% TMPTA. The decrease of the tensile strength of the laminate due to addition of comonomer to the resin matrix implies that the added comonomers are largely cured as a separate aliphatic phase of low strength surrounding the aromatic hyperbranched molecules. For the MUP system, the rate of photocrosslinking can be enhanced by the addition of TMPTA. It can be interpreted that
comonomer TMPTA added is copolymerized firstly with acrylic double bonds at chain ends of MUP polyester and homopolymerized, and then copolymerized with vinylene groups of MUP after a extra amount of comonomer is added, which largely improve the tensile properties of the cured laminates. The same is true for the impact strength after addition of various amounts of comonomer (Figure 9). For the MUP resin, addition of comonomer gives a considerable increase in impact strength which can be explained as the same reson with the tensile strength changes with comonomer added (Figure 8).

Comparison with Thermally Cured UP and UV Cured MUP Laminates

The mechanical properties of laminates with three kinds of cured oligomer resins are shown in Figure 10. "Thermal" refers to a maleate-based unsaturated polyester with styrene added (35 wt%), cured by heating to 80°C for 3 hours and then to 40°C for 30 hours. "MUP" refers to maleate-based unsaturated polyester, modified with epoxy-acrylate, cured by UV irradiation for 10 seconds in UV-CURE at room temperature. "DP" refers to the hyperbranched polyester D-3, modified with epoxy-acrylate and methacrylate anhydride, cured in a Fusion system for 0.10 seconds at room temperature. To the resins "MUP" and "DP" 3 wt% BDK was added. The three resins were cured as laminates with 35 wt% glass fiber mats added. It can be clearly observed that the recently developed hyperbranched polyester laminate (DP) has same level of mechanical properties as the thermally cured and UV cured unsaturated polyester laminates. However, the hyperbranched polyester system was photocrosslinked at much higher speed than the others, especially the thermally cured resin system.

![Comparison of mechanical properties](image)

Fig. 10 Comparison of mechanical properties of the cured hyperbranched polyester with thermally cured UP and UV cured MUP laminates. TS: Tensile strength; TM: Tensile modulus; FS: Flexural strength; FM: Flexural modulus; IS: Impact strength.

CONCLUSIONS

Starburst hyperbranched oligomers endcapped with methacrylic groups have low viscosity which is a function of the functionality of the polyester due to their hyperbranched structure. The flow time for hyperbranched polyesters is only a third of that for epoxy acrylate-modified UP of linear type. The addition of 10 to 40 wt% multifunctional monomer trimethylolpropane triacrylate has small effect on the curing efficiency after prolonged UV irradiation. The mechanical properties of the UV cured laminates with hyperbranched polyesters are comparable with the thermally cured UP and UV cured MUP laminates.
The hyperbranched polyesters have low viscosity and much higher curing rate than corresponding linear UPs and are, therefore, of great interest for industrial applications.

REFERENCES


MECHANISMS OF PHOTOCROSSLINKING OF LOW DENSITY POLYETHYLENE

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ABSTRACT: ESR combined with spin-trapping technique and NMR spectroscopy have been successfully applied to study the mechanisms of photoinitiated crosslinking of low density polyethylene (LDPE). The ESR studies for LDPE and its model compounds show that photoinitiated radical intermediates are of tertiary, secondary, and primary carbon types formed by hydrogen abstraction of the excited triplet state of benzophenone (BP) as photoinitiator. The evidence show that the photocrosslinking of LDPE mainly takes place at both tertiary carbons (branch point) and secondary carbons, especially allylic carbons when available. The solution-state ¹³C NMR studies show that crosslink structures are of H-type crosslinks and Y-type long branches, which are formed by different mechanisms. The former involves radical combination of the primary alkyl and allyl radicals; the latter probably involves addition reactions of the above radicals to vinyl end groups presented in LDPE chain. Photolysis products of BP (PPB) in the photoinitiated crosslinking of LDPE model compounds are also observed by ¹H NMR. The results show that benzpinacol and a small amount of α-alkylbenzhydrols are formed by recombination of two diphenylhydroxymethyl ketyl radicals and by the reactions of ketyl radical and alkyl radical, respectively. These results provide new experimental evidence for elucidating the mechanism of photocrosslinking of LDPE.

Keywords: low density polyethylene, UV irradiation, crosslinking mechanism, ESR, and NMR.

INTRODUCTION

Photocrosslinking of high-density (HDPE), linear low-density (LLDPE), and branch low-density polyethylene (LDPE) in the presence of benzophenone (BP) or its derivatives as a photoinitiator and multifunctional monomer as a crosslinker has been extensively studied for many years.¹-¹⁴ These photochemical method has led to recent technical and industrial applications for manufacturing of crosslinked PE-insulated wire and cable.¹²-¹⁴ However, many basic problems still remain unsolved. For instance, the mechanism of photoinitiated crosslinking, including identification of chemical species responsible for crosslinking reactions as well as the nature of crosslink structures, has not been elucidated yet. On the other hand, the fate of BP as a photoinitiator in the photoinitiated crosslinking of polyethylene, i.e. photolysis products of BP (PPB) has not understood completely. In this paper are presented the mechanisms of photoinitiated crosslinking of LDPE studied by ESR spectroscopy combined with spin-trapping technique and high-resolution solution-state NMR spectroscopy using LDPE model compounds of low molecular weight.
DETECTION AND IDENTIFICATION OF RADICAL INTERMEDIATES

1. Spin-Trapping Reactions from LDPE/BP/BNB

The photoinitiated radical reactions of LDPE have been studied by ESR combined with spin-trapping technique using 2,4,6-tri-tert-butyl nitrosobenzene (BNB) as a spin-trap. BNB has two trapping sites, one on the nitrogen to attach a nonbulky radical to form a nitroxide spin-adduct and another on the oxygen atom of the nitroso group to attach a bulky group to form an anilino spin-adduct\textsuperscript{15-16}, as shown in formula 1. It is possible to distinguish between the anilino and the nitroxide radicals from the differences in the g values and the nitrogen splitting constants.

\[
\begin{align*}
\text{BNB} & \quad \text{Radical} \\
\text{Nitroxide spin-adduct} & \quad \text{Anilino spin-adduct}
\end{align*}
\]

The ESR spectrum observed for the LDPE/BP/BNB system in the melt after UV irradiation for 5 min at room temperature is shown in Figure 1. The spectrum consists of two different components, marked I\textsubscript{B} and II\textsubscript{B} in Figure 1.

\[
\begin{align*}
\text{g} &= 2.0039 \\
J & = 10.3 \text{G} \\
T & = 2.0 \text{G}
\end{align*}
\]

**Figure 1.** ESR spectrum observed at 393 K after UV irradiation (5 min) of an LDPE/BP/BNB sample at room temperature. The stick diagrams, I\textsubscript{B} and II\textsubscript{B}, are spectra of the spin-adducts of tertiary carbon and secondary carbon radicals, respectively.

Component I\textsubscript{B}, which is a triplet of triplets originating from couplings with the single nitrogen (\(J^N = 10.3 \text{ G}\)) and with two meta protons (\(J^H_m = 2.0 \text{ G}\)) of the phenyl group in BNB, is assigned to an anilino-type spin-adduct (I\textsubscript{B}), as shown in formula 2, because the observed g factor (g = 2.0039) is close to the value of the anilino radical reported in the literature.\textsuperscript{17} The spin-adduct I\textsubscript{B} is positive evidence for the presence of the tertiary carbon radical I in the UV-irradiated LDPE which contains a tertiary hydrogen at every branch point.

\[
\begin{align*}
\text{Radical} + \text{BNB} & \rightarrow \text{Spin-adduct I} \\
\text{I (I\textsubscript{B})}
\end{align*}
\]
Another component, II_B, which appears as a double triplet, is attributed to a nitroxide-type spin-adduct (II_B), as shown in formula 3, because its splitting constant with β-H ($a^N_{\beta} = 20.5$ G) and its g factor ($g = 2.0063$) are the characteristic values for the nitroxide adduct. The spin-adduct II_B is assigned to the secondary carbon radical II. These assignments are supported by the characteristic behavior of BNB as a spin trap: a bulky radical is trapped by BNB to form an anilino-type spin-adduct but a non-bulky group is trapped as a nitroxide-type spin-adduct.

$$\text{(3)}$$

2. Spin-Trapping Reactions from MD/BP/BNB

Commercial LDPE polymers usually contain small amount of unsaturated bonds (either as end groups or inner groups) in addition to branch points and paraffin chain segments. The following three kinds of model compounds (MD) have been used in this study: n-paraffins n-C_{24}H_{50} and n-C_{12}H_{26}, branched hydrocarbons isooctane and 3-ethylhexane, and unsaturated hydrocarbons containing allylic hydrogen, 1-hexene, cis- and trans-3-hexene.

**n-Paraffins.** The ESR spectrum for n-C_{24}H_{50}/BP/BNB obtained at 325 K after UV irradiation for 4 min at room temperature and in vacuum (10^{-4} Torr) is shown in Figure 2A. The spectrum contains four components A-D represented by the stick diagrams in Figure 2A. These components are assigned to the anilino or nitroxide spin-adducts A-D, respectively, as shown in Figure 2B.

![Figure 2](image.png)

**Figure 2.** (A) ESR spectrum recorded at 325 K from the n-C_{24}H_{50}/BP/BNB system, UV-irradiated and measured at $1 \times 10^{-4}$ Torr and room temperature; (B) Spin-adducts A-D assigned.

The spin-adducts A and B represent two types of tertiary carbon radicals formed by hydrogen abstraction, which originates from crosslinked dimers of two C_{24}H_{50} molecules. The spin-adduct C, having either an anilino- or a nitroxide-type structure, is assigned to a secondary carbon radical generated by hydrogen abstraction from the CH\textsubscript{2} segments of the model molecule. The spin-adduct D is assigned to the small amount of chain end methylene radicals formed by hydrogen abstraction from methyl end groups, which has not been detected from the LDPE/BP/BNB system. However, it can be seen from the spectral intensities of various components in Figure 2A that the main signal is tertiary carbon and secondary carbon radicals.

The ESR spectrum of the spin-adducts from n-C_{12}H_{26}/BP/BNB at room temperature, recorded after UV irradiation for 5 min is almost the same as that of n-C_{24}H_{50}/BP/BNB and is assigned to radicals shown in Figure 2B. Based on the above analysis, there are two main photoinitiated reactions from n-paraffins: (i) The excited triplet state $^3$(BP)* first abstracts hydrogen from methylene groups to form the $^•\text{-CH}_2$- radicals. (ii) After combination of these radicals, the $^3$(BP)* further abstracts labile tertiary hydrogen to form tertiary carbon radicals.
Branched Hydrocarbons. Isooctane and 3-ethylhexane are used as MD for the branching units of LDPE chains. The two samples iso-octane/BP/BNB and 3-ethylhexane/BP/BNB were UV-irradiated at room temperature for 3-5 min in vacuum or N\textsubscript{2}. Figure 3 presents the ESR spectrum of iso-octane/BP/BNB sample. The main component is a triplet of triplets due to the nitrogen (10.2 G) and the two meta hydrogens (2.0 G) of the phenyl group in the anilino-type spin-adduct, assigned to the tertiary (\(\cdot\text{C} = \cdot\)) radical formed by H-abstraction from a tertiary bonded hydrogen (>CH\textsubscript{3}). The weaker spectral component is assigned to a primary radical \(\cdot\text{CH}\textsubscript{2}\cdot\) formed by hydrogen abstraction from one of the five methyl groups of isooctane. The spectral component is a triplet of triplets of small triplets assigned to nitrogen (13.8 G), the two methylene hydrogens (17.9 G), and the two meta hydrogens (0.8 G) of the phenyl groups in BNB with the spin trap in nitroxide form. Hydrogen abstraction from methyl groups would occur in measurable amounts due to the high concentration of methyl groups in isooctane. There is no indication of hydrogen abstraction from the CH\textsubscript{2} group in isooctane (Figure 3), probably due to steric hindrance of the five methyl groups.

![Figure 3. ESR spectrum of the iso-octane/BP/BNB system, irradiated with UV light under a nitrogen atmosphere.](image)

However, a very weak triplet (\(\alpha^N = 10.1\) G) of doublets (\(\alpha^H = 20.3\) G), have been detected from 3-ethylhexane/BP/BNB system in this work, due to a radical formed by hydrogen abstraction from the CH\textsubscript{2} groups. The above results show that tertiary bonded hydrogen (>CH\textsubscript{3}) is easier to abstract in photocrosslinking with BP than are secondary (–CH\textsubscript{2}–) and primary bonded hydrogens (–CH\textsubscript{3}).

Unsaturated Hydrocarbons. Three kinds of unsaturated compounds, 1-hexene with a double bond at the end group and two with an inner double bond, cis- and trans-3-hexene, were used in this work. The ESR spectrum of a 1-hexene/BP/BNB sample, UV-irradiated for 3 min under nitrogen atmosphere, is shown in Figure 4. Only one spectral component is detected, a triplet of doublets with coupling constants 21.6 and 13.4 G with the g value 2.0061. It is assigned to spin-trapped allylic radicals. The broad lines of this spectrum (Figure 4) may be due to overlap of spin-trapped allylic and secondary carbon radicals, which have similar g values and hyperfine coupling constants.

![Figure 4. ESR spectrum recorded at room temperature for 1-hexene/BP/BNB UV-irradiated under a nitrogen atmosphere.](image)
The EPR spectra recorded for cis- and trans-3-hexene samples after UV irradiation in vacuum have also been studied in this work. The dominant spectral component is due to a spin-trapped allyl radical, a triplet of doublets of small triplets. There is good evidence for assignment of the main radical components to allyl radicals. The assignments of the minor spectral components for cis- and trans-3-hexene have been made with the evidence available.

PHOTONITIATED CROSSLINK STRUCTURES

1. Photoinitiated Crosslinks of n-C_{24}H_{50}

The structure of two C_{24}H_{50} samples with and without UV irradiation have been studied by 50.3 MHz solution ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum of the C_{24}H_{50} sample after irradiation with UV light in vacuum in the melt (70 °C) for 3 min is shown in Figure 5. The new peak, appeared at 41.32 ppm has been assigned to the chemical shift of H-type cross-links as reported for y-irradiation of n-paraffins and polyethylene. A very weak peak at about 39.7 ppm, as indicated by the arrow in Figure 5, may be due to the branches produced by photoinitiated cross-linking of n-C_{24}H_{50} sample. The number of cross-links in the C_{24}H_{50} samples irradiated by UV light in vacuum in the melt for 3–5 min are estimated to be 8.5 to 11.0 per 10 000 C atoms by the relatively integrated intensities.

Figure 5. 50.3 MHz ^{13}C NMR spectrum of n-C_{24}H_{50} sample in solution UV-irradiated for 3 min at 70°C in vacuum.

2. Photoinitiated Crosslinks in UV-irradiated LDPE Samples

The 100.6 MHz ^{13}C NMR spectrum of LDPE sample containing 1 wt% BP, irradiated by UV light at 140 °C for 5 s in vacuum and measured in 20 wt% in TCB/C_6D_6 (1/4) solution at 125 °C, is shown in Figure 6. The spectral assignments for the main components are given by comparing with the data of chemical shifts reported in the literature. The spectrum of the unirradiated LDPE sample in this work is very similar to that reported for LDPE by Bovey et al., but it has much better resolution than before. By comparison with the unirradiated LDPE sample, a new resonance line at 41.53 ppm, as shown by CH_3 in Figure 6, has been assigned to the H-links produced in the photoinitiated cross-linking of LDPE sample. The chemical shift of the H-links is in good agreement with those reported in the model compound, n-alkanes and polyethylene.
Figure 6. 100.6 MHz $^{13}$C NMR spectrum of LDPE sample UV-irradiated for 5 s in vacuum and measured in 20 % TCB/C$_6$D$_6$ solution at 125 °C. The nomenclature L, S, and B refer to long branches, saturated end groups, and short branches; the m, e, b, and a represent methyl, ethyl, butyl, and amyl groups, respectively; the Greek letter describes the position along the chain of the nearest substituent; the CH$_H$ and CH$_Y$ represent the H-links and Y-type branches produced by UV irradiation, respectively.

It is found from Figure 6 that the relative intensities of resonance lines associated with the long branches in the UV-irradiated samples, which are referred to as CH$_L$ at 37.71 ppm, a$_L$ at 34.10 ppm and b$_L$ at 26.84 ppm, are significantly increased by comparing with those of the unirradiated sample in this work. This indicates that the long branches produced by UV irradiation, which are called Y-branches or Y-links (CH$_Y$), are also formed in the photocrosslinked samples. The quantitative determinations by the relative integral intensity of the spectrum in this study show that the H-links and Y-branches are the same order in the XLPE samples. For the 5-10s irradiation time in vacuum or N$_2$, the numbers of H-links and Y-branches thus determined for three different irradiated LDPE samples are 5.7-16.9 and 7.6-21.6 per 10 000 carbon atoms, respectively.

Determination of PPB from LDPE Model Compounds

The 22.49 MHz $^{13}$C NMR spectrum of PPB obtained from n-C$_{24}$H$_{50}$/BP shows exactly the same as that of pure benzpinacol as a standard sample in the present study. The data of chemical shifts at 83.11 ppm from -OH group and at 144.28, 127.37, 128.67 and 127.00 ppm from the substituted-, o-, m- and p-carbons of benzene ring of benzpinacol, respectively, are in good agreement with those reported in the literature. The 500.13 MHz $^1$H NMR spectrum of PPB from n-C$_{24}$H$_{50}$/BP gives the evidence that the weaker peaks at 0.88-2.62 and 7.0-7.4 ppm may be due to various $\alpha$-alkylbenzhydrols, as reported in the literature. These studies show that benzpinacol and a small amount of $\alpha$-alkylbenzhydrols are formed by recombination of two diphenylhydroxymethyl ketyl radicals and by the reactions of ketyl radical and alkyl radical, respectively. The detail identification of PPB products have been presented in the separate paper of RadTech Asia '95 Conference Proceedings.
MECHANISM OF PHOTOINITIATED CROSSLINKING

Based on the above studies of radical intermediates, crosslink structures, and PPB products, the mechanisms of photocrosslinking of LDPE can be proposed as follows. When the photoinitiator BP absorbs a UV quantum and is excited to the singlet state and then rapidly relaxes to the more stable triplet state \(^3\)(BP)\(^*\), it can abstract hydrogen from the LDPE chain to form ketyl and polymer radicals:

\[
BP + h\nu \rightarrow (BP)^* \xrightarrow{k_c} (BP)^* \\
(BP)^* + PH \rightarrow (C_6H_5)_2C\cdot(OH)(K\cdot) + P\cdot \\
P\cdot + P\cdot \rightarrow P-P \text{ (crosslinking)} \\
K\cdot + K\cdot \rightarrow (C_6H_5)_2C(OH)(OH)(C_6H_5)_2 \text{ (benzpinacol)} \\
K\cdot + P\cdot \rightarrow P-K \text{ (\(\alpha\)-alkylbenzhydrol)}
\]

where \(P\cdot\) represents polymer radicals formed by hydrogen abstraction of the excited triplet state \(^3\)(BP)\(^*\) from the LDPE chain; Two polymer radicals \(P\cdot\) combine to form a crosslink; Two ketyl radicals (K\(\cdot\)) form a benzpinacol molecule, while a K\(\cdot\) radical may react with the polymer radical P\(\cdot\) to form \(\alpha\)-alkylbenzhydrol at the given conditions.

The P\(\cdot\) radicals have been identified as being mainly tertiary and secondary carbon radicals, including allylic carbon radicals in the presence of unsaturated double bonds. We did not detect end radical intermediates from the LDPE/BP/BNB although it does have been detected from the model compound systems. So, from the point of view of radical intermediates identified by the spin-tapping ESR technique only H-links would be possible to be formed by the recombination of the above radicals in the photoinitiated XLPE. However, we have determined not only H-links, but also Y-branches in the study of \(^{13}\)C NMR method. This gives the evidence that there must exist another mechanism to form Y-branches, which is not formed by the recombination of two alkyl radicals like H-links. It is well known that LDPE also contains some amount of the structural units of unsaturated double bonds, such as vinyl groups. They can react with the alkyl radicals to form Y-branches, as reported by Randall et al.\(^{19}\) Therefore, the mechanism of photocrosslinking of LDPE can be described clearly as follows:

\[
3(BP)^* + -\text{CH}_2\text{-CH}_2\text{-} \rightarrow -\text{CH}_2\cdot\text{-CH}_2\cdot + \text{Ketyl radical (K}\cdot\text{)} \\
3(BP)^* + -\text{CH}_2\cdot\text{-CH}=\text{CH}_2 \rightarrow -\cdot\text{CH}-\text{CH}=\text{CH}_2 + \text{Ketyl radical (K}\cdot\text{)} \\
3(BP)^* + -\text{CH}_2\cdot\text{-CH}_2\cdot \rightarrow -\text{CH}_2\cdot\text{-CH}=\text{CH}_2 + \text{Ketyl radical (K}\cdot\text{)}
\]

When these radicals thus produced undergo recombination with each other, the H-links will be formed as follows:

\[
-\text{CH}_2\cdot\text{-CH}_2\cdot + \rightarrow -\text{CH}_2\cdot-\text{CH}_2\cdot \\
-\text{CH}_2\cdot\text{-CH}_2\cdot + \rightarrow -\text{CH}_2\cdot-\text{CH}_2\cdot \\
-\cdot\text{CH}-\text{CH}=\text{CH}_2 \rightarrow -\cdot\text{CH}-\text{CH}=\text{CH}_2 \\
-\text{CH}_2\cdot\text{-CH}_2\cdot + \rightarrow -\text{CH}_2\cdot-\text{CH}_2\cdot \\
-\text{CH}_2\cdot\text{-CH}=\text{CH}_2 \rightarrow -\text{CH}_2\cdot-\text{CH}_2\cdot \\
-\cdot\text{CH}-\text{CH}_2 \rightarrow -\cdot\text{CH}-\text{CH}_2 \\
-\text{CH}_2\cdot\text{-CH}_2\cdot + \rightarrow -\text{CH}_2\cdot-\text{CH}_2\cdot \\
-\text{CH}_2\cdot\text{-CH}_2\cdot + \rightarrow -\text{CH}_2\cdot-\text{CH}_2\cdot
\]
At the same time, Y-branches can be produced by addition of these radicals to vinyl end groups:

\[
\begin{align*}
-\text{CH}_2-\cdot\text{CH}-\text{CH}_2- + -\text{CH}_2-\cdot\text{CH}=\text{CH}_2 & \rightarrow -\text{CH}_2-\cdot\text{CH}-\text{CH}_2- \\
\text{CH}_2-\cdot\text{C}-\text{CH}_2- + -\text{CH}_2-\cdot\text{CH}=\text{CH}_2 & \rightarrow -\text{CH}_2-\cdot\text{C}-\text{CH}_2-
\end{align*}
\] (16) (17)

In the photoinitiated crosslinking of LDPE, the photolysis products of BP as a photoinitiator can be mainly benzpinacol and a small amount of α-alkylbenzhydrils, as shown in formulae 7 and 8.

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MECHANISM OF CAMPHORQUINONE - 2 (N,N -DIMETHYLAMINO) ETHYL METHACRYLATE INITIATED PHOTOCURING OF DENTAL MATERIALS

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ABSTRACT

The purpose of this paper is to study the photoinitiated polymerization system of camphorquinone (CQ) with 2(N,N-dimethylamino)ethyl methacrylate (AMH). AMH plays an important role as a diluent in dental composite restorative materials. The CQ-AMH mixture is a binary hybride photoinitiating system for the polymerization of AMH itself. The amine (AM •) radical is formed from the exciplex composed from the excited CQ molecule and AMH in its ground state. The AMH monomer conversion is dependent on the CQ concentration. The induction period was found to increase almost linearly with decreasing light intensity.

INTRODUCTION

Polymerization of commercially available dental restorative materials is usually carried out with the help of binary hybride photoinitiator systems based mainly on camphorquinone (bornanedione, 1,7,7-trimethylbicyclo (2,2,1) heptane -2,3-dione) (CQ) and tertiary amines mainly N,N-dimethyl-p-toluidine and/or 2(N,N-dimethylamino) ethyl methacrylate (AMH). These photoinitiating systems allow the use of visible light over 400 nm, which is not harmful to oral cavity tissues. Radiation below 400 nm is not allowed when using "in vivo" treatment, because it can cause tissue burning and it has photoallergic and carcinogenic effects. The mechanism of photoinitiation of polymerization by camphorquinone (CQ) - amine (AM) is not yet well understood, in spite of many publications on this subject.

Camphorquinone has two absorption regions, 220 - 320 and 400 - 500 nm, due to π, π* and n, π* (Fig. 1). Its spectrum is dependent to some extent on the solvent used, which causes the shift of absorption maxima from 466 nm (ethanol) to 480 nm (cyclohexane), and on the increase in absorption at 260 - 270 nm (ethanol) (Fig. 1).

Camphorquinone (CQ) exhibits strong luminescence from the solid state at 77K, fluorescence at 490 - 550 nm, and phosphorescence at 550 - 600 nm [1, 2]. A weak
fluorescence of CQ can also be observed in benzene [2] and cyclohexane [3], but not in alcohols (due to chemically reactive quenching). Phosphorescence is not observed from the derated solutions in cyclohexane and toluene. Laser irradiation of CQ at 266 nm causes formation of a short lived, transient absorption spectrum (with max at 360 nm), which does not show sensitivity to oxygen. The observed transient spectrum cannot be attributed to the triplet state \( (^3T_1) \) of CQ nor to T - T absorption [4]. Irradiation of CQ with 355 nm laser radiation does not yield formation of any transient spectra.

Proteolysis of QC in degassed 2-propanol or xylene leads to the formation of a strong ESR signals consisting of four main multiples which were assigned to the CQH* radical [2, 5-12]. The chemically induced dynamic electron polarization (CIDEP) measurements show that the CQH* radical is formed from the triplet state of the CQ; however, two excited singlet states \( ^1CQ_1 \) and \( ^1CQ_2 \) may participate in the formation of the \( ^3CQ_1 \) [2]:

\[
\begin{align*}
CQ(S_0) \overset{hv}{\longrightarrow} ^1CQ_1 + ^1CQ_2 \\
^1CQ_2 \overset{IC}{\longrightarrow} ^1CQ_1 \\
^1CQ_2 \overset{ISC}{\longrightarrow} ^3CQ_1 \overset{ethanol}{\longrightarrow} CQH^* 
\end{align*}
\]

Where IC = interval conversion and ISC = inter system crossing.
The present generally accepted mechanism of photoinitiation reaction of CQ-amine
hybrid system involves formation of an exciplex between an excited CQ and an amine
(AMH) in its ground state ($S_0$) \[10, 13, 14\]:

\[
3 \text{CQ} + \text{AMH} (S_0) \rightarrow [\text{CO}:^{\text{---}} \text{AMH}^\ddagger] \rightarrow \text{CQH}^* + \text{AM}^*
\]  

The amine radical ($\text{AM}^*$) is responsible for the initiation of the polymerization reaction,
whereas the CQH$^*$ radical is inactive. The formation of exciplexes between aromatic radical
ketones and amines is well known and described elsewhere \[15\].

The reason for this work was to study the photoinitiating system of CQ with 2(N,N-
dimethylamino)ethyl methacrylate (AMH). The latter substance is itself a polymerizing
monomer. The amine ($\text{AM}^*$) radical formed from the reaction (3) initiates polymerization of
AMH. The AMH also plays an important role as a diluent for the highly viscous di- and tri-
functional methacrylic monomers used in dental restorative materials.

**EXPERIMENTAL**

Camphorquinone (CQ) (Aldrich, Germany) and 2(N, N-dimethylamino)ethyl methacrylate
(AMH) (Aldrich, Germany) containing 2000 ppm hydroquinone monomethyl ether were
purified by crystallisation, and distillation, respectively. The freshly distilled (AMH),
monomer was used directly for polymerization experiments.

Photopolymerization was carried out using a commercially available Luxor ICI dental lamp
with a maximum at 470 nm and at an intensity of 9 $\mu$W/cm$^2$ in the presence of air.

Measurements of the depth of curing were made by using a sandwich configuration of thin
(0.5 mm) layers of monomers placed in a circular spacer 0.5 mm deep between two 0.1 mm
thick glass slides. A number of such prepared samples were placed one on another to obtain
the required total thickness of monomer layers 1.0; 1.5; 2.0; 2.5; and 3.0 mm, respectively
and then irradiated. Monomer conversion has been determined by microgravimetric and or by
FTIR methods. UV/Vis and IR absorption spectra were recorded with Beckman 7500
UV/Vis and Perkin-Elmer 1650 FT-IR spectrometers respectively, using a horizontal leveled
sample attachment device.

**RESULTS AND DISCUSSION**

As photoinitiating hybrid system AMH-CQ at a ratio of 10:1 was used. The UV/Vis
spectrum of this AMH-CQ mixture in ethanol at CQ concentration ($10^{-2}$ M) is shown in
Fig. 2. During irradiation, the maximum band at 468 nm decreases, whereas absorption of
AMH slightly increases (Fig. 2)
These results show that CQ is faster photolysed in the presence AMH, and its absorption maximum at 468 nm decreases continuously with the time of irradiation (Fig. 3), whereas, irradiation of CQ alone in ethanol causes very slow photolysis (with $\phi = 0.16$ according to [10]).

![Absorption spectrum of AMH and CQ](image1)

**Fig. 2** Change of CQ and AMH absorption spectra during irradiation.

![Absorption kinetics](image2)

**Fig. 3** Kinetics of CQ photolysis: in ethanol: (○) without AMH and (●) in the presence of AMH. Ratio of AMH-CQ = 10:1.
Fig. 5 Induction time in air versus relative light intensity, CO concentration:

- ○ 0.05 wt-%, ○ 0.1 wt-%, ○ 0.2 wt-%, ○ 1.0 wt-%.

- Fig. 4 Kinetics of CO photoinitiated polymerization at AMT at different CO concentrations: ○ 0.05 wt-%, ○ 0.1 wt-%, ○ 0.2 wt-%, ○ 1.0 wt-%.
The kinetics of polymerization of AMH photoinitiated by the CQ (Fig. 4) has been determined from the disappearance of the 815 cm\(^{-1}\) band attributed to the presence of double bonds in the monomer. Results presented in Fig. 4 show that monomer conversion (\%), inhibition time and rate of polymerization (\(R_p\)) are evidently dependent on the CQ concentration. The induction period was found to increase almost linearly with decreasing light intensity (Fig. 5).

It was also found that when any of the air-polymerized samples were reirradiated in a nitrogen atmosphere, essentially complete polymerization of remaining monomer occurred at the total monomer conversion for a given CQ concentration. These results suggest that oxygen acts both as an inhibitor (free radical AM\(^*\) scavenger) and as a retarder of polymerization, depending on its concentration.

The monomer conversion was also dependent on the thickness of the irradiated monomer layer, depth of curing (Fig. 6).

![Fig. 6 Monomer conversion as a function of AMH layer thickness exposed to a light, CQ concentration: (\(\triangle\)) 0.05 wt-\%, (\(\bigcirc\)) 0.1 wt-\% and (\(\bullet\)) 1.0 wt-\%.](image)

**CONCLUSIONS**

The 2(N, N\,-dimethylamino)ethyl methacrylate (AMH) is used in dental restorative materials to the amount of 3-10 wt-\%, and plays two important roles: acts as diluent for highly viscous di- and tri-functional monomers such as 2,2-bis(p-(2\,'hydroxy-3\,'-methacryloyloxypropoxy) phenyl propane (bis - GMA), tri-ethylene glycol dimethacrylate (TEGDMA)
and many others, and acts as an important component of binary hybride photoinitiator system
from which reactive amino-radicals are formed. The AMH can, in the presence of bis - GMA
or TEGDMA, be copolymerized into the highly crosslinked network formed due to the
presence of di- and tri-functional monomers. However, AMH homopolymer chains can also
be entangled into these nets. Such nets contain unreacted AMH monomer, (even up to 50 wt %),
depending on the polymerization conditions (Fig. 4). This is a serious disadvantage for the
application of these materials in the oral cavity [16 - 18]. Unreacted monomers slowly diffuse
out of the polymer matrix to the surface and can be further transported by saliva, beverages
and food to the stomach where, if it is not hydrolysed by HCl, it can be accumulated and
resorbed in the circulatory system. It is well known that amines are resistant towards even
concentrated HCl, and that they are toxic. Little is however known about their cancerogenic
and mutagenic effects [19]. For that reason the use of AMH should be limited to amounts
necessary for obtaining effective photoinitiating systems that can initiate polymerization of
other di- and tri-functional monomers, rather than use them as diluents.

Due to space limitations, this paper does not address a detailed discussion of the
polymerization mechanism and its kinetics.

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ABSTRACT

In this paper, the photochemical properties of benzoyl derivatives, e.g. KIP-100F & ESACURE TZT were studied using the N121 UV Curing Tester. It was shown that their photochemical reactivity is higher; the photoactivation of triethanol amine (TEA) upon ESACURE TZT is greater, upon KIP-100F is unexpected; the sensitization of fluorescein upon KIP-100F is larger than upon ESACURE TZT/TEA systems; the synergistic action of them is very effective.

INTRODUCTION

The UV curing market has experienced dynamic growth since its introduction in the late 1960s. Market growth through the 1980s was 10-15% per year (1). Photoinitiators are important components of UV curable systems. Many efforts have been directed towards the understanding of the mechanistic action of photoinitiators under various conditions in order either to improve formulations or to develop more efficient initiator types.

KIP-100F & ESACURE TZT are new photoinitiators introduced in the early 1990s. KIP-100F is a mixture of 2-Hydroxy-2-methylphenyl-1-propanone (HMPP) and its polymer derivative, which has nonyellowing, good solubility and nonmigration characteristics. ESACURE TZT is a mixture of 4-methylbenzophenone and 2,4,6-trimethylbenzophenone, being liquid, the effect of oxygen inhibition is lower.

In this paper, using N121 UV curing tester, we studied on the photo-chemical properties of KIP-100F & ESACURE TZT.

EXPERIMENTAL

1. Materials

The oligomer used in these experiments was polyurethane acrylate (PUA). The reactive monomers were trimethylolpropane triacrylate (TMPTA), tripropylene glycol diacrylate (TPGDA) and hydroxypropene acrylate (HPA). The resins formulation: PUA 42% (w/w), TMPTA 40%, TPGDA 15%, HPA 3%. All the above materials were prepared at our laboratory.

KIP-100F & ESACURE TZT were supplied by Lamberti S.P.A.
2. UV Curing Tester and parameters

Cure measurements were made using a N121 UV Curing Tester from Thomas Swan & Co. Ltd., Consett, Co. Durham, England. The substrate was carton board.

In this work, the tester operating condition was the following:
- UV wavelengths: 254 nm & 355 nm
- Delay distance: 1 cm
- UV intensity: 10 mw/cm²
- Pressure: 4
- Sample speed: 2 cm/min
- Sensitivity: 25
- Sample length: 14 cm
- Atmosphere: Air

The cure tester had been described in more detail (2).

3. Sample preparation

The tested samples were applied uniformly on a strip of carton board, 2 cm x 20 cm, by using K BAR No.4 wire wound applicator. The thicknesses were all of 36 μm. The prepared samples were fixed onto a glass tray, 5 cm x 40 cm, then inserted into the channel. The tester measurements were made automatically, results were showed on the recorder cure trace graphs.

RESULTS AND DISCUSSION

1. The photo-chemical reactivity of KIP-100F & ESACURE TZT/TEA

![Graph 1](image)

![Graph 2](image)

Fig. 1 & 2 show that the photo-chemical reactivity of KIP-100F is lower than that of ESACURE TZT/TEA; additionally, T₁ & T₉ of ESACURE TZT/TEA rise with their content over 6%. These are caused by different initiating-mechanisms of them. KIP-100F depends upon molecular structure to generate free radicals while ESACURE TZT depends upon the presence of a hydrogen donor molecule.
2 The photoactivation effects of TEA upon ESACURE TZT & KIP-100F

Fig. 3  The photoactivation of TEA upon ESACURE TZT

Fig. 4  The photoactivation of TEA upon KIP-100F

Using 5% w/w ESACURE TZT in resins
Using 5% w/w KIP-100F in resins

Fig. 3 & 4 show that the photoactivation effects of TEA upon ESACURE TZT are significantly stronger than that upon KIP-100F; additionally, the photochemical reactivity of ESACURE TZT is reduced as content of TEA over 5%. These results suggest that the best stoichiometric ratio of ESACURE TZT to TEA should be 1:1. Fig. 4 shows that the enhancing effect of TEA upon the photofragmentor KIP-100F is unexpectedly slight.

3. The photosensitization effects of fluorescein upon ESACURE TZT/TEA & KIP-100F

Fig. 5  The photosensitization of fluorescein upon ESACURE TZT/TEA systems

Fig. 6  The photosensitization of fluorescein upon KIP-100F

Using 5% w/w ESACURE TZT & TEA in resins respectively
Using 5% w/w KIP-100F in resins
Fig. 5 & 6 show that the sensitization of fluorescein upon ESACURE TZT/TEA systems is small, but upon KIP-100F, it's greater. It could be concluded that photoactivation enhancement of amine is greater than the sensitization of dye.

4. The synergistic action of KIP-100F & ESACURE TZT/TEA

Fig. 7 & 8 show that the synergistic action of KIP-100F & ESACURE TZT/TEA is effective. These results tell us that the initiating systems consist of different types of photoinitiator must be adopted widely in UV curable formulation.

CONCLUSIONS

This work presents a new method for quick and easy evaluation of photo-chemical properties of photoinitiators. Results obtained are of value to development of UV curable formulation using new photoinitiators.

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PHOTOLYSIS PRODUCTS OF BENZOPHENONE IN THE
PHOTOCROSSLINKING OF LDPE AND ITS MODEL
COMPOUNDS

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ABSTRACT: Photolysis products of benzophenone (BP) as a photoinitiator in the
photocrosslinking of low density polyethylene (LDPE) and its model compounds
have been studied by means of fluorescence spectroscopy, ¹³C and ¹H NMR etc.
Two kinds of photolysis products of BP (PPB) are detected and identified in the
present study: the main product is benzpinacol formed by recombination of two ketyl
radicals (K*); a small amount of α-alkylbenzhydrols are also formed by the
reactions of K* radicals, respectively, with the primary, secondary, and tertiary
carbon radicals produced by hydrogen abstraction of the excited triplet state (BP)*
from the model compounds. These results provide new experimental evidence for
elucidating the mechanism of photocrosslinking of polyethylene.

INTRODUCTION

Benzophenone (BP) and its derivatives can efficiently initiate photocrosslinking of high-density
polyethylene (HDPE), low-density polyethylene (LDPE) and linear low-density polyethylene
(LLDPE).¹² The mechanism of the photocrosslinking of LDPE and its model compounds has been
studied by spin-trap ESR ¹³ and ¹³C NMR ¹⁴ However, the photolysis products of BP as a
photoinitiator during the photocrosslinking of polyethylene have not been investigated yet.

On the basis of the photolysis studies of BP in secondary alcohols,⁷⁸ it has been deduced¹⁰ that
benzpinacol should be formed during the photocrosslinking of polymers. Therefore, it should be
possible to detect benzpinacol formed in the photocrosslinked polyethylene (XLPE) with fluorescence
spectroscopy. However, the fluorescence spectra only give very limited structure information because
it is very difficult to resolve different photolysis products of BP (PPB) in the insoluble XLPE. In order
to obtain detailed structure information from the crosslinked system, several model compounds with
low molecular weight are used in this work. According to our previous work,¹¹ commercial LDPE
polymers usually contain small amounts of unsaturated bonds (either as end groups or inner groups) in
addition to branch points and paraffin chain segments. Therefore, the following three kinds of LDPE
model compounds have been used in this study: n-paraffins, branched hydrocarbons and unsaturated
hydrocarbons containing allylic hydrogen.

The purpose of this study is to detect and identify the photolysis products of BP as a photoinitiator
in the photocrosslinking of LDPE and its model compounds by fluorescence spectroscopy, ¹³C and ¹H
NMR etc., and thus to elucidate the mechanism of BP-photoinitiated crosslinking of polyethylene.
EXPERIMENTAL

Materials

Three kinds of PE resins, branch LDPE, linear LDPE (LLDPE), and HDPE; five model compounds: two n-paraffins, n-tetracosane (C_{24}H_{50}) and dodecane (C_{12}H_{26}); two paraffins with branched structure, squalane (C_{30}H_{62}) and isooctane (C_{8}H_{18}); one unsaturated compound, 1-hexene (C_{6}H_{10}) were used in the present work. Benzophenone (BP) was used as a photoinitiator. Benzpinacol was used as a standard sample in the study of fluorescence. All these chemicals were commercially available without further purification.

Sample Preparation

XLPE Films. Fifty grams of HDPE, LDPE or LLDPE powder or granules with 1-4 wt% BP were mixed at 160-200 °C for 10 minutes in a Brabender Plasticorder, respectively. The mixture was hot-pressed at 160 °C for 4-5 minutes to obtain 0.1-0.2 mm sample films. Samples in the melt and N_{2} atmosphere were UV-irradiated in a UV-CURE device with Philips HPM 15 lamp operated at 2 kW.

PPB Samples. BP (5 wt%) was mixed with an amount of model compound in a quartz tube at 60 °C. Oxygen in the mixture was driven away by filling with highly pure nitrogen for 0.5 h. The sample was then irradiated with UV light (high-pressure mercury lamp, GGU-500, made in Shanghai, China) at 60 °C for about one hour. The white crystal called the photolysis products of BP (PPB) was formed during UV irradiation. The PPB products were filtered and purified by repeatedly washing with isooctane at 60 °C, and then dried in a vacuum desicator at the same temperature to constant weight.

Fluorescence Spectroscopy

The emission fluorescence spectra were recorded on a Hitachi fluorescence model 850 spectrophotometer. The excited wavelength was 260 nm, and the measurement range was from 270 nm to 500 nm.

NMR Measurements

{superscript}13C and {superscript}1H NMR spectra for the PPB products were observed with JEOL FX-90Q and Bruker DMX500 spectrometers at room temperature. The operation frequency is 89.55 MHz and 500.13 MHz for {superscript}1H and 22.49 MHz and 125.77 MHz for {superscript}13C, respectively. The spectrum widths were 900 Hz and 5 000 Hz for {superscript}1H and 4 500 Hz and 25 000 Hz for {superscript}13C, respectively. For {superscript}13C NMR measurements, the flip angle was 30° (3 μs) and 90° (9.5 μs); data points were 16 K and 64 K; and the FID's accumulation was 4 000 and 1 000 on FX-90Q and DMX500, respectively. CDC_{3} was used as the internal standard.

Other Measurements

The ratio of carbon and hydrogen in the PPB products was determined with an element analyzer (Model 240C, Perkin-Elm Ltd., USA). The melt point was measured on a SHIMAODU thermal analyzer (DSC). IR spectra were recorded on a NICOLET model 170 SX FT-IR spectrometer.

RESULTS AND DISCUSSION

Fluorescence Detection of Benzpinacol

Figure 1 shows the fluorescence spectra of pure benzpinacol, the PPB products obtained from different sample systems, and pure benzophenone. It can be seen that pure benzpinacol (Figure 1a) has an emission spectrum with a maximum at wavelengths between 295 and 310 nm, whereas no such an emission spectrum was observed from pure benzophenone (Figure 1d) under the same
measurement conditions. Figure 1b and c show the fluorescence spectra of PPB obtained from n-C_{12}H_{26}/BP and isooctane/BP systems, respectively. Apparently these two fluorescence spectra with a maximum between the wavelength 300 and 310 nm are similar to that from pure benzpinacol (Figure 1a). Therefore, the peaks shown in Figure 1b and 1c can be associated with benzpinacol.

![Fluorescence spectra](image)

Figure 1 Fluorescence spectra: a: pure benzpinacol; b: PPB from n-C_{12}H_{26}/BP; c: PPB from isooctane/BP; d: pure benzophenone.

Figure 2 Fluorescence spectra of HDPE/1%BP films for different irradiation time: a: 160s; b: 80s; c: 20s; d: 0s

Figure 2 shows typical fluorescence spectra from HDPE/1%BP films with different UV irradiation time. For the unirradiated film, no emission spectrum was observed (Figure 2d). With shorter irradiation (less than 20 s), a peak with a maximum at about 290 nm began to emerge (Figure 2c); for longer irradiation, such as 80 s and 160 s, fluorescence intensity at 290 nm increases rapidly (Figure 2b and a). Moreover, the relative intensities of fluorescence peaks at 290 nm increase with increasing concentrations of BP in the samples. All the data from the LDPE/BP, LLDPE/BP, and HDPE/BP systems in the present studies show the same results, i.e., the increases of the relative fluorescence intensities at 290 nm with the increases of irradiation time and concentrations of BP, which means the increase of benzpinacol. The above results from the fluorescence spectroscopy give the evidence of benzpinacol formed in the photoinitiated cross-linking of PE samples.

In order to further study the structures of benzpinacol and other possible PPB products separated from the model samples as described in the experimental section, detail structures are determined by various analytical methods, such as \(^{13}\)C and \(^1\)H NMR, IR, DSC etc.

### Structural Identification of Benzpinacol

The 22.49 MHz \(^{13}\)C NMR spectrum of PPB obtained from C_{12}H_{26}/BP system is shown in Figure 3, which is almost the same as that of pure benzpinacol as a standard sample in this study. The resonance line at 83.11 ppm is assigned to the carbons associated with -OH group of benzpinacol. The peaks at 144.28, 127.37, 128.67 and 127.00 ppm are due to the substituted-, \(\alpha\)-, \(m\)- and \(p\)- carbons of benzene ring of benzpinacol, respectively, as shown in the up right of Figure 3. The signals at 75.69, 77.10 and 78.51 ppm are due to the solvent CDCl\(_3\). These data are in good agreement with those of pure benzpinacol in this study and reported in the literature.\(^1\)

The 22.49 MHz \(^{13}\)C NMR spectra of PPB products from the other systems of model compounds, such as n-C_{12}H_{26}/BP, squalane C_{30}H_{62}/BP, isooctane C_{8}H_{18}/BP, and 1-hexene C_{6}H_{10}/BP are the same as that from n-C_{12}H_{26}/BP. The assignments of corresponding \(^{13}\)C chemical shifts associated with -OH group and benzene ring of benzpinacol are similar to the above analysis from C_{12}H_{26}/BP system.
The element analysis shows that the carbon-hydrogen ratios of PPB products obtained from all the above model compound systems are 13:11. The melt point of PPB obtained by DSC measurement is 184-186°C. The evidence from IR spectra also shows the hydroxyl groups presented in PPB. These data are in complete agreement with those of pure benzpinacol reported in the literature. Apparently the main photolysis product of BP can be confirmed to be benzpinacol.

![NMR Spectrum](image)

**Figure 3** 22.49 MHz $^{13}$C NMR spectrum of PPB from n-C$_{24}$H$_{50}$/BP system.

**Detection of α-alkylbenzhydrol**

Figure 4 displays the 500.13 MHz $^1$H NMR spectrum of PPB from n-C$_{24}$H$_{50}$/BP. The peak at 3.02 ppm is due to $^1$H of -OH group, and the stronger peaks at 7.0-7.4 ppm are due to various $^1$H of phenyl group in benzpinacol, as reported in the literature. The weaker peaks at 7.0-7.4 ppm and the ones at 0.88-2.62 ppm have been tentatively assigned to various $^1$H of three kinds of α-alkylbenzhydrols (I), (II) and (III), as shown in the formulae (6) to (8). The assignments of $^1$H NMR spectra of various α-alkylbenzhydrols obtained from n-C$_{24}$H$_{50}$/BP system are listed in Table 1. These data of chemical shifts in this work fit well with those reported for α-alkylbenzhydrol (I) in the literature. The weak peaks at 7.4-7.9 ppm are due to the residual BP in the systems. However, the detailed analysis and identification of $^1$H peaks in these α-alkylbenzhydrols (I), (II) and (III) needs to be further done.

![NMR Spectrum](image)

**Figure 4** 500.13 MHz $^1$H NMR spectrum of PPB from n-C$_{24}$H$_{50}$/BP system.
Table 1 Assignments of 500.13 MHz \(^1\)H NMR Spectra of \(\alpha\)-alkylbenzhydrols during the Photocrosslinking of Model Compound Systems

<table>
<thead>
<tr>
<th>Structures of (\alpha)-alkylbenzhydrols</th>
<th>n-Paraffin n-C(<em>{24})H(</em>{50})</th>
<th>n-Paraffin n-C(<em>{12})H(</em>{26})</th>
<th>C(<em>{30})H(</em>{62}) squalane</th>
<th>C(<em>{8})H(</em>{18}) isooctane</th>
<th>C(<em>{6})H(</em>{10}) 1-hexene</th>
</tr>
</thead>
<tbody>
<tr>
<td>(e{\begin{array}{c} HO \ CH_2(CH_2)_nCH_3 \ d, c, b, a \end{array}})</td>
<td>(a = 0.88)</td>
<td>(a = 0.86)</td>
<td>(a = 0.83-0.87)</td>
<td>(a = 0.88)</td>
<td>(a = 0.82-0.92)</td>
</tr>
<tr>
<td>(\begin{array}{c} a = 1.2-1.6 \ b = 1.0-1.6 \ c = 2.14-2.26 \ d = 2.14 \ e = 7.0-7.4 \end{array})</td>
<td>(b = 1.0-1.6)</td>
<td>(c = 2.14-2.26)</td>
<td>(d = 2.0-2.05)</td>
<td>(e = 7.0-7.4)</td>
<td>(b = 1.0-1.7)</td>
</tr>
<tr>
<td>(\begin{array}{c} f \end{array})</td>
<td>(\begin{array}{c} a = 1.2-1.6 \ b = 1.0-1.6 \ c = 2.59 \ d = 1.86 \ e = 7.0-7.4 \end{array})</td>
<td>(\begin{array}{c} a = 1.2-1.6 \ b = 1.0-1.6 \ c = 2.62 \ d = 1.86 \ e = 7.0-7.4 \end{array})</td>
<td>(\begin{array}{c} a = 1.83 \ e = 7.0-1.83 \end{array})</td>
<td>(\begin{array}{c} a = 1.83 \ e = 7.0-7.6 \end{array})</td>
<td>(c = 2.58)</td>
</tr>
<tr>
<td>(\begin{array}{c} a = 0.83-0.87 \ a' = 0.90-0.94 \end{array})</td>
<td>(\begin{array}{c} a = 0.88 \ a' = 0.90 \end{array})</td>
<td>(\begin{array}{c} a = 0.88 \ a' = 0.90 \end{array})</td>
<td>(\begin{array}{c} a = 0.88 \ a' = 0.90 \end{array})</td>
<td>(\begin{array}{c} a = 0.88 \ a' = 0.90 \end{array})</td>
<td>(b = 1.0-1.7)</td>
</tr>
<tr>
<td>(\begin{array}{c} b = 1.0-1.6 \ c = 1.1-1.6 \ d = 1.5-1.6 \ e = 7.0-7.6 \end{array})</td>
<td>(\begin{array}{c} b = 1.0-1.6 \ c = 1.1-1.6 \ d = 1.5-1.6 \ e = 7.0-7.6 \end{array})</td>
<td>(\begin{array}{c} b = 1.0-1.6 \ c = 1.1-1.6 \ d = 1.5-1.6 \ e = 7.0-7.6 \end{array})</td>
<td>(\begin{array}{c} b = 1.0-1.6 \ c = 1.1-1.6 \ d = 1.5-1.6 \ e = 7.0-7.6 \end{array})</td>
<td>(\begin{array}{c} b = 1.0-1.6 \ c = 1.1-1.6 \ d = 1.5-1.6 \ e = 7.0-7.6 \end{array})</td>
<td></td>
</tr>
</tbody>
</table>

In order to determine the chemical shifts of -OH in Figure 4, D\(_2\)O was added to the system to exchange the active \(^1\)H atoms in -OH. It was found that the peaks at 3.02 ppm, 2.14 ppm and 1.86 ppm completely disappeared. In addition, the peak at 1.5-1.6 ppm became more narrow, which indicates that \(^1\)H signal of -OH at about 1.58 ppm disappeared. Therefore, we can conclude that the signal at 3.02 ppm is from -OH group in benzpinacol, whereas those at 2.14, 1.86, and 1.58 ppm are due to different -OH groups in \(\alpha\)-alkylbenzhydrols (I), (II) and (III), respectively.

The observed changes of \(^1\)H chemical shifts of -OH groups in different \(\alpha\)-alkylbenzhydrols \(((C_6H_5)_2C(OH)R)\) can be explained as follows. When R in alkylbenzhydrols is primary, secondary or tertiary carbon, respectively, the steric hindrance increases in order, which makes -OH group to approach the shielding region of phenyl group of \(\alpha\)-alkylbenzhydrol. Therefore, the chemical shift of -OH \((\delta_{OH})\) becomes smaller, which leads to the \(^1\)H signal of -OH in \(\alpha\)-alkylbenzhydrol (III) appeared at 1.58 ppm and overlapped with those of -CH\(_2\)- in \(\alpha\)-alkylbenzhydrols.

It is estimated from the intensities of \(^1\)H NMR spectra that the concentrations of benzpinacol, \(\alpha\)-alkylbenzhydrols (I) and (II) in the above PPB of Figure 4 are roughly 90%, 2% and 8%, respectively. However, the concentration of \(\alpha\)-alkylbenzhydrol (III) could not be quantitatively detected because of its overlapping with the signals of -CH\(_2\)- group of \(\alpha\)-alkylbenzhydrols. These results show that the secondary carbon radicals as the precursors of \(\alpha\)-alkylbenzhydrol (II) are dominant intermediates.

In n-C\(_{12}\)H\(_{26}\)/BP system, the same four kinds of PPB products are also detected and identified from the \(^1\)H NMR spectrum: benzpinacol, \(\alpha\)-alkylbenzhydrols (I), (II) and (III). Their corresponding analysis and assignments of the spectrum are also given in Table 1.
Figures 5 shows $^1$H NMR spectrum of PPB obtained from the squalane/BP system. Again four spectral components are detected and identified. However, the $\alpha$-alkylbenzhydrol (III) in this system is produced by the addition reaction of K• radical with tertiary carbon radical formed by hydrogen abstraction from the tertiary carbon in squalane. The $^1$H NMR spectrum of PPB from the isooctane/BP system shows the similar results. The $^1$H chemical shifts of -OH ($\delta_d$) of $\alpha$-alkylbenzhydrols (I), (II) and (III) in Figure 5 are identified to be 2.03-2.05, 1.86 and 1.5-1.6 ppm by adding D$_2$O, respectively. The other data are shown in Table 1.

The concentration of $\alpha$-alkylbenzhydrol (III) from the squalane/BP or isooctane/BP system is much more than those of (I) and (II) by comparing their relative integral intensities of $^1$H NMR spectra. This gives the evidence that the tertiary carbon radicals as the precursors of (III) are predominant species during the photocrosslinking of squalane and isooctane systems. These results are in good agreement with those obtained from ESR studies.

The $^1$H NMR spectrum of PPB obtained from 1-hexene/BP system is shown in Figure 6. The similar four kinds of PPB are identified by the detailed analysis of the spectrum as being benzpinacol and $\alpha$-alkylbenzhydrols (I), (II) and (III), as given in Table 1.
Mechanism of Photoinitiated Crosslinking

Based on the above studies of PPB products and crosslink structures\(^5\), the mechanism of photoinitiated crosslinking of LDPE can be proposed as follows. When the photoinitiator BP absorbs a UV quantum and is excited to the singlet state and then rapidly relaxes to the more stable triplet state \(3^*(BP)\), it can abstract hydrogen from the model compounds to form the ketyl (K\(\circ\)) and M\(\circ\) radicals:

\[
\begin{align*}
BP + h\nu &\rightarrow (BP)^\circ \xrightarrow{ISC} 3^*(BP)^* \quad (1) \\
3^*(BP)^* + MH &\rightarrow (C_6H_5)_2C(OH)(K\circ) + M\circ \quad (2) \\
M\circ + M\circ &\rightarrow M-M \text{ (Cross-linking)} \quad (3) \\
K\circ + K\circ &\rightarrow (C_6H_5)_2C(OH)C(OH)\text{(benzpinacol)} \quad (4) \\
M\circ + K\circ &\rightarrow M-K (\alpha\text{-alkylbenzhydrol}) \quad (5)
\end{align*}
\]

where M\(\circ\) represents model compound radicals; K\(\circ\) represents ketyl radicals. Two K\(\circ\) radicals combine to form a benzpinacol molecule. Radicals M\(\circ\) can be described as follows:

\[
\begin{align*}
\text{CH}_2^\cdot - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \\
\text{CH}_2^\cdot - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \\
\text{CH}_2^\cdot - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \\
\end{align*}
\]

These M\(\circ\) radicals can react with K\(\circ\) radicals to form \(\alpha\)-alkylbenzhydrols (I), (II) and (III):

\[
\begin{align*}
K\circ + \text{CH}_2(\text{CH}_2)_n\text{CH}_3 &\rightarrow (C_6H_5)_2C(OH)\text{CH}_2(\text{CH}_2)_n\text{CH}_3 \quad (6) \\
K\circ + -\text{CH}_2(\text{CH}_2)_n\text{CH}_3 &\rightarrow (C_6H_5)_2C(OH)\text{CH}_2(\text{CH}_2)_n\text{CH}_3 \quad (7) \\
K\circ + -\text{CH}_2(\text{CH}_2)_n\text{CH}_3 &\rightarrow (C_6H_5)_2C(OH)\text{CH}_2(\text{CH}_2)_n\text{CH}_3 \quad (8)
\end{align*}
\]

CONCLUSION

1. In photoinitiated crosslinking of polyethylene and model compounds using benzophenone (BP) as initiator, the main photolysis product of BP (PPB) is benzpinacol formed by the combination of two ketyl radicals (K\(\circ\));
2. The results obtained from the model compounds also show that a small amount of \(\alpha\)-alkylbenzhydrols are also formed by the reactions of K\(\circ\) radicals with the primary, secondary, and tertiary carbon radicals produced by hydrogen abstraction of \(3^*(BP)\) from model compounds;
3. As far as \(\alpha\)-alkylbenzhydrol is concerned, \(\alpha\)-alkylbenzhydrol (II) and \(\alpha\)-alkylbenzhydrol (III) are the main products for the \(n\)-paraffins and branched hydrocarbon systems. On the other hand, the double bond of unsaturated hydrocarbons such as 1-hexene can be opened to form the saturated \(\alpha\)-alkylbenzhydrols by the addition reactions with K\(\circ\) radicals.

Acknowledgments

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(15) Nuclear Magnetic Resonance Spectra, Sadtler Research Laboratories, Inc., 1976, 35, 22430M; 22432M; 22436M.
ABSTRACT

Crosslinks formed by photoinitiated crosslinking of dodecane, squalane, isooctane and 1-hexene as the model compounds of low-density polyethylene in the presence of benzophenone as photoinitiator have been studied for the first time by solution-state $^{13}$C NMR spectroscopy. H- and Y-type crosslinks have been observed and identified for the photo crosslinked samples. The quantitative studies show that H- and Y-links are both formed for photo crosslinked dodecane and branched hydrocarbons (squalane and isooctane), and the double bond of unsaturated hydrocarbons such as 1-hexene can be opened to form Y-links by the reaction between a terminal vinyl group and an alkyl radical. These results give new evidence for elucidating the mechanism of photoinitiated crosslinking of polyethylene.

INTRODUCTION

The mechanism of photoinitiated crosslinking of polyethylene (PE) has been widely investigated. However, many fundamental problems, such as the structure and nature of crosslinking, are still indistinct. Therefore, there is considerable interest in the direct observation and detection of the crosslinks in the photo crosslinked PE.

High-resolution solution $^{13}$C nuclear magnetic resonance (NMR) spectroscopy has been successfully used to measure the crosslinks of PE and its model compounds produced by high-energy irradiation (either γ-rays or electron beam). In order to study the crosslinking structure of PE, we have used $^{13}$C NMR to make a direct observation and detection of H-links during the photoinitiated crosslinking of tetradecane as a model compound of low-density polyethylene (LDPE) in the presence of benzophenone (BP) as photoinitiator. However, the Y-links were not detected in this system.

The purpose of this work is to observe and detect the photo crosslinks of various model compounds of LDPE. The advantage using the relative low-molecular-weight model compound is in that it is able to accept large UV irradiation doses without gel formation. Because commercial LDPE polymers usually contain small amount of unsaturated bonds in addition to long-chain branches and paraffin chain segments, branched hydrocarbons and unsaturated carbon as well as n-paraffin were selected as model compounds of LDPE in this study.

EXPERIMENTAL

Materials

Four model compounds of LDPE were used in the present work. n-paraffin, dodecane (C_{12}H_{26}, purity ≥ 98%, d=0.748, bp 209-212°C ) from Fluka; two paraffins with branched structure, squalane (C_{30}H_{62}, MW 422.83, d=0.809, bp 210-215°C ) from Fluka and isooctane (C_{8}H_{18}, purity ≥ 98%, d=0.688-0.693) from Hangzhou Refinery, China; one unsaturated compound, 1-hexene ( purity ≥ 98%) from Fluka.

Benzophenone (BP) (mp 48.1°C) as a photoinitiator was purchased from KEBO Lab, Sweden. All these chemicals were commercially available without further purification.

Sample Preparation
Photoinitiator BP (5% by weight) was dissolved in a quartz tube with 10ml liquid model compound at 60°C to produce the samples for irradiation. Oxygen in the mixture was driven away by filling with highly pure nitrogen for 0.5h. The sample was then irradiated with UV light (high-pressure mercury lamp, GGU-500, made in Shanghai, China) at 60°C for one hour. The crosslinked compounds were obtained by filtering the insolubles at room temperature.

NMR Measurements

$^{13}$C NMR spectra were observed with a Bruker DMX500 spectrometer at room temperature. The pulse sequence was inverse gated decoupling. The operation frequency is 125.77MHz; the spectrum width was 25000Hz; pulse delay (PD) after free induction decay (FID) was 7.5s; the flip angle was $38^\circ$ ($\mu$s); data points were 178K; and the FID's accumulation was 1000. CDCl$_3$ was used as the internal standard for isooctane and 1-hexene, and C$_6$D$_6$ for others.

RESULTS AND DISCUSSION

1. Characteristics of Photoinitiated Crosslinks

(1) Crosslinked C$_{12}$H$_{26}$ Sample

For the C$_{12}$H$_{26}$ samples with and without UV irradiation, five strong resonance lines were clearly observed in their $^{13}$C NMR spectra. Figure 1 shows the $^{13}$C NMR spectrum of the C$_{12}$H$_{26}$ sample with UV-irradiated.

![Figure 1. $^{13}$C NMR spectrum of the C$_{12}$H$_{26}$ sample with UV-irradiated](image)

In Figure 1, new peaks at the chemical shift 39.47-41.63 ppm originating from the methine carbon atoms are associated with the H-links in the photo crosslinked C$_{12}$H$_{26}$ sample while the new methine carbon resonance peaks at 37.65-38.63 ppm are due to the Y-links of the sample. The resonance lines of $\alpha$-, $\beta$- and $\gamma$- carbon atoms of H- and Y-links are also clearly resolved. The structure and their chemical shifts of H- and Y-links are shown in Figure 2, and the nomenclature is expressed on the basis of the pioneering works.$^3$
Figure 2. The structure and their chemical shifts of H- and Y- links of crosslinked C₁₂H₂₆

This result is different from those for γ-irradiated crosslinking systems of model compounds of LDPE and the photo crosslinking system of C₂₄H₅₀. Horii et al. reported that H-links were formed preferentially at high temperature and in the melt for γ-irradiated crosslinking systems of model compounds of LDPE[3]; Y-links were not detected for the photo-crosslinked n-C₂₄H₅₀ sample[2], either. However in this work, H- and Y- links are both detected in the crosslinked C₁₂H₂₆.

(2) Crosslinked Squalane and Isooctane Samples

Figure 3 shows the ¹³C NMR spectrum of the crosslinked squalane sample. In comparison with the unirradiated sample, new peaks appeared in Figure 3 can be assigned to structural units of two kinds of H- links of crosslinked squalane as shown in Figure 4.

Figure 3. ¹³C NMR spectrum of the squalane sample with UV-irradiated

Figure 4. Crosslinks and their chemical shifts of the crosslinked squalane sample
The chemical shifts of H-links and their α-, β- and γ-carbon atoms are also marked in Fig. 4, and those in parentheses are theoretical values calculated according to Lindeman-Adams' equation[4]. Apparently, the data show good agreement of the experimental values with those calculated.

A series of new resonance lines due to structural units of various Y-links of the crosslinked isooctane sample are observed in its $^{13}$C NMR spectrum (Figure 5). The crosslinks and their neighboring carbon atoms together with their chemical shifts are expressed in Figure 6. In parentheses in Fig. 6 are shown the theoretical chemical shifts which are in good agreement with the observed values.

Figure 5. $^{13}$C NMR spectrum of the crosslinked isooctane sample

Figure 6. Crosslinks and their chemical shifts of the crosslinked isooctane sample

(3) Crosslinked 1-Hexene Sample

No remarkable difference between the $^{13}$C NMR spectral of the 1-hexene samples with and without UV-irradiated was observed. However, the concentrations of carbon atoms of the double bond in 1-
hexene decrease after irradiation. This change indicates that the double bond of 1-hexene may have involved reactions, in which the double bond is opened to form the Y-link as shown in Figure 7.

\[
\begin{align*}
\text{CH}_{\gamma} & \\
\downarrow & \\
\text{CH}_2=\text{CHCHCH}_2\text{CH}_2\text{CH}_3 & \\
\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3
\end{align*}
\]

Figure 7. The Y-link of crosslinked 1-hexene sample

2. Measurements of Cross-Link Concentration and Error Analysis

It is assumed that the relative intensity of the NMR spectrum is directly proportional to the number of contributing carbon atoms if the proper parameters are used, such as consideration of satisfying of "Nuclear Overhauser Effects (NOE)" and the spin lattice relaxation times (T₁) requirements. Usually the pulse delay after FID requires a pulse spacing 5T₁ for the 90° flip angle for the $^{13}$C NMR quantitative measurement.

In this work, the pulse delay is 7.5s and not sufficient for the $^{13}$C NMR quantitative measurement of certain kinds of structural units such as -(CH₂)_n- (T₁ ~ 3.30s). However, for the quantitative measurement of H-links (T₁ ~ 0.30s) and Y-links (T₁ ~ 1.50s), the signal intensities are not affected because of their short T₁ and the lower flip angle (38°) used. In addition, the pulse sequence of inverse gated decoupling can reduce the errors caused by NOE. Therefore, the quantitative analytical results in this work should be reliable.

Table 1 presents the relative integrated intensities and the measurement errors calculated according to the ratio of carbon atoms in the various units of n-C₁₂H₂₆ without UV-irradiated. It appears that the errors are within the error range of $^{13}$C NMR measurements.

<table>
<thead>
<tr>
<th>Structural units</th>
<th>-(CH₂)_n-</th>
<th>1S</th>
<th>2S</th>
<th>3S</th>
<th>4S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative integrated intensities</td>
<td>1.8480</td>
<td>1.0380</td>
<td>1.0063</td>
<td>1.0000</td>
<td>0.8755</td>
</tr>
<tr>
<td>Errors (%)</td>
<td>-3.9</td>
<td>8.0</td>
<td>4.7</td>
<td>3.9</td>
<td>-8.9</td>
</tr>
</tbody>
</table>

Based on the quantitative analysis of $^{13}$C NMR spectra, the yielding concentrations of H- and Y-links for various photo crosslinking systems are estimated and listed in Table 2.

<table>
<thead>
<tr>
<th>Crosslinked Compounds</th>
<th>Crosslinks</th>
<th>No. of Links per 10,000 C</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₂H₂₆</td>
<td>H-link</td>
<td>31.8</td>
</tr>
<tr>
<td></td>
<td>Y-link</td>
<td>33.0</td>
</tr>
<tr>
<td>Squalane</td>
<td>H-link</td>
<td>9.0</td>
</tr>
<tr>
<td>Isooctane</td>
<td>Y-link</td>
<td>22.2</td>
</tr>
<tr>
<td>1-Hexene</td>
<td>Y-link</td>
<td>34.0</td>
</tr>
</tbody>
</table>
From Table 1, it seems that that H- and Y- links have almost equal yielding probability during the photo crosslinking of C\textsubscript{12}H\textsubscript{26}.

3. Mechanism of Photo Crosslinking

The above results show that both H- and Y- links are formed during the photo crosslinking of n-paraffin and branched compounds. The formations of H- and Y- links can be explained in following ways:

\begin{align*}
\text{3.} & (\text{BP})^* + \text{CH}_2\text{CH}_2\text{CH}_2\rightarrow -\text{CH}_2\cdot\text{CHCH}_2^- + \text{Ketyl radical (K\bullet)} \\
\text{3.} & (\text{BP})^* + \text{CH}_2\text{CH}_3 \rightarrow -\text{CH}_2\cdot\text{CH}_2 + \text{K\bullet} \\
\text{3.} & (\text{BP})^* + \text{CH}_2\text{CHCH}_2\rightarrow -\text{CH}_2\cdot\text{CCH}_2^- + \text{K\bullet} \\
\text{H-link} & \quad \text{-CH}_2\cdot\text{CHCH}_2^- + \text{CH}_2\cdot\text{CHCH}_2\rightarrow -\text{CH}_2\cdot\text{CHCH}_2^- + \text{CH}_2\cdot\text{CHCH}_2^- \\
\text{H-link} & \quad \text{-CH}_2\cdot\text{CCH}_2^- + \text{CH}_2\cdot\text{CCH}_2^- \rightarrow -\text{CH}_2\cdot\text{CHCH}_2^- + \text{CH}_2\cdot\text{CHCH}_2^- \\
\text{Y-link} & \quad \text{-CH}_2\cdot\text{CHCH}_2^- + \text{-CH}_2\cdot\text{CH}_2 \rightarrow -\text{CH}_2\cdot\text{CHCH}_2^- + \text{CH}_2\cdot\text{CH}_2 \\
\text{Y-link} & \quad \text{-CH}_2\cdot\text{CCH}_2^- + \text{CH}_2\cdot\text{CCH}_2^- \rightarrow -\text{CH}_2\cdot\text{CHCH}_2^- + \text{CH}_2\cdot\text{CH}_2 \\
\end{align*}

During the photo crosslinking of 1-hexene, the decrease of carbon atoms of the double bond indicates that double bond can react with alkyl radicals and form Y-links:

\begin{align*}
\text{Y-link} & \quad \text{-CH}_2\cdot\text{CHCH}_2^- + \text{CH}_2\cdot\text{CCH}_2^- \rightarrow -\text{CH}_2\cdot\text{CHCH}_2^- + \text{CH}_2\cdot\text{CCH}_2^- \\
\text{Y-link} & \quad \text{-CH}_2\cdot\text{CCH}_2^- + \text{-CH}_2\cdot\text{CH}_2 \rightarrow -\text{CH}_2\cdot\text{CHCH}_2^- + \text{CH}_2\cdot\text{CH}_2 \\
\end{align*}

CONCLUSIONS

H- and Y-links are both formed for photo crosslinked dodecane and branched hydrocarbons (squalane and isooctane), and they have almost equal yielding probability; the double bond of 1-hexene can be opened to form Y-links. These results are different from those reported\cite{3-4} and give new evidence for elucidating the mechanism of photo crosslinking of polyethylene.

REFERENCES

THE USE OF VINYL ETHERS IN FREE RADICAL UV CURING SYSTEMS

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Singapore Science Park, Singapore 0511

ABSTRACT

This paper describes the use of vinyl ethers as reactive diluents in radiation curable coatings and includes newly developed concepts for formulation. The use of vinyl ethers in free radical photoinitiated clear wood coating systems was evaluated. The experimental results obtained are being discussed.

INTRODUCTION

Vinyl ethers in cationic UV curing systems have been extensively investigated over the past few years (ref. 1-3). By utilizing iodonium or sulphonium salt as photoinitiator, this technology is already used in coil coatings, printing inks and adhesives based on epoxy/vinyl ether systems.

Vinyl ether monomer can also be used with acrylate oligomers to afford hybrid curable systems which combines the advantages of both vinyl ethers and acrylate chemistries including a wide selection of acrylate-based oligomers, low viscosity formulations permitting a range of application techniques, high cure speeds and excellent coating properties (ref. 4). Subsequent work suggests that in certain cases, it is possible to omit the cationic photoinitiator. Such systems are cured by UV generated free radicals alone (ref. 5). This finding is confirmed by high conversion rates obtained in monomer conversion studies performed (ref. 6).

Free radical UV curing systems have traditionally been based on acrylated pre-polymers and oligomers. In order to achieve viscosities which are suitable for industrial applications, such as spray, curtain or roller coating, dilution with acrylate monomers is often required. The combined benefits of vinyl ether diluents and acrylate oligomers would widen formulation latitude for the coating formulator. This formulation concept is demonstrated in the following experiments which evaluate the effect of varying major ingredients in free radical UV formulations for wood based on vinyl ether/acrylate blends.

VINYL ETHERS

Vinyl ethers are exceptionally reactive compounds, the chemistry of which is dominated by the fact that the vinyl ether double bond is highly electron rich and thus can form stable carbocations. Consequently, vinyl ethers readily undergo acid catalyzed polymerizations. Vinyl ethers are also reactive comonomers for free radical polymerizations. The vinyl ether electron-rich double bond associates with highly electron-deficient maleate or fumarate unsaturated polyesters forming charge transfer complexes which, on polymerization, afford alternating copolymers.

The key features of vinyl ethers are their excellent toxicity profiles, with LD-50s (oral - 5g/1000g and dermal - >2g/1000g) and no skin-sensitising effects. As reactive diluents, vinyl ethers are well known for their low viscosity, low odour and efficient diluency. They are available in various molecular structures that are capable of imparting a wide variety of chemical and physical properties to the formulation.

Of the vinyl ethers designed for use as reactive diluents in radiation-curable systems, RAPICURE® DVE-3 triethylene glycol divinyl ether from ISP provides excellent solvency and high degree of flexibility to cured films. 1,4-cyclohexane dimethanol divinyl ether (RAPICURE® CHVE) imparts hard but brittle coatings. Judicious blending of RAPICURE® DVE-3 vinyl ether and RAPICURE® CHVE vinyl ether permits formulation of coatings with the desired level of flexibility and hardness.

EXPERIMENTAL

To determine the level of vinyl ether at which optimum cure performance and cured film properties can be obtained, RAPICURE® DVE-3 vinyl ether was incorporated as a reactive diluent at levels between 10-30% into a series of epoxy acrylate (Actilane 320 from Akcos Chemicals) and urethane acrylate (Ebecryl 4858 from UCB Radcure) based coating systems. Free radical photoinitiators representing both the Norrish Type I and Type II mechanisms were used at levels 1-3% to achieve commercially viable clear coating systems. The free radical systems were suitable for use as top coats on birchwood or ply panels. A similar set of formulations were also prepared with the acrylate monomer diluent for comparison purposes.
Three consecutive layers of each of the wet formulations were applied and cured on wood panels that were dried and sanded before each application. The films were cured by exposure to a Fusion System standard "H" UV bulb (180 W/cm). Dose was varied by varying the rate of conveyance under the lamp. The total dry film thickness was approximately 25 - 30 microns. The cured films were stabilized for 24 hours before the panels were evaluated for surface gloss, pencil hardness, water resistance and MEK resistance. Thermal cycle tests over a temperature range -15 to 50°C were also carried out.

Upon determination of the optimum level of vinyl ether in free radical UV systems, the effects of varying other components in the vinyl ether/acrylate formulations were evaluated. Maximum cure speeds were determined with single coating of the formulation on aluminium substrates. Cured film properties were evaluated with coatings on printed paper substrates.

RESULTS & DISCUSSION

Viscosities of the formulations diluted with RAPICURE® DVE-3 vinyl ether and the acrylate monomer were plotted against the levels of diluents. Figure 1 shows viscosity reduction in formulations based on epoxy acrylate oligomer. Figure 2 shows viscosity reduction in urethane acrylate oligomer system.

In both cases, RAPICURE® DVE-3 vinyl ether diluent provided significant reduction in viscosities, when compared to the acrylate monomer. This demonstrates RAPICURE® DVE-3 vinyl ether's efficient diluency, that is capable of providing blends with viscosities below those obtainable from the 100% acrylate formulations. Hence, for a desired formulation viscosity, lower level of monomer can be used by substituting acrylate monomer with RAPICURE® DVE-3 vinyl ether diluent. This affords better end-product properties, eg. film toughness and flexibility. RAPICURE® DVE-3 vinyl ether offers good resin compatibility allowing more flexibility in viscosity adjustments to meet end-use requirements.

Figures 3 and 4 illustrates the effect of RAPICURE® DVE-3 vinyl ether on throughout, ie. maximum curing speed, of the coating formulations.
The maximum cure speed curves indicate decreasing cure speed with increasing RAPICURE® DVE-3 vinyl ether concentration. The results suggest an upper limit of 20% RAPICURE® DVE-3 vinyl ether in free radical formulations. Exceeding this limit may detract from acceptable film properties. In cases where higher levels of RAPICURE® DVE-3 vinyl ether diluent are required to achieve lower application viscosities, selection of oligomer with higher acrylate functionality and/or incorporation of a portion of acrylate monomer would help accomplish this.

The cured films were also evaluated for performance characteristics and results are summarized in Tables 1 and 2.

### Table 1: Cured Film Properties of Epoxy Acrylate Systems

<table>
<thead>
<tr>
<th>No.</th>
<th>Resin /Monomer Conc</th>
<th>Viscosity (Poise)</th>
<th>Max Curing Speed (m/min)</th>
<th>Gloss (60°)</th>
<th>Pencil Hardness</th>
<th>Water Resist, 6hr, 25°C</th>
<th>MEK Resist</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>83%/10% RAPICURE® DVE-3 diluent</td>
<td>106</td>
<td>&gt; 150</td>
<td>93.7</td>
<td>5B</td>
<td>VG</td>
<td>140</td>
</tr>
<tr>
<td>2</td>
<td>73%/20% RAPICURE® DVE-3 diluent</td>
<td>20</td>
<td>80</td>
<td>97.9</td>
<td>2B</td>
<td>VG</td>
<td>&gt; 500</td>
</tr>
<tr>
<td>3</td>
<td>83%/10% acrylate</td>
<td>426</td>
<td>&gt; 150</td>
<td>90.4</td>
<td>&lt; 6B</td>
<td>VG</td>
<td>40</td>
</tr>
<tr>
<td>4</td>
<td>73%/20% acrylate</td>
<td>80</td>
<td>113</td>
<td>93.1</td>
<td>&lt; 6B</td>
<td>VG</td>
<td>94</td>
</tr>
</tbody>
</table>

All the cured films had negligible odour. The films based on formulations containing RAPICURE® DVE-3 vinyl ether show overall improvement in performance properties as compared with those based on 100% acrylate chemistry. Such performance improvements are attributed by optimum conversion of reactive components in the formulations, eg. RAPICURE® DVE-3 vinyl ether reactive diluent.

As shown in Table 1, the epoxy acrylate films give excellent performance properties. MEK resistance was improved by using RAPICURE® DVE-3 vinyl ether. This is a significant improvement over the cured films based on 100% acrylate chemistry. Improvement in pencil hardness and surface gloss were also noted. The urethane acrylate based cured films exhibited excellent MEK resistance and good surface gloss.

Thermal cycling test results based on visual assessment of panels after 10 thermal cycles are shown in Table 3. Both the urethane acrylate and epoxy acrylate based cured films, employing 10-20% RAPICURE® DVE-3 vinyl ether exhibited good stability.

### Table 3: Thermal Cycle Stability of Cured Films

<table>
<thead>
<tr>
<th>No.</th>
<th>Formulation</th>
<th>Visual Assessment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Epoxy acrylate / 15% DVE-3</td>
<td>No apparent effects</td>
</tr>
<tr>
<td>2</td>
<td>Epoxy acrylate / 20% DVE-3</td>
<td>Slight cracking at edges after 10 cycles</td>
</tr>
<tr>
<td>3</td>
<td>Urethane acrylate / 10% DVE-3</td>
<td>No apparent effects</td>
</tr>
<tr>
<td>4</td>
<td>Urethane acrylate / 15% DVE-3</td>
<td>No apparent effects</td>
</tr>
</tbody>
</table>

From the results obtained, an upper limit of 20% RAPICURE® DVE-3 vinyl ether is suggested for optimum film properties. Maintaining at 20% vinyl ether, further evaluations and observations were made by varying the other formulation components.
Table 4: Influence of Vinyl Ether type on Epoxy Acrylate Coatings

<table>
<thead>
<tr>
<th>Coating</th>
<th>Cure speed, m/min</th>
<th>Surface gloss</th>
<th>Pencil Hardness</th>
<th>MEK resistance</th>
<th>Cured film odor</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1*</td>
<td>60</td>
<td>Good</td>
<td>H</td>
<td>&gt;100</td>
<td>none</td>
<td>Clear, low viscosity</td>
</tr>
<tr>
<td>2**</td>
<td>88</td>
<td>V good</td>
<td>B</td>
<td>&gt;100</td>
<td>mild</td>
<td>Cloudy, higher viscosity</td>
</tr>
</tbody>
</table>

* 73% Actilane 320, 20% RAPICURE® DVE-3, 3.5% benzophenone, 1% Darocure 1173 and 2.5% NMDEA
** 73% Actilane 320, 20% RAPICURE® CHVE, 3.5% benzophenone, 1% Darocure 1173 and 2.5% NMDEA

As shown in Table 4, replacing RAPICURE® DVE-3 vinyl ether with RAPICURE® CHVE vinyl ether improved cure speed of the wet formulation and surface gloss of the cured film. Film cured with RAPICURE® CHVE vinyl ether however, had mild odor whilst that cured with RAPICURE® DVE-3 vinyl ether had none. The superior diluency of RAPICURE® DVE-3 vinyl ether is again demonstrated.

Table 5: Effect of Free Radical Photoinitiators on Epoxy acrylate/RAPICURE® DVE-3 Systems*

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Benzo-phenone</th>
<th>Rapi-cor</th>
<th>PI507</th>
<th>Darocure 1173</th>
<th>Irgacure 184</th>
<th>Irgacure 651</th>
<th>Quantacure ITX</th>
<th>Quantacure DMB</th>
<th>Quantacure MCA</th>
<th>NMDEA</th>
<th>Pencil Hardness</th>
<th>Cure speed, m/min</th>
<th>MEK rubs</th>
<th>Odor</th>
<th>Cured film color</th>
<th>Visual gloss</th>
<th>Visual gloss</th>
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<tbody>
<tr>
<td>1</td>
<td>2.5</td>
<td>2.5</td>
<td>4.0</td>
<td>4.0</td>
<td>3.0</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>H</td>
<td>32</td>
<td>&gt;100</td>
<td>none</td>
<td>water white</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>2</td>
<td>2.5</td>
<td>2.5</td>
<td>4.0</td>
<td>4.0</td>
<td>3.0</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>HB</td>
<td>88</td>
<td>&gt;100</td>
<td>mild</td>
<td>water white</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>3</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
<td>3.0</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>H</td>
<td>32</td>
<td>&gt;100</td>
<td>mild</td>
<td>water white</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>4</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
<td>3.0</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>HB</td>
<td>88</td>
<td>&gt;100</td>
<td>none</td>
<td>water white</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>5</td>
<td>3.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>H</td>
<td>32</td>
<td>&gt;100</td>
<td>none</td>
<td>water white</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>6</td>
<td>3.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>HB</td>
<td>88</td>
<td>&gt;100</td>
<td>none</td>
<td>water white</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>7</td>
<td>3.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>H</td>
<td>32</td>
<td>&gt;100</td>
<td>none</td>
<td>water white</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>8</td>
<td>2.0</td>
<td>2.5</td>
<td>4.0</td>
<td>4.0</td>
<td>3.0</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>HB</td>
<td>88</td>
<td>&gt;100</td>
<td>mild</td>
<td>water white</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>9</td>
<td>2.0</td>
<td>2.5</td>
<td>4.0</td>
<td>4.0</td>
<td>3.0</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>HB</td>
<td>32</td>
<td>&gt;100</td>
<td>none</td>
<td>water white</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>10</td>
<td>2.5</td>
<td>2.5</td>
<td>4.0</td>
<td>4.0</td>
<td>3.0</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>HB</td>
<td>88</td>
<td>&gt;100</td>
<td>none</td>
<td>water white</td>
<td>Good</td>
<td>Good</td>
</tr>
</tbody>
</table>

*73-77% Actilane 320/20% RAPICURE® DVE-3 vinyl ether

As observed in Table 5, the type of free radical photoinitiators used in the vinyl ether/ acrylate coating systems will affect the color, odor and speed of the formulated product. Of the monomolecular types, Darocure 1173 provided the fastest cure speed.

With formulations containing bimolecular photoinitiators, application of RAPICURE® PI507 as an amine synergist for benzophenone gave faster cure speed than NMDEA with benzophenone. This observation is made after comparing results obtained in formulations 1 and 2. The coating that was cured with Quantacure ITX and Quantacure MCA, as in formulation 9, provided the fastest cure speed. However, it was also noted that the resultant cured film was yellow and would not be suitable for colorless coating application. Apart from the formulations cured with Irgacure 651 and Quantacure DMB, all the cured films were odorless.
CONCLUSION

The positive results obtained from the study has certainly proven the commercial viability and formulation versatility of using vinyl ether in free radical UV curing coating systems. The following conclusions are apparent:

- **Total substitution of acrylate monomer with vinyl ether in UV curing clear coat formulation can be achieved, particularly noteworthy are the very low viscosities achievable using vinyl ether diluents, compared with acrylate monomers. This enables the use of higher molecular weight acrylate oligomers, improving final film properties.**

- **Essential and desirable characteristics both in the wet formulation and cured film are not compromised.**

- **Performances of cured films, employing vinyl ether diluent, are equal or superior to those obtained from 100% acrylate formulations in epoxy acrylate and urethane acrylate systems.**

- **Cured film performances, such as, surface gloss, hardness, chemical and water resistance are improved.**

- **Cure speeds of the free radical formulations can be greatly improved by careful selection of photoinitiator combinations.**

- **RAPICURE® PI507 photoaccelerator is an excellent amine synergist in systems cured using photoinitiator of Norrish Type II mechanism.**

- **Toxicity profiles of the coating formulations are improved attributed by the excellent profile of vinyl ether (LD-50s, oral 5g/1000g and dermal >2g/1000g, non-sensitising).**

- **Vinyl ether can be incorporated into free radical UV curing formulations at levels up to 20%.**

REFERENCES

PRIMARY STUDY ON SYNTHESIS AND CHARACTERIZATION OF THE NEW TYPE EB CURABLE RESINS
I. ACRYLIC RESINS MODIFIED BY LIGHT-OIL

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Abstract

An acrylic resin modified by vegetable oil with high degree of unsaturation level has been synthesized. The characterization of coating film EB cured by the modified acrylic resin was studied primarily. The new type of EB curable acrylic resin is possessed of many merits such as cheap raw materials, simple synthesis technique and pretty characteristics of coating film. It is especially fit for timber surface coatings cured by EB radiation.

Introduction

Among all the oligomers used in EB curing of coatings, acrylate resins are the optimum with the merits of high reactivity, great variety and excellent adhesion [1]. The coating films with this kind of resin are possessed of high gloss, pretty hardness and fair toughness. In addition, its resistance to chemicals, water and so on are satisfied as well. However, because of high price, it is difficult, to some degree, to be used widely in many fields. One has suggested to use oil with epoxy group, such as epoxy bean oil to produce acrylated oil [2]. This type of oligomer has the advantage of low price, strong adhesion, light skin stimulus and so on, whereas, low curing speed and soft coating film make its use limited.

The acrylic resin synthesized in author's lab with the vegetable oil of high unsaturation level is a new type of EB curable resin. It is possessed of low price of raw materials, simple synthesis technique, excellent performance and higher reactivity because of its high unsaturation [3]. It has wide practical use especially for timber surface coating.
Experimental

1. Raw materials

The vegetable oil used in this work is light oil. The rest chemical reagents, such as pentaerythritol et al. are all products of Beijing Chemical Works, without purification.

2. Performance testing

Gloss: KG2-1A Mirror Facing Glossmeter (Material Test Machine Factory, Tianjing, China).

Hardness: QBY Swing Link Paint Film Sclerometer (ibid).

Adhesion: QFD Electric Paint Film Adhesion Tester (ibid).

3. EB curing: $^{60}$Co γ source facility, Peking University, accelerator, Beijing Normal University, acceleration voltage: 4 MeV, beam current: 100 μA

Synthesis of resin

The synthesis procedure is divided into three steps as follows in Fig. 1.

1. Synthesis of polymer containing light-oil

2. Synthesis of polymer containing light-oil
Both 860g of light-oil and 272g of pentaerythritol were added into a four-mouth bottle equipped with agitator condenser and thermometer. The polymerization reaction would be started by the aid of catalyst. The reaction system should be agitated efficiently and reaction temperature was raised sharply up to 230°C to reduce the decomposition of oil. After keeping the temperature for 0.5 hr. the methanol tolerance of the reaction system was checked at each 15 mins. until it equaled 3.0. If the reaction was not completed jet, additional catalyst should be added and the reaction continued at 230°C for another 0.5 hr. After the procedure, the main product was obtained as follows:

![Chemical structure diagram](image)

2. Synthesis of acrylic oligomer

13.17g of acrylic acid, 190.3g of styrene and 183.0g of methyl methacrylate were loaded in a four-mouth bottle. After adding proper amount of initiator, beginning agitation and raising the temperature, the reaction would be started and kept at 138°C for 5 hrs. The structure of the obtained product should be as follows:

![Chemical structure diagram](image)

3. Acrylation reaction

190g of light-oil polymer and 314g of acrylic oligomer were taken in a four-mouth bottle. The reaction began after starting the agitation and raising the temperature up to 230°C. One hour later, the product was obtained. The structure formula was like that:

![Chemical structure diagram](image)
4. Synthesis of acrylic-light-oil alkyd resin

After cooling the above product to room temperature 145g of TDI-monoHEA was added in the system and the reaction would continue at 80°C for 1h. and then, the final product was obtained as follows. Because of containing double-bonds in terminal groups the resin is rather reactive.

\[
\text{OH} \quad \text{C} \quad \text{CH} \quad \text{CH} \quad \text{St} \quad \text{MMA} \quad \text{LFA} \\
\text{\text{OCH}} \quad \text{\text{CH}} \quad \text{CH} \quad \text{CH} \quad \text{NH} \quad \text{NH} \\
\]

Preparation of coating

The formulation of the coating was made as shown in Table 1.

<table>
<thead>
<tr>
<th>Component</th>
<th>Content, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copolymer</td>
<td>46</td>
</tr>
<tr>
<td>HDDA</td>
<td>30</td>
</tr>
<tr>
<td>TDI-diHEA</td>
<td>20</td>
</tr>
<tr>
<td>Inhibitor</td>
<td>2.0</td>
</tr>
<tr>
<td>Additives</td>
<td>2.0</td>
</tr>
</tbody>
</table>

* Proper amount of ethyl acrylate (EA) may be added to adjust the viscosity of the system

Coating and curing

The talcum powder and synthesized coating by ratio 2.2 : 3 : 1 were put together, while proper amount of diluent was added in order to control the viscosity to a favorable level and then, the paste was spreaded uniformly on the test panel surface as primer which was cured by 60Co γ-rays with dose rate of 71.3 Gy/Min. total dose of 60 kGy in vacuum to cure the primer. And then, the cured primer was treated as described in experimental part of this work to paint the surface layer of timber as the top coating. The coated film covered by PET film was cured again by EB from accelerator with total dose of ~ 70 kGy.
The property tests after EB curing showed that the films have gloss of 88.5, hardness of 0.85 and adhesion of one grade.

Conclusion and discussion

1. Using coating synthesized in this work the paint film cured by EB irradiation on timber surface is possessed of a good level of main performances, such as gloss, hardness and adhesion.
2. Because of the large amount of vegetable oil with high unsaturation used as the raw material in the synthesized resin, the cost of the coating descended apparently.
3. The electron beam energy of the accelerator utilized is higher (~ 4 MeV) than that is needed in the work, so the actually required absorbed dose ought to be smaller than it was reported here.

References

"Electron Beam Curing of Polymeric Materials"
Radiation Curing of Polymeric Materials Edited by Charles E. Hoyle and James F.Kinstle, ACS symposium Series 417 P.17 (1990)
Another new type of alkyd resin modified by linseed oil fatty acid (LFA) was synthesized and the EB curable coating was prepared in this work. After EB curing on timber surface, the coating film is possessed of good performances.

Compared with the previous work [1] where vegetable oil was used as main raw material to synthesize a new type of EB curable resin, in this paper the corresponding fatty acid was used. This process has two merits at least. As for coating, vegetable-oil fatty acid is a kind of leftover cull from refining process of corresponding oil, so it has a much lower price; in respect of synthesis, using oil as the raw materials it needs to take an ester exchanging reaction, however, the final effective component in the resin is the corresponding unsaturated fatty acid. The synthesis process was simplified whereas the performance of the cured coating film was similar to the former.

The raw materials, reagents, EB curing conditions and the test methods of coating films were similar to those shown in previous paper.

Synthesis of resins

By using oil fatty acid, two kinds of resins were synthesized.

Synthesis of alkyd-urethane acrylate

LFA (or soybean-oil fatty acid), pentaerythritol and phthalic anhydride, in equal mole ratio (1:1:1), were added into a four-mouth bottle equipped with agitator, condenser and thermometer followed by filling super pure nitrogen gas in order to prevent LFA from being oxidized by air. The xylene solvent was dripped into separator to make the pentaerythritol detained on the bottle wall be cleaned continuously by xylene reflux during the course of reaction, so as to make the reaction complete.

In this experiment, the temperature of reaction system was raised quickly up to 180 °C under the condition of full agitation and then up to 230 °C gradually within 1.5 hs and kept for 1 h. The reaction would be complete when acid value of the system became less than 20. The product obtained finally was still thick and proper amount of diluent such as ethyl acrylate (EA) should be added in to adjust the viscosity of system.
When temperature of the system dropped down to 50 °C, 0.5 mole of TDI-monoHEA was dripped slowly in during the period of 1 h and then, the temperature was raised up to 80 °C with agitation for another 1 h. The proportional crosslinking agent, TDI-diHEA (or HDDA) and proper amount of diluent was added in product system to regulate viscosity. The coating prepared was stored for use (sample 1). The structural formula of the product is as follows:

\[ \text{TH : TDI-monoHEA} \]

The formulation of coating was shown in Table 1.

<table>
<thead>
<tr>
<th>Component</th>
<th>Content, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modified resin</td>
<td>50</td>
</tr>
<tr>
<td>TDI-diHEA</td>
<td>45</td>
</tr>
<tr>
<td>Inhibitor</td>
<td>2</td>
</tr>
<tr>
<td>Additives</td>
<td>2</td>
</tr>
<tr>
<td>EA</td>
<td>Proper amount</td>
</tr>
</tbody>
</table>

Synthesis of acrylic-linseed alkyd

The synthesis procedure was divided into 4 steps as shown in Fig. 1:

1. Synthesis of acrylic oligomer

The synthesis of acrylic oligomer can also be seen in the previous work

2. Reaction of TMP with acrylic oligomer

1.0 mole of trimethylolpropane (TMP, illustrated as \(-\text{-}-\)) was added in a four-mouth bottle where 1.83 mole of acrylic oligomer was at 100 °C. The temperature of reaction system was raised up to 230 °C for initiating esterification reaction. This reaction could be formulated as follows.
3. Esterification between TMP and LFA

When above reaction was completed, 0.8 mole of LFA was dripped at 230℃ for 1h. The reaction formula is

\[ \text{LFA} + \text{Acrylic oligomer} \rightarrow \text{O-} - \text{AA-(St-MMA)_{10}} \]

4. Reaction of product with phthalic anhydride

After above reaction the temperature in reactor was decreased down to 100℃ and then, 0.8 mole of phthalic anhydride (PA) was poured into the reaction system which has been filled with nitrogen gas. The reactor was heated up to 230℃ for 2 hs to complete the reaction. The structural formula of the product was as sample 2.

5. Summary of the reactions:

The above reactions could be summarized in Table 2.

<table>
<thead>
<tr>
<th>Reaction step</th>
<th>Component</th>
<th>Content, mole</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AA</td>
<td>0.183</td>
<td></td>
</tr>
<tr>
<td></td>
<td>St</td>
<td>1.83</td>
<td>In xylene</td>
</tr>
<tr>
<td></td>
<td>MMA</td>
<td>1.83</td>
<td></td>
</tr>
<tr>
<td></td>
<td>BPO</td>
<td>2.5% / monomer</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>TMP</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>LFA</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>PA</td>
<td>0.8</td>
<td>Proper amount of EA</td>
</tr>
</tbody>
</table>
Preparation of coating

Lower the temperature of the product down to 150°C and added 1,6-hexanediol diacrylate (HDDA) as crosslinking agent. When the temperature dropped gradually down to 60°C, the viscosity of the reaction system may be still sluggish, then EA, as the diluent, may be used to adjust the viscosity. The formulation of the coating was shown in Table 3.

Table 3. Formulation of coating

<table>
<thead>
<tr>
<th>Component</th>
<th>Content, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oligomer</td>
<td>50</td>
</tr>
<tr>
<td>HDDA</td>
<td>40</td>
</tr>
<tr>
<td>Inhibitor</td>
<td>2</td>
</tr>
<tr>
<td>Additives</td>
<td>3</td>
</tr>
<tr>
<td>EA</td>
<td>Proper amount</td>
</tr>
</tbody>
</table>

Performance of EB curing coating film
The method and experimental conditions of EB curing was the same as the previous work. The main characteristics of the cured test panels was checked as follows in Table 4.

Table 4. Main characteristics of prepared coatings

<table>
<thead>
<tr>
<th>Sample</th>
<th>Gloss</th>
<th>Hardness</th>
<th>Adhesion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>86</td>
<td>0.85</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>90</td>
<td>0.88</td>
<td>1</td>
</tr>
</tbody>
</table>

In respect of above main performances, the results of EB curing resins using LFA as the raw material was much similar to that using corresponding oil. The primary results indicated that the products made from vegetable oil with high degree of unsaturation and corresponding fatty acid as main raw materials could be classified into a new type of EB curing resin which is possessed of both oil and alkyd resins and can be cured by EB radiation easily. This new type of resin is worthy of making further investigation and development.

References

[1]. Wei Jinshan, Yi Min et al.  
"Primary study on synthesis and characterization of the new type EB curable resins 1. Acrylic resin modified by light-oil"  
To be published.
RADCURE DEVELOPMENTS IN RUSSIA

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125124 Moscow RUSSIA

ABSTRACT

The survey dwells on three main parts:

1. Insight into the state of radiation curing technology in Russia.
2. Scope of the scientific potential.
3. Certain regard on forecasts, opportunities and prospects for Russian RadTech market.

INTRODUCTION

Dynamics of radcure technologies' dissemination is docketed in Table 1. In 70's Russian scientific institutes had successfully developed radcure process due to the lavish state subsidizing. The laboratories that these institutes had at their disposal had used state-of-the-art equipment. It had broadened the plants horizons as well. EB coatings on TV set bodies, UV coatings and inks for chipboards and printed circuit boards, materials for photopolymer printing plates were implemented to the industry.

In 1980's, when the Russian economics has been almost collapsed, RadTech sector also plunged into turmoil. The lack of acrylic monomers became the decisive factor of radcure stalling. Nevertheless some radcure processes and systems had been developing even in this recession period (Table 1).

Nowadays, despite the great changes in the country, clouds continue to hang over the Russian RadTech market. However, the second advent of RadTech technology could be envisaged.

Our market data is based mostly on own information retrieval as well as on information collected by RadTech devotees.
Table 1. Dissemination of radcure technologies in Russia

<table>
<thead>
<tr>
<th>1970's</th>
<th>1980's</th>
<th>1990's</th>
</tr>
</thead>
<tbody>
<tr>
<td>UPS wood coatings</td>
<td>UPS wood coatings</td>
<td>UPS wood coatings</td>
</tr>
<tr>
<td>UPS building adhesives</td>
<td>UPS building adhesives</td>
<td>UPS building adhesives</td>
</tr>
<tr>
<td>Acrylic flexographic plates</td>
<td>Acrylic flexographic plates</td>
<td>Acrylic flexographic plates</td>
</tr>
<tr>
<td>Optical fiber coatings</td>
<td>Optical fiber coatings</td>
<td>Optical fiber coatings</td>
</tr>
<tr>
<td>Optical discs coatings</td>
<td>Optical discs coatings</td>
<td>Optical discs coatings</td>
</tr>
<tr>
<td>Adhesives for laminated glass production</td>
<td>Adhesives for laminated glass production</td>
<td>Adhesives for laminated glass production</td>
</tr>
<tr>
<td>Dental resins</td>
<td>Dental resins</td>
<td>Dental resins</td>
</tr>
<tr>
<td>Materials for printing plates</td>
<td>Materials for printing plates</td>
<td>Materials for printing plates</td>
</tr>
<tr>
<td>Photoresists</td>
<td>Photoresists</td>
<td>Photoresists</td>
</tr>
<tr>
<td>Acrylic wood coatings</td>
<td>Acrylic wood coatings</td>
<td>Acrylic wood coatings</td>
</tr>
<tr>
<td>Jet Inks</td>
<td>Jet Inks</td>
<td>Jet Inks</td>
</tr>
<tr>
<td>LCD adhesives</td>
<td>LCD adhesives</td>
<td>LCD adhesives</td>
</tr>
<tr>
<td>Aspherical lenses coatings</td>
<td>Aspherical lenses coatings</td>
<td>Aspherical lenses coatings</td>
</tr>
</tbody>
</table>

RAW MATERIALS

Table 2 summarizes the market data monomers, olygomers and photoinitiators. It reveals the range of commercial products as well as their annual growth rates for the consumption in 1991-1994.

As it is seen the domestic range of raw materials is extremely limited. For many years Russian plants have been making the simple acrylic monomers with no risk and no competition and as a result they have become complacent. The only plant to be reckoned is the acrylic plant, built by Japanese license, not launched since 1987.

In this particular situation the weak players should be weeded out and the growing demand of the RadTech customers could be satisfied by the import. From this point of view Russia is an unparalleled prospect for sales of western-made acrylic monomers and olygomers.

It should be mentioned, that the general falling down of raw materials manufacturing in 1991-1994 does have some exceptions. The growth of monofunctional acrylic monomers, urethaneacrylates and 2,2-DIPAPH photoinitiator manufacturing is connected with the wide promotion of the domestic urethaneacrylate adhesives in multilayer glass production technology.
Table 2. Radcure Raw Materials in Russia

### COMMERCIAL PRODUCTS

<table>
<thead>
<tr>
<th>COMMERICAL PRODUCTS</th>
<th>VOLUME, M.T.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomers</td>
<td></td>
</tr>
<tr>
<td>Acrylic Acid</td>
<td>1000</td>
</tr>
<tr>
<td>Acrylic Ethers Monofunctional</td>
<td>1000</td>
</tr>
<tr>
<td>(MA, BA, 2-EHA, MA, BA, HEMA, MA, DMAEM)</td>
<td></td>
</tr>
<tr>
<td>Acrylic Ethers Multifunctional</td>
<td>8400</td>
</tr>
<tr>
<td>(TGM-3, DMEG, TGM-13T)</td>
<td></td>
</tr>
<tr>
<td>Oligomers</td>
<td></td>
</tr>
<tr>
<td>Unsaturated Polyesters</td>
<td>5100</td>
</tr>
<tr>
<td>Polyesteracrylates</td>
<td>2000</td>
</tr>
<tr>
<td>(PEA 7-1, PEA 7-29, MGF-1, MGF-2, MGF-8, BPAEDM)</td>
<td></td>
</tr>
<tr>
<td>Epoxycrylates</td>
<td>800</td>
</tr>
<tr>
<td>(EAS-28A, BISGMA)</td>
<td></td>
</tr>
<tr>
<td>Urethaneacrylates</td>
<td>300</td>
</tr>
<tr>
<td>(UA-1052, UA-2102, UA-3592, UA-6003)</td>
<td></td>
</tr>
<tr>
<td>Carbonatemethacrylates</td>
<td>100</td>
</tr>
<tr>
<td>(OCM-2)</td>
<td></td>
</tr>
<tr>
<td>Photoinitiators</td>
<td></td>
</tr>
<tr>
<td>Irgacure 651</td>
<td>10.5</td>
</tr>
<tr>
<td>2,2-Diisopropanyacetophenone</td>
<td>~</td>
</tr>
</tbody>
</table>

### MAJOR USE SEGMENTS

#### HIGH VOLUME CATEGORY

Wood coatings

As described earlier the market of wood coatings is the major Russian radcure market.

There are about 120 UV process production lines (95 are of foreign origin) at furniture plants. Their potential production capacity averages 750,000 square meters per year. Nowadays these production lines are charged not more than on 50% (Picture 1)
Utilization of Wood Coating Materials

The part of import materials becomes prevailed. Interim results this year likely to reflect recession of domestic market and the buoyant demand for import.

UPS systems have traditionally been the major basis for wood coating market. For time being they are being partially substituted by more sophisticated acrylic materials. However, the positions of UPS systems remain strong. The matter is that low quality of Russian wood materials hardly enables the usage of roll coating finishing technology for the front panels of furniture. As to acrylic curtain coatings, they are too expensive.

As to EB formulations for wood, they were used mostly for finishing the TV set bodies and as adhesives for laminating particle boards and concrete shuttering. Nowadays these applications dramatically decreased (Picture 2).

Picture 1. Utilization of Wood Coating Materials

Picture 2. Dynamics of EB Wood Coatings market
Glass laminates

Automotive, security, bulletproof and acoustic multilayer glass are widely produced in Russia by pouring UV formulations between two glass sheets and then curing with low pressure UV lamps through the glass. The technology successfully competes with lamination, using polyvinylbutyral (PVB) films, offering the possibilities of enormously reduced costing.

A novel photopolymerizable urethaneacrylate adhesive for glass lamination has been developed by DIPOL. It confers the excellent variety of properties (Table 3).

Table 3. Properties of the Novel Urethaneacrylate Adhesives for Multilayer Glass Bonding.

<table>
<thead>
<tr>
<th></th>
<th>+20°C</th>
<th>-20°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength, kg/cm²</td>
<td>336</td>
<td>295</td>
</tr>
<tr>
<td>Elongation, %</td>
<td>445</td>
<td>360</td>
</tr>
<tr>
<td>Volume Shrinkage, %</td>
<td>max 5</td>
<td>min 10</td>
</tr>
<tr>
<td>Adhesion, MPa</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Its production enables to reach viable prospect for the Russian customers involved in this specific niche with the overall demand, surpassing 500 MT per year.

Photopolymer printing plates

Photopolymer printing plates (PPP) have become very popular in the Russian flexographic and letterpress printing since the beginning of 70's. Nowadays the shift towards web offset printing is noticeable. However, flexo printing liquid photopolymer systems are still used including some rather effective tap water washout systems. Declining of photopolymers demand is presented on Picture 3.
LOW VOLUME CATEGORY

Table 4 describes the Russian market segments where UV/EB curable materials are used in the low volumes. The most growing areas among them are optoelectronic materials (coatings and inks for optical discs, fibers, lenses) and offset inks.

Table 4. Areas of Low Volume application

<table>
<thead>
<tr>
<th>Application</th>
<th>Annual Tonnage</th>
<th>No of Installations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Offset inks for plastic lids</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Screen print inks for CD</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>Ink</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>Photoresists</td>
<td>250</td>
<td>25</td>
</tr>
<tr>
<td>Conformal coatings</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>Aspherical lenses coatings</td>
<td>0.3</td>
<td>5</td>
</tr>
<tr>
<td>Videodiscs replicate coatings</td>
<td>0.4</td>
<td>2</td>
</tr>
<tr>
<td>CD protective coatings</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>Optical fiber coatings</td>
<td>20</td>
<td>8</td>
</tr>
<tr>
<td>Protective coatings for holograms</td>
<td>0.2</td>
<td>3</td>
</tr>
<tr>
<td>Dental restoration</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>LCD adhesives</td>
<td>0.3</td>
<td>2</td>
</tr>
</tbody>
</table>

Novel UV-curable monomers for optical coatings

At the beginning of RadTech boom Russian scientists had revealed that carbonate acrylates (CA) are extremely suitable for radiation curing (increasing reactivity, decreasing volume shrinkage). Some years ago we discovered also that multifunctional CA are characterized by drastically increased birefringence. It enabled the development of the specific range of monomers for optical properties with the unique variety of characteristics (Table 5).

Table 5. Properties of the Novel Carbonate Acrylate Monomers

<table>
<thead>
<tr>
<th>Property</th>
<th>Min</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refractive Index</td>
<td>1.53</td>
<td></td>
</tr>
<tr>
<td>Birefringence</td>
<td></td>
<td>10 nm/mm</td>
</tr>
<tr>
<td>Volume Shrinkage</td>
<td></td>
<td>6%</td>
</tr>
<tr>
<td>Moisture Absorption</td>
<td></td>
<td>1%</td>
</tr>
<tr>
<td>Flame Retardance</td>
<td>V-1 according to the Vertical Burning Test</td>
<td></td>
</tr>
<tr>
<td>Impact Resistance</td>
<td></td>
<td>20 kg/cm</td>
</tr>
<tr>
<td>Scratch Resistance</td>
<td></td>
<td>5000 rev/min</td>
</tr>
</tbody>
</table>
FORECASTS, OPPORTUNITIES, PROSPECTS

No question the legal, technical, financial situation is rather vexing to the western companies. No wonder that import acrylic monomers have seen so little spot business. It is really difficult to recon on making an immediate profit or to commit profit to this field.

Nevertheless, the contrasts of Russia are as usually tremendous. The traditions, scientific potential, prospects of RadTech market were mentioned above. Moreover, two months ago Russia revamp its rules for foreign investors to facilitate their participation in its business. Mitigating circumstances appear in financial sphere also. To experience the vicissitudes of the Russian transport systems is not yet so risky.

DIPOL’s strategy, focused on creating and strengthening the Russian RadTech market, is trying to take into account all these points.

CONCLUSIONS

1. THE BASIS FOR THE RUSSIAN RADTECH: Traditions
   Scientific potential
   Growing market

2. THE MAJOR RETARDING FACTORS: Lack of modern
   radcure technologies
   and acrylic monomers

3. DEBOTTLENECKING SOLUTIONS
   A. The specialized retrieval of the potential radcure technologies and
      materials customers.
   B. Establishing of joint ventures between customers from one side,
      suppliers of technologies and materials from other side
Influence of Catalysts in the Structures and Performance of Meta-Cresol Novolacs

Wu Lin Yu Shangxian
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Beijing, 100875, P.R. China

ABSTRACT
The different influences of catalysts (Zn(AC)$_2$, P-toluene sulfonic acid and oxalic acid) on the structures and performance of meta-cresol novolacs were researched by quantitative $^1$C-NMR spectroscopy and infrared spectrophotometry. It was found that the resin catalyzed by Zn(AC)$_2$ is high ortho-ortho type, the resin catalyzed by oxalic acid is mainly ortho-para type and the structure of resin catalyzed by p-toluene sulfonic acid is between that of the above two novolacs.

In practical synthesis, the integrated use of Zn(AC)$_2$ and oxalic acid should be considered, and the resins resulted from this consideration possess excellent performance when used as the binder resins of positive photoresists.

INTRODUCTION
By $^1$C–NMR spectroscopy and infrared spectrophotometry it was found that a high ortho-ortho m-cresol novolac was obtained using Zn(AC)$_2$ as catalyst, an ortho-para m-cresol novolac was obtained using oxalic acid as catalyst and a novolac whose structure is between that of the above two novolacs was obtained using p-toluene sulfonic. The positive photoresist, in which the m-cresol novolac catalyzed by Zn(AC)$_2$ is used as binder resin, has nice imaging feature, high alkali resistance and high contrast. However the novolac catalyzed by Zn(AC)$_2$ is liable to crosslink and this drawback appears obviously in after-treatment of the product. On the otherhand, the resin catalyzed by oxalic acid is light colored and has less tendency to crosslink in after-treatment. So in order to take advantages of these two catalysts a two-step catalyzing method to synthesize novolac was designed and our expectation of using obtained products as binder resins for positive photoresists have been achieved.

EXPERIMENTAL
In a 250 ml 4-neck round bottom flask a definite quantity of m-cresol and
catalyst was added, the reactants were heated to 90°C with vigorous stirring under N<sub>2</sub> protection.

Then 37% aqueous solution of formalim was dropped in the flask over 1 hour at 90°C. After that, the reactants were kept on reacting for 8–10 hours. Then the reactants were washed with water for several times and dehydrated to obtain solid resin. The specific synthesis examples and reaction conditions were listed in table 1.

Table 1 Synthesis examples of m-cresol novolacs with different catalysts

<table>
<thead>
<tr>
<th>serial number</th>
<th>m-cresol: formaldehyde ratio of molar number</th>
<th>kind and quan. of act. (wt% m-cresol)</th>
<th>average reaction temperature(°C)</th>
<th>softening point of product (°C)</th>
<th>yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B0-1</td>
<td>3:2</td>
<td>zinc acetate 2%</td>
<td>91</td>
<td>91</td>
<td>89</td>
</tr>
<tr>
<td>B0-2</td>
<td>3:2</td>
<td>P-toluene sulfonic acid 0.1%</td>
<td>60</td>
<td>60</td>
<td>86</td>
</tr>
<tr>
<td>B0-3</td>
<td>3:2</td>
<td>oxalic acid 1%</td>
<td>85</td>
<td>85</td>
<td>85</td>
</tr>
</tbody>
</table>

reaction time: 13 hours

RESULTS AND DISCUSSION

1. Solvents solubility

Resins catalyzed by the above catalysts are all soluble in alcohol, ethers, ketones, esters, amines, 5% Na<sub>2</sub>SiO<sub>3</sub> aqueous solution and 0.1% NaOH, while insoluble in toluene, xylene, chloroform, tetrachloro-methane and gasoline.

2. Analysis of the <sup>13</sup>C–NMR spectra of the resins

Fig.1 and Fig.2 give <sup>13</sup>C–NMR spectra of m-cresol and resin B0-1, respectively.

Fig.1 <sup>13</sup>C–NMR spectrum of m-cresol
The 1, 2, 3, 4,—positions in the above spectra represent the positions of the following carbons respectively:

\[
\begin{align*}
\text{Fig. 2 } {}^1\text{C—NMR spectrum of } B_{2-1}.

\text{The } {}^1\text{C—NMR spectra of the resins are quantitatively analyzed by DEPT method [1] using a ARX 400 type nuclear magnetic resonance spectrometer. In DEPT method, } {}^1\text{C—NMR spectrum gives no signals for carbons not connected with hydrogen atoms, such as 1,3—carbons. In o—o resin structure, 4—carbon is free of } -CH_2—\text{bridge. In o—p structure, 2-carbon or 6-carbon is free of } -CH_2—\text{bondage. So the resonance peak area of 4—carbon in every resin can tell us the main connection pattern of this resin. The specific quantitative method is as follows:}

\[
\text{Si}= \frac{A_i \times 100}{A_5 \times f_i}
\]

(1)

where \( Si \)—the ratio of vacant \( i \)—carbon

\( A_i \)—the peak area of \( i \)—carbon in \(^1\text{C—NMR spectrum of a resin}

\( A_5 \)—the peak area of 5-carbon in \(^1\text{C—NMR spectrum of a resin}

\( f_i \)—correction factor

The calculated \( Si \) values are listed in table 2.

From table 2, we can see:

(1) The descending order of \( S_i \) is: \( B_{2-1}, B_{2-2}, B_{2-3}, \), which means that Zn(AC)
is an effective catalyst for obtaining high ortho-ortho novolac, while oxalic acid is the least effective catalyst for such purpose and p-toluene sulfonic acid tends to give a novolac having a structure between that of ortho-ortho and ortho-para novolacs.

(2) The vacant ratio of 2-carbon is higher than that of 6-carbon. This is due to the higher steric hindrance of 2-carbon by methyl and hydroxyl groups.

### Table 2 Si values of B₀₋₁, B₀₋₂, and B₀₋₃

<table>
<thead>
<tr>
<th>resin</th>
<th>Si</th>
<th>S₁</th>
<th>S₂</th>
<th>S₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>B₀₋₁</td>
<td>52.9</td>
<td>47.4</td>
<td>15.1</td>
<td></td>
</tr>
<tr>
<td>B₀₋₂</td>
<td>26.8</td>
<td>63.9</td>
<td>26.2</td>
<td></td>
</tr>
<tr>
<td>B₀₋₃</td>
<td>19.1</td>
<td>61.0</td>
<td>40.1</td>
<td></td>
</tr>
</tbody>
</table>

3. Analysis of the infrared spectra of the resins

In the spectra the absorption at 770 cm⁻¹ is the characteristic of C-H group at the 4-position of benzene ring, and the absorption at 850 cm⁻¹ is the characteristic of the C-H group at 2-position of benzene ring. According to the Lambert-Beer Law, the results in table 3 are obtained through specific calculation.

If p is used to represent C-H at the 4-position, o is used to represent C-H at the 2- and 6-positions and A is used to represent optical density, Aₚ/Aₒ can be used to determine the main connection pattern between m-cresol and CH₂O.

### Table 3. The analytical results from IR spectra

<table>
<thead>
<tr>
<th>resin</th>
<th>Aₚ</th>
<th>Aₒ</th>
<th>Aₚ/Aₒ</th>
</tr>
</thead>
<tbody>
<tr>
<td>B₀₋₁</td>
<td>0.132</td>
<td>0.0725</td>
<td>1.82</td>
</tr>
<tr>
<td>B₀₋₂</td>
<td>0.0726</td>
<td>0.0947</td>
<td>0.767</td>
</tr>
<tr>
<td>B₀₋₃</td>
<td>0.0308</td>
<td>0.0827</td>
<td>0.372</td>
</tr>
</tbody>
</table>

Comparing the data in table 3 and table 2, we can see that the descending order of the ratio of Aₚ/Aₒ is B₀₋₁, B₀₋₂, B₀₋₃ which is the same as the results from ¹³C-NMR spectra.

From the above experimental results, the following reaction mechanism of using two valent metal ions as catalysts can be postulated [2].
It is well known that in the acidic medium, the reaction is ready to occur in the para position of hydroxyl group. This is due to the high activity in this position. If the acid is very strong, for example p-toluene sulfonic acid, the activity of ortho positions will be increased, while oxalic acid is a medium strong acid, it mainly produces ortho-para m-cresol novolacs.

4. The imaging features and alkaline resistance of the positive photoresists prepared using the above novolacs as binder resins

The compositions of the positive photoresists are as follows:

- binder resin: B₁₋₁, B₂₋₂, B₃₋₃, B₄₋₄,
- solvent: EGMA
- photo-active compound (PAC): NT—155 (TOYO GOSEL. CO.)
- solid cont. (wt. %): 15
- ratio of resin to PAC: 2:1

The imaging results of the photoresists are listed in table 4.

From table 4 we can see the concentrations of developing solution have to
be diluted with the descending of $S_4$ values in order to achieve the same imaging results, so the resins with higher $S_4$ value have higher alkaline resistance. This can also be seen from the film retaining rate of resins after dipping in 5% $\text{Na}_2\text{SiO}_3$ for 5 min. The film retaining rates (%) of $\text{B}_{0-1}$, $\text{B}_{0-2}$ and $\text{B}_{0-0}$ are 98, 51 and 46 respectively.

<table>
<thead>
<tr>
<th>resin</th>
<th>developing condition</th>
<th>result</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cont. (%)</td>
<td>t/sec</td>
</tr>
<tr>
<td>$\text{B}_{0-1}$</td>
<td>5</td>
<td>60</td>
</tr>
<tr>
<td>$\text{B}_{0-2}$</td>
<td>4</td>
<td>60</td>
</tr>
<tr>
<td>$\text{B}_{0-0}$</td>
<td>3</td>
<td>40</td>
</tr>
</tbody>
</table>

temperature of prebake: 100°C, time of prebake: 25 min, developer: aqueous solution of $\text{Na}_2\text{SiO}_3$, developing temperature: 18°C

* 2 represents that the washing off grade is 2. 7 represents that the color changing grade is 7.

** 2 represents that the lowest grade where no dot is washed away. 12 represents that the highest grade where no dot is connected with others.

In alkaline solution the diazo group in PAC coupled with the vacant 4-position carbon, so the alkaline solubility of novolacs was reduced greatly. Thus, the more vacant 4-position the resin has, the lower solubility the resin possesses in alkaline solution.

Although resins catalyzed by $\text{Zn(AC)}_2$ have high alkaline resistance and contrast, we still can not use $\text{Zn(AC)}_2$ singularly to prepare novolacs, because it was found that such resins are liable to crosslink and this drawback appears obviously during after-treatment. On the other hand, the resins obtained using oxalic acid are almost colorless and have less tendency to crosslink. Therefore in order to take advantages of both $\text{Zn(AC)}_2$ and oxalic acid, we designed a two-step catalyzing method to prepare novolacs and achieved our expectation of using them as binder resins for positive photoresists.

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DIVINYLBENZENE—RESORCIN RESINS
FOR UV CURING
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Beijing 100875, P.R. China

ABSTRACT

The Friedel–Crafts reaction between divinylbenzene (DVB) and resorcin produced a new series of photopolymer: DVB—resorcin (DVBR) resins. The modified DVB—resorcin (MDVBR) resins are also obtained after the reaction between other olefin hydrocarbon and DVBR resin. The photosensitive system including DVBR or MDVBR and a photosensitizer such as 2,6-bis (4'-azidobenzal)-4-methyl cyclohexanone (BAC-M) can be used as a type of UV curing negative photoresist. Through the analysis of the $^{13}$C–NMR spectra of resorcin—formaldehyde resins and DVBR resins, we discuss the influence of different catalyst on the structures of the resins. We also found a method by which we can determine the structures of the resins through the cheap and convenient IR spectrometre.

INTRODUCTION

Some UV curing photoresists formed with phenolic or novolac resins and azides can be developed by dilute alkaline aqueous solution. Because of their high resolution and good resistance to etching, this type of photoresists is still one of the main interesting subjects [1,2]. Our laboratory has successfully prepared a series of resorcin—type UV curing photoresists, among which tung oil—resorcin resin (TRR) is a perfect one [3]. In order to increase the softening point and to further improve the performance of the photosensitive film, we successfully synthesized a new kind of photopolymer: divinyl benzene—resorcin (DVBR) resin. We also successfully synthesized the modified DVBR resins.

EXPERIMENTAL

1. Synthesis of divinyl benzene—resorcin (DVBR) resins.

Use a special way to make DVB and resorcin perform homogenous reaction in the presence of a kind of acidic catalyst (SC). Then, maintain about
2—4 hours at some narrow range of temperature. Finally, A series resins were obtained after purging disposal.

Table 1 Influence of different synthesis conditions on the properties of A series resins

<table>
<thead>
<tr>
<th>Resin No.</th>
<th>Resorcin:DVB ratio</th>
<th>Colour</th>
<th>Softening point (°C)</th>
<th>Solubility</th>
<th>Alcohol</th>
<th>Acetone</th>
<th>Ethyl cellosolve</th>
<th>NaOH-H₂O (1%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1</td>
<td>3:2</td>
<td>red-brown</td>
<td>25</td>
<td>soluble</td>
<td>soluble</td>
<td>soluble</td>
<td>soluble</td>
<td></td>
</tr>
<tr>
<td>A-2*</td>
<td>4:3</td>
<td>bright yellow-brown</td>
<td>74</td>
<td>easily</td>
<td>easily</td>
<td>easily</td>
<td>easily</td>
<td></td>
</tr>
<tr>
<td>A-3</td>
<td>5:4</td>
<td>yellow-brown</td>
<td>78</td>
<td>soluble</td>
<td>soluble</td>
<td>soluble</td>
<td>soluble</td>
<td></td>
</tr>
<tr>
<td>A-4</td>
<td>1:1</td>
<td>red-brown</td>
<td>25</td>
<td>soluble</td>
<td>soluble</td>
<td>soluble</td>
<td>soluble</td>
<td></td>
</tr>
<tr>
<td>A-5*</td>
<td>4:5</td>
<td>bright yellow-brown</td>
<td>90</td>
<td>soluble</td>
<td>soluble</td>
<td>soluble</td>
<td>soluble</td>
<td></td>
</tr>
</tbody>
</table>

* The products were dealt with under vacuum condition.

2. Synthesis of modified divinyl benzene-resorcin (MDVBR) resins

Make resin A-1 soften fully then add toluene sulfonic acid. Finally, add monoene or diene to carry modified reaction.

2.1 Using styrene to modify

The reaction was carried out in accordance with the reaction formula (1):

After purging disposal, C series resins were obtained, which are red-brown, transparent solid and are soluble in alcohol, acetone, ethyl cellosolve and dilute alkaline aqueous.

2.2 Using isoprene to modify

D series resins could be obtained after purging disposal, whose appearance and solubility like those of C series resins.

3. Testing photosensitivity

The photosensitive system made up of DVBR or MDVBR and BAC-M was...
exposed with SYYA polyfunction plate-making machine, then developed with five percent sodium silicate aqueous.

RESULTS AND DISCUSSION

1. Catalyst of DVBR resin synthesis

Use inorganic acid such as sulfuric acid or organic sulfonic acid such as toluene sulfonic acid as the reaction catalyst, then we can obtain rapid reaction rate but thick coloured products.

Use zinc acetate as the reaction catalyst, then the reaction hardly performs.

Use aluminium resorcinate as the reaction catalyst, then the reaction rate is low, moreover, the colour of the product is thick, and its solubility is not good.

After a lot of experiments, we found a special catalyst – SC which can make us obtain relatively rapid reaction rate. The product has light colour, good transparency and good solubility.

2. Influence of different catalyst on the structure of the products

Most phenolic alkylation is para-position alkylation, but in the presence of some metal phenate, ortho-position alkylation may occur. Phenol occurs ortho-position alkylation in the presence of aluminium phenate and the mechanism of the reaction has been well studied [4]. In order to study the influence of aluminium resorcinate and SC on the structure of DVBR resins, we firstly studied the $^{13}\text{C}-\text{NMR}$ spectrum of resorcin and the influence of aluminium resorcinate and SC on the structure of the resorcin-formaldehyde resins.

In the spectra, 1, 2, 3, 4, 5, 6 represent the kinds of carbons of resorcin as formal (2):

\[
\begin{align*}
\text{OH} & \\
\text{H} & \\
\text{OH} & \\
\end{align*}
\]

In the $^{13}\text{C}-\text{NMR}$ spectrum of resorcin, the absorptions of carbon 1, 3 don't appear. Carbon 2 is unshielded greatly because of the influence of the two hydroxy groups. Its chemical shift has the lowest value. Carbon 4, 6 are equal, so they have the same chemical shift. Carbon 5 is on the meta-position of the two hydroxy groups. Its chemical shift has the highest value.

Having studied the $^{13}\text{C}-\text{NMR}$ spectra of resorcin-formaldehyde resins, we got information about the influence of aluminium resorcinate and SC as catalyst. Resin $E_1$ was synthesized without catalyst. Resin $E_2$ was synthesized in the presence of SC. Resin $E_3$ was synthesized in the presence of aluminium.
In resorcin-formaldehyde resin, the position of methylene group is not constant. It may connect with carbon 2, 4 or 6. So comparing the resonance area of carbon 2, 4 and 6, we can know the probability of the reaction taking place on the position 2, 4 or 6 through DEPT method [5]. In the method, Si represents the empty ratio on position i of the benzene ring of these resins, Ai represents the resonance area of the carbon on the position i in the $^{13}\text{C} - \text{NMR}$ spectrum of the resins. Fig.1 shows the $^{13}\text{C} - \text{NMR}$ spectrum of resin E.

Table 2 Analytical results of the $^{13}\text{C} - \text{NMR}$ spectra of resin E

<table>
<thead>
<tr>
<th>Resin</th>
<th>Si</th>
<th>S4(S4)</th>
<th>S2</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>0.175</td>
<td>0.774</td>
<td></td>
</tr>
<tr>
<td>E2</td>
<td>0.278</td>
<td>0.486</td>
<td></td>
</tr>
<tr>
<td>E3</td>
<td>0.162</td>
<td>0.701</td>
<td></td>
</tr>
</tbody>
</table>

Table 2 shows that the values of S4(S4) of the three kinds of resins are all low. This indicates that in the three kinds of resins the main connective way is 4(6)–6(4) connection. In another word, most carbon 4 and 6 are connected with methylene group. The main connective way of resin E3 is also 4(6)–6(4) connection. Moreover, the ratio of 4(6)–6(4) connection in E3 is higher than that in E2. There may be two reasons causing the results: First, position 2, 4 and 6 are all the ortho-positions of the hydroxy groups. In the presence of aluminium resorcinolate, the reaction takes place mostly on the ortho-position of the hydroxy groups. So the reaction takes place mostly on position 4 and 6.
while the position 2 has big steric hindrance. Second, aluminium hydrat reacts with resorcin to form aluminium resorcinate whose structure may be drawn as formulor (3)

![Diagram](image)

the structure blocks carbon 2, then its reactive chance will be decreased. This may be the cause of the $S_4$ value of resin $E_2$ higher than that of $E_3$.

Using SC as catalyst, we also found that the reaction takes place mostly on position 4 and 6, but because the existence of hydrogen ion, the ratio of occupying position 2 increases.

Because DVB was introduced, then the carbons of its benzene ring disturb carbon 5 of DVBR resins, we only could get the precise value of $S_2:S_4(6)$. We know: $S_2:S_4(S_6) = A_2:A_4(A_6)$. So we got: $A-2^* S_2:S_6(S_6) = 1.666$; $A-6 S_2:S_6 = 1.544$. Resin $A-6$ was synthesized in the presence of aluminium resorcinate. Fig.2 shows its $^{13}$C—NMR spectrum.

From the result we found that the reaction still takes place mostly on position 4 and 6. The probability of the reaction on position 4 and 6 in $A-6$ is higher than that in $A-2^*$. This is same as the results of the analysis of resorcin-formaldehyde resins.

Because the cost of testing $^{13}$C—NMR spectra is very high, we looked for a cheap and convenient method, infrared spectrometry, to testify the structure of the products.

Through analysis and justification, we make it sure that in IR spectra of resin E the absorption at 865cm$^{-1}$ is the absorption of the interplane wag vibration of carbon-hydrogen on position 2 of resorcin, and the absorption at 765cm$^{-1}$ is the absorption of the interplane wag vibration of carbon-hydrogen on position 4 and 6.

After calculation it is known that the order of the probability of the reaction occurring on position 4 and 6 is $E_3 > E_1 > E_2$. The tendency is same as the result of the analysis of the $^{13}$C—NMR spectra. This indicates that the method of using IR spectrometry to testify the structure of the products is very practical.

But when we analysis the IR spectra of DVBR resins, we found it is difficult to determine the absorption of the interplane wag vibration of carbon-hydrogen on position 2, 4(6) of resorcin, because the benzene rings of DVB and resorcin affect each other. It can't be known to which group the absorption
bands in the fingerprint region belong separately. The further work need carrying out in future.

3. Influence of modification

Because the polymer chain was introduced with alkane group the molecular weight and the softening point increase. For example, the softening point of resin C - 2 and D - 2 are 75°C and 84°C respectively.

4. Influence of M/A index on the photosensitivity of the resins.

M/A index of resin is closely relevant to the photositivities of resin. M represents resinal molecular mass. A represents the hydroxy group mass of the resinal molecule.

Table 3 Influence of M/A index on photosensitivity

<table>
<thead>
<tr>
<th>Resin</th>
<th>M/A</th>
<th>photosensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>A - 2*</td>
<td>6.1</td>
<td>nothing left</td>
</tr>
<tr>
<td>A - 5*</td>
<td>8.0</td>
<td>clear image</td>
</tr>
<tr>
<td>C - 1</td>
<td>7.5</td>
<td>part image left</td>
</tr>
<tr>
<td>C - 2</td>
<td>8.0</td>
<td>clear image</td>
</tr>
<tr>
<td>C - 3</td>
<td>8.5</td>
<td>film left</td>
</tr>
<tr>
<td>D - 1</td>
<td>8.0</td>
<td>film left</td>
</tr>
<tr>
<td>D - 2</td>
<td>7.4</td>
<td>clear image</td>
</tr>
<tr>
<td>D - 3</td>
<td>7.2</td>
<td>nothing left</td>
</tr>
</tbody>
</table>

Table 3 has shown that when the value of M/A index equals to 8.0, the resins have good photosensitivity and developing property. Based on this, we testify that practical M/A value of resin D - 2 is about 8.0. So we make it sure that during the reaction, D series resin don’t cyclize completely and they only cyclize partly. But the concret direction of the disappearance of the double bond of isoprene is waiting for further research.

CONCLUSION

1. Resist systems composed of DVBR or MDVBR and azide compound (BAC - M) can be used as UV curing negative photoresists
2. Influence of all kinds of catalysts on the structure of DVBR resin is same. They also make the reaction mostly take place on the position 4 and 6 of resorcin.
3. Cheap and convenient IR spectrometry can substitute expensive 13C – NMR spectrometry to analyse the structures of products.
4. The value of M/A of resin is closely relevant to the photosensitivity of resin so it can be a reference basis of synthesis of resin.

REFERENCES

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The Mechanism Study on Overcoming Oxygen Inhibition of Polyether Type Multifunctional Acrylate

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INTRODUCTION

The radiation process on EB cured coatings without inert gas is an important problem. In 1985, Holl et al. investigated EB cured coating without inert gas (Holl et al. 1985). In 1987, Reese's studies showed that under certain coatings the oxygen does no inhibit the electron beam curing of films (Reese, 1987). Since 1988 the studies have been conducted using amine compounds and resins possessing multifunctional groups at our Institute. The polyester type multifunctional acrylic resin (MAR) and polyether type multifunctional acrylate (MFA) were formulated and used for EB cured coatings of some decorative materials (Zhou et al. 1993).

EXPERIMENTAL

Materials

(1) Oligomer.

The oligomer is polyether type polyurethane acrylate. This oligomer was synthesized by reaction of toluene diisocyanate with polyether and hydroxy ethyl acrylate.

\[
\text{OCN} - \bigcirc - \text{NC} + \text{HO-} \bigcirc - \text{CH}_2 - \bigcirc - \text{CH} - \bigcirc - \text{H} + \text{CH}_2 = \text{C} - \text{O-CH}_2 \text{CH}_2 \text{OH}
\]

(2) Monomers.

The diluent for the oligomer is methyl methacrylate (MMA). In order to increase the reaction activity, TMPTA and TEGDA were added in the formulation.

(3) Additives.

TiO$_2$, pigment, antioxidant and photostabilizer.
Coating and Irradiation

Coating specimens of 50-200 μm thickness and 10 × 10 cm size were prepared and irradiated by 0.3 MeV electron beam.

Performance Measurement and Testing.

The hardness of radiation cured coating specimen was measured with pendulum hardometer.

RESULTS AND DISCUSSION

In our early work we formulated the polyester type multifunctional acrylic resin (MAR) paint for the cured coatings of gypsum decorative materials. In this paint we also added radiation sensitizer and photostabilizer, but a deeper study of oxygen inhibition hasn't been performed. Therefore, the irradiation dose was higher. The value of dose was usually 90 kGy. However, we still get a better result with this paint.

Afterwards we improved the paint formulation through adding to antioxidants and photostabilizers, and prepared new polyester type multifunctional acrylic risen (MAR) system. When the critical absorbed dose is decreased to 60 kGy, not only the same technical performances come to previous ones, but also the hardness kept to 76%. The investigation indicated that the hardness of radiation cured coating without inert gas is better than result of similar coating at oxygen concentration to 50 ppm (crailik, 1989). In recent years, the high reactive polyether type multifunctional acrylate (MFA) was prepared for rapid curing coating in which the trimethylol propane triacrylate and triethylene glycol diacrylate were utilized. The experimental results have showed that when the absorbed dose reaches 60 kGy, the hardness kept to 80%.

In order to perform further study of radiation process, we focused on the preventive oxidation by the addition of oligomer, photostabilizer and antioxidant. As we know, benzamine type compounds can serve as antioxidant and antiozonant. The oligomer has the similar structure and thus may play an important role in antioxidation and antiozonation. Besides, the added photostabilizer 2-hydroxy-4-methoxybenzophenone not only functions as sensitizer, but also may play an essential role in antioxidation. One possibility is the formation of dual radicals from carbonyl group (C=O) under irradiation just as in photoirradiation, followed by its reaction with oxygen in air, so as to overcoming oxygen inhibition.
Mechanism of antioxidation using hydroxyl benzophenone and bisphenol A

\[
\begin{align*}
\text{HO-} & \quad \text{O} \quad \text{CH_3} \\
\text{CH_3} & \quad \text{CH_2} \\
\text{CH_3} & \quad \text{CH_2}
\end{align*}
\]

This reaction is realized by hydrogen abstraction from the hydroxyl benzophenone or bisphenol A. The mechanism of hydroxyl benzophenone is similar to that of phenol compound. Hydroxyl benzophenone is used not only as photostabilizer but as antioxidant in the process of irradiation as well.

Mechanism of amine antioxidant and antoironant (aniline)

\[
\begin{align*}
\text{Ar-} & \quad \text{NH-} \quad \text{Ar} + \text{RO_1} \rightarrow \text{ROOH} + \text{Ar,N}
\end{align*}
\]

There is aniline type structure in our used oligomer. Therefore, it may serve as an antioxidant component in the irradiation system. But here the oligomer, we think, functions mainly as antiozonant during irradiation.

The irradiation of 2-hydroxyl-4-methoxy benzophenone leads to formation of dual radicals at carbonyl group (C=O). Then the hydrogen abstraction take place to form the radical A, followed by reaction with O_2 to obtain peroxide B. This way O_2 is consumed and oxidation on the polymer is prevented. The peroxide B, under irradiation, is easily disintegrated into two radicals which may facilitate polymerization and crosslinking of the polymer.
REFERENCE


UV Curing Materials for the Printing and Electronics*

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UV Curing Materials and
Photoinitiators for Printing Circuit Boards
Electronic industry is one of the newly arisen industry in China. It was rapidly developed from the end of 1980s to the 1990s. Among which the market demand for printing circuit boards become greater and greater and the requirements on its quality become higher and higher. The demand also varied from single-faced boards in 1980s to the current double-faced and multiple layer boards. The flexo boards are also begun to be used practically. With the increasing of the memory storage of integrated circuits and the miniaturization of parts, the circuit lines are required to be finer and finer, which put forward good chances for the development of UV curing technique. Most resists, solder resists, electroplating resist inks, marking inks, hole sealing inks and protecting coatings for printing circuit boards used to use thermally cured materials, which were printed on circuit boards by screen leaking method and cured by baking and drying. In recent 2~3 years such thermally cured materials were eliminated and replaced by UV curing materials.

The following requirements are normally put on the UV curing materials for printing circuit boards:
• High sensitivity and the fastest curing speed for increasing the production efficiency
• High resolution and fine lines
• High performance suitable to be used for special purpose

Usually for UV resists ink the requirements are that they have good adherence to the base and high acid resistance. For UV solder resist inks, the cured coatings are required to have excellent heat resistance.

* During the preparation of this article, Dr. Yangzhi Jin, associate professor of Beijing University of Chemical Technology and Dr. Fubao Gu, senior engineer of Beijing Institute of Electro-light Sources provided us with a good deal of useful information.
and adherence. For marking inks, their spectrosensitivity are required to possess broader range than 400nm as well as high sensitivity.

Because the excellent performance of UV curing materials for printing circuit boards is what mainly concerned, their price is allowed to be much more expensive than those UV materials for printing and the requirement on the price of photoinitiators is not critical. So long as the sensitivity is high, thermal stability is good and yellow changing is slight under some situations the high priced ones can also be considered for practical purpose, for example, the excellent photoinitiators like I−369, CGI−1700 and I−907 of CIBA GEIGY Co. are attractive candidates.

1. The general international situation of printing circuit boards

Prior to 1990s, the most developed printing circuit boards industry was in Japan and America. In entering 1990s, with the development of electronic industry the printing circuit boards industry began to develop rapidly in some Asian countries and areas. According to the statistics of 1993 the first 7 main countries and areas in printing circuit boards production were Japan, America, Taiwan, Korea, Germany, Singapore and Hongkong. The corresponding output in Japan, America, Taiwan and Hongkong is listed in Table 1.

Table 1. (expression output in ten thousand m²)

<table>
<thead>
<tr>
<th>country and area</th>
<th>single-faced board</th>
<th>double-faced board</th>
<th>multiple layer board</th>
<th>flexo board</th>
<th>total output</th>
<th>the percentage in world output (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Japan</td>
<td>4571</td>
<td>753</td>
<td>854</td>
<td>250</td>
<td>6428</td>
<td>32.3</td>
</tr>
<tr>
<td>America</td>
<td>442</td>
<td>710</td>
<td>1210</td>
<td>256</td>
<td>2618</td>
<td>13.1</td>
</tr>
<tr>
<td>Taiwan</td>
<td>734</td>
<td>217</td>
<td>238</td>
<td>18</td>
<td>1207</td>
<td>6.1</td>
</tr>
<tr>
<td>Hongkong</td>
<td>756</td>
<td>210</td>
<td>135</td>
<td>5</td>
<td>716</td>
<td>3.6</td>
</tr>
</tbody>
</table>

From table 1, we can see that in highly developed countries, the multiple layer and double-faced boards are main products. For instance in U.S., the production of multiple layer boards is the greatest and that of double-faced boards is the next, the production of single-faced boards occupies only a small proportion. In Japan, the production of double-faced boards increases at a high speed, while that of multiple layer boards is also considerable. In other countries and areas, single-faced boards are still predominant, but double-faced boards and multiple layer boards will undoubtedly be developed greatly. It is reported that by the end of 1994, the output of double-faced boards and
multiple layer boards had occupied an increasingly greater proportion in the total output in Japan, Korea and Taiwan province.

In view of the variety of UV curing materials, in the primary stage the products were mainly screen printing materials and dry film resists. In recent years, liquid resists, solvent type solder resists for double-faced boards and dry film solder resists began to develop rapidly. The resists and solder resists for flexo boards with high resolution, high adherence and strong deflection also came on stage. In order to guarantee the quality of UV curing materials, the binder resin monomers and oligomers with high performance should be selected, on the other hand, excellent photoinitiators should be used, CGI-1700 and I-369 photoinitiators of CIBA GEIGY Co. began to be choosed by many manufacturers in Japan, Taiwan, Hongkong and Singapore. The prices of the photocompositions for double-faced and multiple layer boards are all higher than RMB.500/kg and the quantity of photoinitiators used is quite small, so the adoption of a photoinitiator with a price of about RMB.1000/kg is acceptable in price. This is quite different from the low cost principle for adopting photocompositions for printing. It is anticipated that in China, the selection of photoinitiators will be also in this trend. Presently some joint ventures with Hongkong and Taiwan in Guangdong and Fujian have begun to perform in this way.

2.Recent development of printing circuit boards in China

In China the industrilization of printing circuit began in 1960s. This industry has now become quite large in scale and it has developed into an important part of electronic industry. The gross output value of printing circuit boards in 1989 was RMB. 8.17 hundred million which occupied 8% of the gross output value of electronic device industry. It possessed 52 imported production lines and 1394 machines. The workers were more than 20,000, among whom the engineering technicians were more than 3000. The production capability of single-faced boards was over 4 million m². The production and technique level of the backbone factories equaled that of foreign countries in the end of 1970s and the beginning of 1980s.

Due to the above developmental situation 211 enterprises joined the trade union of printing circuit boards when it was set up in 1990. Since then industry of printing circuit boards have been developed more rapidly.

In 1992 the total output of 3.8 million m² single-faced boards, 730,000m² double-faced boards, 47,000m² multiple layer boards was obtained. The output of 15 biggest enterprises was 2.09 million m² single-faced boards, 385,000 m²
double-faced boards and 31,500 m² multiple layer boards. The gross output value was RMB 10.57 hundred million. It was estimated that 150 tons UV curing solder resists, 40 tons UV curing marking inks, 500,000 m² dry film solder resists, and 1.2–1.5 million m² dry film resists were needed.

In 1993 the 67 main units in this trade produced 2.31 million m² single-face boards, 600,000 m² double-faced boards, 39,000 m² multiple layer boards and 6,000 m² flexo boards. The gross output value of the whole trade reached RMB 18 hundred million.

The above data did not include the productivity and the output value of the printing boards of sole proprietorships built by Hongkong, Taiwan in Guangdong and Fujian. The estimated output of the sole proprietorships was about 3 million m², so the total output of all kinds of printing circuit boards was about 6 million m², among which the majority were single, double-faced boards and multiple layer boards took a small part. With the development of computer and communication industries the proportion of double-faced and multiple layer boards will be gradually increased.

In 1994, an unprecedented heartening prospect emerged in printing circuit boards industry. The output of all kinds of printing circuit boards was greatly increased, especially double-faced boards. The estimated total output of all kinds of printing boards including that of those sole proprietorships and joint ventures in 1995 will exceed 10 million m², which surpasses that of Hongkong and approaches that of Taiwan province in 1993.

There are more than ten main manufacturers of UV curing materials for printing circuit boards in China.

UV Curing Materials and Photoinitiators for Printing

1. Photopolymer plates for printing

The study on photopolymer plates began in the late 1960s and the early 1970s in China. At that time the main research was on the study and application of photopolymer relief plates. In 1994, the demand of liquid photopolymer relief plates was about 50,000 m², and the yearly consumption of liquid photopolymers was more than 20 tons. The major manufacturers of it are Guangdong Xinhui Xinqin Fine Chemical Plant and Xian Organic Chemical Plant. The resins they produced were unsaturated polyesters and polyester-amides. The only photoinitiator used by them is benzyldimethyl ketal (BDK, I–651). The output of solid photopolymer relief plate has been increasing since 1990, and the number of the manufacturers has been increased from 3,4 to more
than 20. Almost all kinds of the resins for the solid photopolymer plates are PVA, the main crosslinking monomer is \( \alpha \)-methylol benzoin methyl ether or \( \alpha \)-methylol benzoin ethyl ether. The commonly used BDK (I-651) abroad is not used by anyone in China, the reason is that the monomer that foreigners mainly used is HEMA and BDK is readily dissolved in it, while the crosslinking monomer on domestic market is N-hydroxymethyl acrylamide which has poor miscibility with BDK so the \( \alpha \)-methylol benzoin ether with the stronger water solubility is often used. In 1994, 300,000 quarter plates, ie, 80,000 – 10,0000\( \text{m}^2 \) PVA type solid photopolymer relief plates were put into markets. The biggest manufacturers of it are Jiangsu Taixing Instrumental Plant, Tianjin Institute of Printing Technology etc. The anticipated output of it in 1995 will be increased further. Presently some units use water soluble nylon plates, which is mainly imported from Japanese TOYO BOSEKI Co., The study on the above plates is made by a number of units, but until the end of 1994 was the first sample of such plates created by Beijing Normal University. The alcohol soluble nylon plates were used by many units in 1970s and 1980s, but in 1990s such plates are rarely used.

The domestic demand for flexo plates has increased recently and continues to rise, half of that was imported from DOPONT Co. and the other half was supplied by Shanghai Institute of Printing Technology. It totaled about 30,000 \( \text{m}^2 \) in 1994. The technique was transferred from Beijing Institute of Printing Technology to Taixing Instrumental Plant and the products co-manufactured by a Japanese company and Taixing Instrumental Plant came to the market in 1995. It is reported that DUPONT Co. and Shanghai Institute of Printing Technology use SIS rubber as main resin. The domestic output of flexo plates in 1995 will probably increase by one time. It is anticipated that Chinese flexo plates yearly output will approach that of the U.S., Japan and the other advanced countries by 2000. At present flexo plates are mainly applied on packaging printing. In future the application of it will be extended to newspaper printing etc.

One of the fastest developing field of photopolymer plates is offset PS printing plate. In recent years it was doubled every two years. In 1994 the output of it was more than 6 million \( \text{m}^2 \), added to the reproducible plates, the total output was about 8~9 million \( \text{m}^2 \). It was anticipated that the output of it would reach 15 million \( \text{m}^2 \) in 1995 and the production scale would approach that of Japan in 2000. However, the main type of PS plates in China is photo-decomposing positive one belonging to naphthoquinone diazide sulfonyl ester.
system. The photoinitialized polymerizing negative PS plates are still of laboratory stage without being transferred to productive forces. In the past the small quantity of negative PS plates appearing on markets was mainly diazo resin type photo-decomposed crosslinking system.

The development of screen printing in China is also very fast. The photopolymer used on screen printing is diazo resin type. Recently the MURAKAMI Screen Printing Co. began to produce and sell SBQ type screen printing UV curing material. The study of the application of photosensitive polymers on screen printing material was done only by Beijing Normal University and Beijing Institute of Printing Technology. Recently the water soluble nylon screen printing material is under research in Beijing Normal University who uses α-methylol benzoin ethers and CGI-1700 as photoinitiators.

Presently the photopolymers for gravure printing are also under exploration in some units, but the commercialized products have not appeared on markets till now and its future is still hard to anticipate.

2. UV curing inks and overcoatings for paper
In China the development on offset printing UV curing inks is relatively slow. Although the research work began in 1970s, and the obtained products were already used on iron printing, yet the formal products were not obtained until the end of 1980s. The commercialization of UV curing offset ink was formally begun by Tianjin Ink Plant in 1992. But the present output of it is still very low. It accounts for a small percentage in UV curing materials made in this plant. Especially the UV curing offset ink for paper is on a beginning stage presently. Such material requires broad spectrosensitivity on photoinitiators, usually the long boundary wavelength should be greater than 400 nm, so the I-369, I-907 and CGI-1700 of CIBA GEIGY Co. are idealized initiators. Under the situation where the requirement on yellow changing is not very strict the other initiators as thioxanthone and the complex of 4,4'-diakyl amino benzophenone and tertiary amines can also be used, but the total quantity is small.

It was anticipated that UV curing offset ink would hold some markets in China in the future with the development of the technique of high speed offset printing.

The research on UV curing ink for gravure printing has not started yet.

The development of the UV curing ink for screen printing is becoming
faster in China in recent years. However the main use of it is on electronic industry, especially on the processing of printing circuit boards, which will be discussed elsewhere. Besides that the demand and the output of other UV curing screen inks is very limited. The future tendency of their development is also not very clear.

The development on the overcoatings for paper surface treatment is very rapid, the reason for which is that with the exporting of Chinese products to the world market under the opening up policy of China, the grade of packaging and decorating is progressively improved and therefore the needs for paper surface treatment by UV curing method are increasingly raised. The output of overcoatings for paper surface treatment in 1994 was increased by 100% than in 1993. The yearly output of it was more than 50 tons. It was anticipated that the increasing rate of it would still be 100% in 1995 on the basis of 1994. Besides, some of these coatings are to be imported from Hongkong, Taiwan and Japan. The coatings are used on following aspects:

- Overcoating for colour offset printing products
- Overcoating for cosmetics cases and other thin sheet cases
- Overcoating for cover paper
- Overcoating for packaging paper

Because the photosensitive compositions for paper surface treatment are required to be colourlessly transparent and not easily to change yellow after UV curing, thus such photoinitiators as I-184, I-369, D-1173 had better be used. Presently the domestic plant who uses the above photoinitiators is Hunan Yada High Polymer Chemical Plant. Yet some plants still use the thermally unstable benzoin ethers. However, with the requirement on printed paper surface getting stricter, the photoinitiators with less tendency of becoming yellow will gradually dominate in future.

In a word, the demand and output of UV curing materials in the field of printing in China is not very large, but the recent development is quick and the prospect is optimistic. Presently the types of UV curing monomers and oligomers are rare, which is the main contradiction of the development. The mainly used photoinitiators on Chinese market are domestically produced derivatives of benzoin ethers, BDK(I-651) and some small quantity of I-184, D-1173. Some other initiators with higher performance such as I-369, CGI-1700 can not be accepted by customers because of their higher price.
Photoresists for Integrated Circuits

In the past the main negative photoresists were polyvinyl cinnamate and polyisoprene, whose resolution was greater than 3μm, and they were mainly used for processing silicon wafers no greater than 64K. The annual output of them was tens of tons. Their main makers were Beijing Institute of Chemical Reagents, Suzhou Electro-Chemical Material Plant and Huangyan Organic Chemical Plant. The photoetching using positive photoresists is able to meet requirements of making integrated circuits more than 256K. In the past, positive photoresists were mainly imported from the U.S., Japan. The main systems of positive photoresists are naphthoquinone diazide sulfonates. During the Seventh-five year plan period Beijing Institute of Chemical Reagents had completed the research on products similar to AZ system, then put them into practical uses. During the Eighth-five year plan period, Beijing Institute of Chemical Reagents and Suzhou Electro-Chemical Material Plant had explored some new products respectively. Basic research and exploration work on the positive photoresists have been done by Beijing Normal University and Shanghai Jiaotong University under the corporation with above units. The yearly output of positive photoresists is more than 10 tons presently. The import amount of positive photoresists is far greater than domestic yield. There's remarkable tendency that besides the usage on large scale integrated circuits more and more positive photoresists are also used in liquid crystal parts and grating holograph etc. So the output of positive photoresists is redoubled per year, and the demand still becomes greater and greater.

One front edge of photoresists - chemical amplification photoresist has been studied initially by Tsinghua University and Beijing Normal University. Their research results were reported at some concerned international conferences. Nowadays some novel products with special structures are under research and exploration. The effort is also put on their practical usage.

The concerned references were left out.
PHOTOCURING OF DENTAL MATERIALS - PRACTICAL APPLICATIONS

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ABSTRACT

Photocurable polymeric materials have found wide applications in dentistry as composite restorative materials, adhesives, glass-ionomer cements, cavity liners, and as protective sealants for pits and fissures in teeth. However, there are a number of problems in using photocurable polymeric composite resins in restorative dentistry, which include low polymerization conversion, huge shrinkage, inferior mechanical properties, allergiological problems, and short longevity in comparison with dental amalgam fillings. This lecture focuses on the practical aspects of using commercially available photocurable dental restorative materials.

INTRODUCTION

In 1992, the Swedish Parliament proposed to discontinue the use of amalgam as dental filling material during the next five year period. The classical, old type of dental amalgam filling consists of silver (40-60%), mercury (30-50%) tin (8-15%), copper (3-10%) and traces of other metals e.g. zink [1]. The mercury can be released from amalgams in the oral cavity due to the effect of e.g. chlorides [2].

\[ \text{Sn}_7\text{Hg} + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + \text{Cl}^- \rightarrow \text{Sn}_4(\text{OH})_6\text{Cl}_2 + \text{Hg} \]

Release of mercury to the saliva and uptake in the body raised the questions of its biological and toxicological effects. In figure 1 are some typical symptoms expressed by patients who claim that they are suffering from effects of mercury from amalgam fillings.

Fig.1 The six most common subjective symptoms from patients (in %) referring to problems with dental amalgams. Filled bars = all fillings removed, open bars = not treated [3].
Besides the amalgam problems of patients, dental personnel are constantly exposed to not only the mercury vapour from their own amalgam fillings, but also to the mercury vapour in their environment. [4-8]. Mercury is released as an invisible and odourless vapour, and is constantly accumulated in the body. Women tend to show higher mercury levels and longer half-times in the body than men. The threshold limit value for mercury vapour in dental clinics in Sweden is 30mg Hg per m$^3$ of air. Due to a parliament decision (resolution), the use of amalgams in dental clinics will be abandoned from the 1st of July 1996. However, exposure to mercury vapour for the dental personnel will not stop abruptly since 84% of the Swedish population have amalgam restorations that will be treated in the future.

Replacing of amalgam fillings by composite polymeric materials is a future task for the 2000 century. This can be performed by using chemical or radiation curing procedures. The last subject is discussed in this presentation.

**PHOTOCURABLE POLYMERIC COMPOSITE FILLING MATERIALS**

The essential constituents of commercially dental composites are [9-12]:

1. A vinyl (mainly methacrylates) mono-, di- and tri-functional monomer systems, which on diluents for highly viscous di- and tri-functional monomers. free radical polymerization provide a solid crosslinked matrix. The most typical monomers used are shown in the Appendix. The mono-functional monomers are mainly used as reactive diluents for highly viscous di- and tri-functional monomers.

2. A photoinitiator system based on a mixture of champhorquinone-tertiary amines such as N,N-dimethyl-p-toluidine or 2(N,N-dimethylaminoethyl) methacrylate that are effective under clinical conditions.

3. Reinforcing fillers, such as silanised quartz, glass, ceramics, metallic and hybrid organic-inorganic fillers.

4. Surface active agents capable of reacting or interacting with two disparate phases forming an interfacial bonding phase.

5. Various types of inhibitors and stabilizers for optimizing the storage stability of the uncured material and its color and also to improve the general chemical stability against degradative processes.

6. Pigments and fluorescence agents which aid in harmonizing the appearance of the restoration with respect to that of the tooth.

In order to increase adhesion of polymeric composite restorations to enamel and dentin, several ancillary materials are used in the clinic. Such materials are cleansers, etchants, bonding agents, protective liners, surface coatings, and fluoride releasing agents.

**PHOTOCURABLE POLYMERIC DENTAL SEALANTS**

Dental sealants have similar compositions, but are unfilled or lightly filled composite materials and usually contain a higher portion of diluent (mono-functional monomer, e.g. 2(N,N-dimethyl)aminoethyl methacrylate.

**MONOMERS AND POLYMER MATRIX PHASE**

The commercially available filling materials are based on a mixture of different monomers (mainly Bis-GMA) (see Appendix), and their composition is a subject of secrecy for the producers. A number of publications discuss the relation between monomers used and the properties of the polymer matrix phase [9-14]. For dental applications the polymer matrix has to withstand a number of requirements, like low shrinkage during monomer polymerization, high elastic moduli, low solubility, relatively low water absorption, have good thermal properties, be aesthetic, have high biocompatibility, and last but not least meet very strict demands on toxicological, carciogenic and mutagenic effects.
One of the major problems in polymer restorative dentistry is the contraction of the polymer matrix during polymerization. This shrinkage is due to the reduction in volume brought about by an increase in density. This phenomenon is observed during both monomer polymerization and polymer curing, and arises from a number of factors. One of the major causes of shrinkage is that in the monomer form, the molecules are located at van der Waals distances from one another, while in the polymer form, the corresponding monomeric units move within a covalent distance from each other. The monomeric units are, therefore, closer together in the polymer form than in the monomer units. Lesser, yet significant, factors which affect volume change are the change in entropy in transformation from monomer to polymer, the reduced free volume in amorphous polymers, and also how monomers, macromolecules and additives are packed in the polymer matrix phase. The resulting shrinkage introduces serious limitations for the use of UV-curable composites in clinical dentistry. The clinical problems with shrinkage include the following (Fig. 2)

1. Material shrinkage creates gaps between the cavity walls of the tooth and the cured restorative. These gaps result in microleakage with accumulation of liquid, food debris and microorganisms, which produce toxins and acids during their fermentation. This can lead to hypersensitivity and pain reactions in the tooth pulp.

2. Shrinkage may result in the formation of unwanted stresses in the tooth substance, in the resin matrix, and at the resin/filler particle interfaces. These built-in stresses can cause acute clinical problems, such as post-operative pain, fracture of tooth substance, and later when the stresses are released, cracks (delamination) in the filling and appearance of gaps in the margins of the restoration.

3. Further effect of shrinkage include void formation in the polymer matrix, poor adhesion of the polymer to the tooth substance, delamination of the polymer matrix, and warping of the composite.

Fig. 2 Typical problems of shrinkage in dental filling materials; a) void formation, b) stress cracking, c) poor adhesion, d) delamination and e) composite warping

In IN VITRO measurements of polymerization reactions, the contraction of dental composites ranges from 0.2 to 2.9% linear shrinkage, and 1.7 to 5.5% volumetric shrinkage.
Since Bis-GMA shrinks by 6.5% when cured and the lower viscosity diluents shrink by greater amounts, it was reasoned [15] that the limited bonding to tooth enamel and unsatisfactory wear characteristics were related to stress states in the matrix, and that lower shrinking resin systems would be of great use in the dental restorative materials. Stresses up to 6 MPa are formed during shrinkage and the process can continue for 3-4 weeks after the clinical application of a dental composite filling. Obviously, the shrinkage can open gaps in the dentin/adhesive interface beneath fillings. This is a very serious problem since it is impossible to detect in the clinical situation. Factors that have a direct effect on shrinkage include:

1. Size of restoration
2. Cavity configuration
3. Placement technique (incremental or bulk)
4. Curing procedure
5. Types of monomers used in restorative composites

Several different approaches can be considered to reduce the shrinkage of the dental composite filling materials:

1. Use of the high molecular weight starting monomers (oligomers and prepolymer) which reduces the exotherm caused by the polymerization process. This exotherm is a well known problem, especially when large volume polymerizations are made;
2. Use of well designed photocuring, under optional conditions (which can control initiation and propagation rates);
3. Use of fillers. Their effect on shrinkage is usually more dependent on the amount used than on the type of filler used, because the reduction in shrinkage is due to replacement of resin with a material that does not undergo permanent changes in dimensions during photocuring.

Since the polymeric dental materials have to work continuously in a water-saliva environment, a higher water uptake by a polymer matrix and hygroscopic expansion can seriously influence dimensional stability. However high water uptake may be beneficial in closing margin gaps existing at the restorative-tooth interface and in reducing stresses in the composite [16-19].

In order to prevent microleakage due to gap formation, it is necessary to prevent capillary penetration of oral fluids by use of composites having contact angles versus saliva of greater than 90° [20-24]. This can be achieved by using highly fluorinated monomers like FPMA, PFEMA and PFUMA (see Appendix). Dental composites based on these monomers show reduced microleakage and high improved stain resistance, but have relatively low mechanical strength and high contraction on polymerization [23-29].

A serious problem observed during the photo-curing is the formation of porosities caused by entrapped air [30,31], especially during polymerization of high viscous monomers, leading to inferior characteristics. Porosities enhance abrasion [32], surface instability, plaque accumulation, and bacterial colonization in surface irregularities [33,34]. The air bubbles in the photocured fillings are therefore mainly a result of mixing and insertion procedures. A clinically acceptable way of reducing porosities is by using encapsulated or syringed materials for insertion.

RESISTANCE OF POLYMERIC COMPOSITES IN THE ORAL CAVITY

There are number of serious disadvantages of polymeric restorative composite materials:
1. The poor resistance of composite resins to mechanical stress (high load, flexural tension, and grinding wear).
2. Limitations due to chemical and biological degradation for the use as posterior fillings.
3. Polymeric materials are also exposed to often rapid thermal changes from -7°C (ice-creme) to +70°C (hot beverages). A typical damage to such forces is formation of microcracks, cavities, giving a rough and corrugated surface.

4. The saliva and fluid food-stuffs may also cause hydrodynamic damage of the surface and participate in the removal of materials. Such damaged surfaces serve as retentive areas for food debris, bacterial plaque, and discolorations.

The wear of polymeric dental composites is a complex process and no single "In vitro" test has found to duplicate clinical wear. IN VIVO studies have shown that wear of conventional dental polymeric composites proceeds by loss of polymer matrix followed by a dislodging of filler particles [30,35-37]. The softening of the polymer matrix by saliva and food fluids will increase the sensitivity to wear of dental composites. An increase in degree of polymerization decreases the diffusion rates of fluids in the polymer matrix.

Mechanical (physical) degradation of dental restorative composites in the oral cavity is always accompanied by chemical- and biodegradation processes [38]. Chemical degradation is caused by rapid changes of pH in the oral cavity (bases and acids present in food), oxidation processes in which oxygen from air, disclosed in liquids, and present in food is involved, and fermentation processes in which lactic acid is produced. Many polyacrylyic materials are susceptible to biodegradation caused by microorganisms as bacteria and fungi.

**HUMAN FACTORS INFLUENCED PHOTOCURING**

In order to obtain a good compatibility of a photo-cured polymer filling composition with enamel and dentine, the dentist must obey strict procedures. One major duty is to remove the decayed tooth substance and prepare a cavity for the filling material. In a general procedure, depending on the anatomy of the tooth, the depth and localisation of the decay, and the ease of access for preparation and filling, the dentist must achieve a restoration of sufficient dimensions, and quality in increments of a maximum of 1mm, in order to completely replace the removed part of the tooth substance.

Before filling the cavity with composite material, the prepared surface should be carefully cleaned from saliva and debris and dried in order to attain a good adhesion between polymer matrix and tooth.

The depth of curing of polymeric filling materials is limited to 1mm due to very high content of fillers (up to 60-% by volume) which limits approach of light to the deeper layers. The approach of light from the commercially available dental curing lamps (visible light at max. 470nm, blue region) must be strictly directed towards the applied material (Fig. 3), in order to cure the whole layer.

![Fig. 3 Positioning of a light source over the material in the cavity during photocuring procedure: a) correct and b) incorrect.](image-url)
In practice, however, many dentists, limited by time and cost/benefit demands, do not follow the recommended photocuring procedure. This leads to curing layers which are too thick. When a composite layer is thicker than 1mm and not completely polymerized and irradiations exposures are too short, and contaminated by air (causing porosity) and moistured, the result is a low degree of conversion and poor quality of restoration. The final consequence is dental restorations which fail to meet the standards expected, or those offered by the producer.

TOXIC CONSIDERATIONS

Acrylic monomers can cause both systematic allergic and local chemical reactions. Typical reactions are the "burning mouth syndrome" and redness, and erosions of the tongue and the oral mucousa [39-42]. Leachable substances from fillings (like acrylic monomers and additives photo-initiators and their photolysis products, antioxidants, inhibitors, photostabilizers) dissolved in water or saliva are transported to the stomack where they can be resorbed and distributed to the circulatory system, where it can cause potential biologic effects [43-45].

The photoinitiating systems in all commercially available dental compositions are based on camphorquinone-amines. The latter are considered to be cancerogenic and may also cause mutagenic transformations (distortion of a genetic code of DNA). The free radicals formed from camphorquinone can survive in the polymer matrix even 4 hours [46]. Free radicals in contact with tissues may eventually cause neoplastic reaction (cancer formation). There is still lack of a statistically confirmed research on allergic symptoms from polymeric dental materials, and so is the case for the effects of dental amalgams (Fig. 1).

CONCLUSION

The use of polymeric dental filling materials has not been entirely successful. The poor mechanical properties, compared to amalgam fillings, limit their application to anterior restorations that are not subjected to high mechanical stresses. The shrinkage of polymerization, high coefficient of thermal expansion, poor abrasion resistance, and flow under occlusal load, however, prevented them from displacing dental amalgam as posterior filling materials.

It can also be concluded that there is a need for more extensive academic research on radiation curing of polymeric materials and developing new monomers. This can be achieved only by dental material science research units, which facilitate the mutual scientific cooperation of polymer scientists with dentists. The future is in the development of such research units and adequately supporting them with sophisticated equipment together with sufficient financial support. There is also a need for more practical education of dentists in the application of radiation curing methods and more information on new materials and progress in this field. The dental personnel must have access to appropriate teaching courses dealing with the knowledge on polymeric materials science. More effort and thorough strategies are required in these areas. Also, a program for studying toxicological, cancerogenic and mutagenic properties of polymeric materials used in the dentistry is necessary. The discontinuance of amalgam from the dental practice without developing new and better polymeric restorative materials is far from satisfactory.

REFERENCES


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APPENDIX

Examples of the most common mono-, di- and tri-functional monomers used in commercially produced composite filling materials:

\[ \text{HEMA} \]

\[ CH_2 = C - \overset{\|}{O} - \overset{\|}{C} - CH_2 - OH \]

\[ \text{FPMA} \]

\[ CH_2 = C - \overset{\|}{C} - O - CH_2 - (CF_2)_n - H \]

\[ \text{DMAEMA} \]

\[ CH_2 = C - \overset{\|}{O} - CH_2 - CH_2 - NH \]

\[ \text{HDDA} \]

\[ CH_2 = C - \overset{\|}{C} - O - (CH_2)_m - O - \overset{\|}{C} = CH_2 \]

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DERIVATIVES OF BIS-GMA

URETHANE DERIVATIVES OF BIS-GMA

URETHANE METHACRYLATES
RECENT PROGRESS IN THE STUDY OF THE DEVELOPMENT-FREE VAPOR PHOTOLITHOGRAPHY*

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ABSTRACT

Development-free vapor photolithography (DFVP) is a unique all-dry pattern transfer technique, which is based on the reaction of SiO2 with HF vapor under a polymer film in the presence of accelerators at a temperature of above 100°C. It can simultaneously overcome the diffraction limitation and the problems arisen from wet process to offer a high resolution and high aspect ratio pattern. This paper will present a review of the results of researches on the DFVP process, including the studies of the reaction mechanism, explanations of high resolution and high aspect ratio, polymer accelerators, the latest progress, approaches to create a great difference of accelerator concentration between exposed and unexposed areas, and so on.

INTRODUCTION

An unusual phenomenon of etching under exposed but not developed photoresist film was disclosed fifteen years ago, which we call the development-free vapor photolithography (DFVP). It is a unique all-dry pattern transfer technique, and has been successfully used in manufacturing microelectronic devices [1]. Seemingly, this phenomenon is similar to the vapor etching process reported by Holmes and Snell as early as in 1966 [2], and more recently by others [3-4], however, they differ from each other greatly.

The general procedure of DFVP is illustrated in Fig.1. A silicon wafer with a SiO2 surface is coated with cinnamate-type photopolymer containing 5-nitroacenaphthene, followed by masking and exposed to UV light. Then an etching gas (hydrofluoric acid vapor) is passed over the wafer in a chamber at a temperature of above 100°C for a definite time. The SiO2 under the polymer film in the exposed area is etched and removed completely. However, the SiO2 in the unexposed area remains and forms a clear positive pattern.

The advantages of the development-free vapor photolithography technique over the conventional wet process include: (1) offering higher resolution (0.4 um etching lines can be obtained) and a high aspect ratio (1:12), it is capable of producing submicrometric feature; (2) omitting three steps: prebaking, development, and postbaking; (3) overcoming problems induced in the development and etching step, such as loss of adhesion, high pinhole density, isotropic etching, poor end point control and so on; (4) saving large volume of organic solvent and corrosive chemicals, etc.. The plasma etching is an important dry etching technique, which can offer high resolution and a good aspect ratio. It has been widely used in manufacturing very large scale integrated circuit. This technology can etch

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* This project is supported by the National Natural Science Foundation of China.
** Corresponding author.
many materials, such as silicon dioxide and silicon nitride. However, some problems still exist in this technology. When SiO₂ was etched out, plasma can go on to etch silicon. It can result in serious damage to the microelectronic devices. However, DFVP technique offers absolute selectivity with zero silicon etching and high SiO₂ etching rate. Moreover, the equipment for plasma is much more expensive than that for DFVP (shown in Fig. 2).

The drawbacks of DFVP are: (1) the high requirement of exposure dose; (2) the limitation to the etching of SiO₂; (3) the loss of resolution when applied to a complex topographic feature substrate. Although the DFVP is a promising process, it has not received sufficient attention. In this paper we will present a review of the results of researches conducted by us and others.

![Schematic illustration of the DFVP](image1)

![Schematic illustration of etching system](image2)

1, hot plate 2, temperature controller 3, hydrofluoric acid 4, flowmeter 5, nitrogen source 6, pressure meter 7, silicon wafer.
2. THE PRINCIPLE OF DFVP

The question why a polymer film that resists etching in conventional wet photolithography becomes an etch-inducing film in DFVP has attracted the attention of researchers.[5-14] Obviously, the study of the mechanism of the etching reaction would be helpful for overcoming drawbacks and further developing this technique.

At present, a mechanism (illustrated in Scheme 1) has been proposed that during the DFVP process the reaction of SiO₂ with HF vapor can only occur when etching accelerators exist. These accelerators are compounds containing polar functional groups that can absorb and ionize HF vapor at high temperature. This is because the controlling step of the reaction of SiO₂ with HF vapor is the formation of fluorine anions. At low temperature the gaseous HF readily dissolves in the water layer existing on the surface of SiO₂ and dissociates to form fluorine anions and thus the etching reaction occurs. However, at high temperature there is no water layer on the surface of SiO₂, the reaction takes place only in the presence of accelerators which can assist the formation of fluorine anions. After exposed to UV light, the photopolymer is cross-linked and its Tg is increased. This prevents the rapid escape of small molecular accelerators contained in the film, such as 5-nitroacenaphthene that has been confirmed to be an effective accelerator. Consequently, there is a difference of accelerator concentration between exposed and unexposed areas. In the exposed areas the HF vapor can etch SiO₂ with a measurable rate in the presence of accelerators. In the unexposed areas the etching reaction cannot occur because the accelerators escaped from the film at high temperature. This procedure is shown in Scheme 2.

\[
\text{SiO}_2 (s) + \text{HF} (g) \xrightarrow{\text{Accelerator}} \text{SiF}_4 (g) + \text{H}_2\text{O} (g)
\]

Scheme 1

\[
\text{SiO}_2 (s) + \text{HF} (g) \xrightarrow{100^\circ \text{C}} \text{SiF}_4 (g) + \text{H}_2\text{O} (g)
\]

Scheme 2
3. HIGH RESOLUTION AND HIGH ASPECT RATIO

The question why this technique can simultaneously overcome the diffraction limitation and the problem of isotropic etching to offer a high resolution and high aspect ratio pattern were puzzles for long time. However, now it can be explained reasonably with the model we proposed. It is well known that the Tg of polymer is affected by crosslinking density, however, only high crosslinking density can markedly increase Tg, while slight crosslinking does not obviously affect Tg. On the other hand, slight crosslinking does greatly affect the solubility. Therefore, in the conventional photolithography less crosslinking density and in turn less exposed dose is enough for the solubility differential, and even the slight crosslinking caused by diffraction of light can result in loss of solubility and hence the resolution is limited. By contraries, in DFVP the requirement of high Tg needs high crosslinking density and the high exposure dose, the slight crosslinking in the diffraction areas does not affect the Tg and can not prevent the escape of accelerators. UV/Vis spectrometer was ever used to monitor structural changes of the photopolymer during the exposure to the 351nm XeF excimer Laser. (Fig. 3) The strong peak centered at 328nm in Fig.3 can well be attributed to conjugated double bonds in poly(glycol cinnamalmalonate) backbone[15]. As the Laser-exposure proceeds, the intensity of the peak at 328nm decreases. This indicates a loss of the conjugated structures. We found out that the etching reaction occurs only when the exposure energy is higher than 250mJ/cm², which corresponds to a 60% loss of the conjugated double bonds; the optimum exposure energy is 600-1000mJ/cm². This research result suggested that a highly crosslinked polymer is a prerequisite for the etching reaction to occur.[16]

The high aspect ratio of DFVP is related to the intimate contact between SiO₂ and polymer film during the etching period. The film on the SiO₂ in the exposed area should fall down with the removal of SiO₂, and at the same time the connected unexposed film will flow along the wall of etched channel. Therefore, the wall will be covered by slight crosslinked or uncrosslinked film, thus it can not be etched. As a result, a high aspect ratio is obtained.

![Fig. 3 UV spectra for a resist film of poly(glycol cinnamalmalonate) with 5-nitroacenaphthene](image)

<table>
<thead>
<tr>
<th>No.</th>
<th>Exposure energy (mJ/cm²)</th>
<th>Conjugate double bond disappearance %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>45.3</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>125.7</td>
<td>32</td>
</tr>
<tr>
<td>3</td>
<td>262.3</td>
<td>65</td>
</tr>
<tr>
<td>4</td>
<td>524.6</td>
<td>83</td>
</tr>
<tr>
<td>5</td>
<td>802.3</td>
<td>87</td>
</tr>
<tr>
<td>6</td>
<td>1726.3</td>
<td>95</td>
</tr>
</tbody>
</table>
4. ACCELERATORS AND POLYMER ACCELERATORS

Hydrogen fluoride can react with SiO₂ only when accelerators exist. The etching rate depends on the type and the concentration of accelerators. For a given set of fixed parameters, the etching rate of SiO₂ was found to increase with the increase of the concentration of 5-nitroacenaphthene in the photopolymer film. In the commercial camphorquinone type photoresist the 5-nitroacenaphthene concentration is 3% or so (based on photopolymer). Higher concentration are not favourable to the rate of crosslinking. However, in the DFVP process a concentration of photosensitizer of more than 10% is required in order to achieve a high etching rate. In our experimental condition the optimum concentration is 15-20% [12]. In addition, we found out that different functional groups greatly affected the etching rate. The strong dipolar aprotic compounds (e.g. DMF, DMSO, HMPA) can result in an evident etching of SiO₂, while compounds with hydroxyl groups or carboxyl groups only give minor etching; carbonyl and nitro groups also exhibit an evident accelerating role in the etching reaction. This is because dipolar aprotic accelerators can ionize HF and generate active fluorine anions. Hydroxyl and carboxyl groups are polar in nature, but the acidic hydrogen atom decreases the activity of fluorine anions, thus, the accelerating function becomes minimal.

Our recent work shows that polymer with carbonyl, nitro, amino formacyl, and other polar functional groups behave the same as small molecular accelerators [14]. These polymers which act not only as film formers but also accelerators of the etching reaction are called polymer accelerators. The relationship between the polymer functional group content and the etching rate is: the higher the functional group content, the higher the etching rate. However, the small molecular accelerators may gradually escape from that polymer film and diffuse in the film at an etching temperature above 100°C, even when the film is crosslinked. This is unsuitable for the DFVP process. On the other hand, once the accelerator groups are attached to the polymer through covalent bonding, they cannot escape. Therefore, polymer accelerators can etch thicker SiO₂ layer.

In summarizing our research results we could reasonably draw a conclusion that hydrogen fluoride can react with SiO₂ only when fluorine anions exist, and the etching rate was affected not only by the concentration of fluorine anions formed under the help of accelerators, but also by the activity of fluorine anions.

5. IRRADIATION SOURCES

UV, electron beam and ion beam can be used as the irradiation sources. The results showed that diffraction of the UV light and the electron reflect or scattering do not obviously affect the resolution of pattern [9,10]. Even the photolithography can make a 0.4 micron line. However the required dose are much higher than the conventional photolithography and electron beam lithography, for example, it was reported that when KPR was used as photoaccelerator, the exposure doses were 5.4 J/cm² or so for photolithography and 3.2 mC/cm²/20 Kev or so for electron beam lithography.[7] Compared with 180mJ/cm² exposure energy for the conventional photoetching, it is too high.

However, it is desirable to make patterns of high resolution at a relatively low exposure energy. Recently, by using the 351nm XeF excimer Laser, etched lines of 0.4um in width have been produced for poly(glycol cinnamalmalonate) /5-nitroacenaphthene system at an exposure energy as low as 650mJ/cm² (shown in Fig. 4). [16]

6. APPROACHES TO CREATE HIGH ACCELERATOR CONCENTRATION DIFFERENTIAL
In summarizing research results we could reasonably draw a conclusion that the etching rate depends on the type and the concentration of the accelerator. Therefore, our research will focus on creating a high concentration differential through three major approaches as follows:

1. Photoinduced Tg difference approach: If a polymer film is photocrosslinkable and contains an evaporable accelerator, the photocrosslinking reaction is able to create a Tg difference in the film, and in turn a difference of evaporation rate between exposed and unexposed areas, that leads to a difference of accelerator concentration.

2. Photoinduced accelerator approach: If a film contains a nonaccelerator compound (A) which can be turned into an accelerator (C) which can be turned into a nonevaporable accelerator via photoreaction (e.g. 2 plus 2 photocyclomerization reaction or photopolymerization), a concentration differential of accelerators can be created through irradiation.

(3) Photoinduced accelerator approach: If a film contains a nonaccelerator compound (A) which can be turned into an accelerator (C) which can be turned into a nonevaporable accelerator (B) via a photochemical reaction, irradiation may create a high differential of accelerator concentration. Thus, a film containing A will be a positive photoaccelerator film, while that containing C will be negative. It can be expressed as follows:

$$A \xrightarrow{hv} \text{C}_1 \quad \text{or} \quad C \xrightarrow{hv} \text{B}$$

$$\text{HF}(g) + \text{SiO}_2(s) \xrightarrow{c} \text{SiF}_4(g) + \text{H}_2\text{O}(g)$$

By these ways, more sensitive accelerator systems have been found out, and the etched thickness of SiO₂ is more than 1400nm.

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Fig. 4 Photographs of 0.4μm line obtained by DFVP process, at an exposure dose of 650 mJ/cm², etched at 135°C for 30 min gas pressure of HF with N₂ (2.5g/cm²).
REFERENCES

LASER INDUCED SURFACE MODIFICATION OF POLYDIMETHYLSILOXANE AS A SUPER-HYDROPHOBIC BLOOD COMPATIBLE MATERIAL

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ABSTRACT

With the purpose of improving, a polydimethylsiloxane (PDMS) based vulcanize surfaces exposed to, at room temperature, CO\textsubscript{2}-pulsed laser as the excitation source without photosensitizer. Modified surfaces have been studied by performing scanning electron microscopy (SEM) combined with energy dispersive X-ray analysis (EDXA) and attenuated total reflectance infrared (ATR-IR) spectroscopy to evaluate the surface morphology and surface functional groups. To evaluate the surface property, the water drop contact angle was measured. An important increase of the O/Si atomic ratio of the surface layer was seen on all exposed surfaces. The dependence of -Si-O- infrared peak intensity, O/Si ratio and water drop contact angle of the treated PDMS on laser pulses were studied. SEM micrographs and water drop contact angle variations show the uniform porosity and super-hydrophobic nature on the surface of PDMS respectively. The bulk mechanical properties of PDMS after being laser-treated did not change as shown by dynamic mechanical thermal analysis (DMTA).

In vitro blood compatibility assays showed insignificant platelet adhesion and aggregation onto the surface of the modified PDMS.

INTRODUCTION

Laser induced surface modification of polymers provides a unique and powerful method for the surface modification of polymeric materials without altering their bulk properties. This technique offer possibilities to improve the performance of existing biomaterials and medical devices and for developing new biomaterials\cite{1-4}. However, irradiating a polymeric material with a continuous laser beam heats the surface and may damage both the surface and the bulk, whilst pulsed lasers allow short exposure times and less thermal damage by optimizing the time intervals between pulses (repetition rate), laser fluency and pulse number\cite{5}.

Rubbers based on polydimethylsiloxane have some excellent properties such as high structural resistance towards heat, ozone and chemicals\cite{6}. Medical-grade silicone rubber is a widely used biomaterial for different applications including tubing, catheters, vascular grafts, plastic reconstruction, encapsulation of electronic components and voice prostheses. However, further long term application of the silicones used, the stability and the biocompatibility of the polymer are crucial\cite{7,8}.

It has been reported that the polymer surface, either super-hydrophilic or super-hydrophobic which indicate very high and very low surface free energy respectively, may possess excellent blood compatibility. It is well known that the thrombus formation is triggered by an interaction between blood components and the foreign polymer surface. On the other hand, the protein adsorption depends greatly upon the surface energy of the substrate\cite{9}.

In the present work we have utilized a line tunable pulsed CO\textsubscript{2}-laser to induce surface modification of PDMS to create a super-hydrophobic polymer to reducing the surface free energy of the PDMS to improve blood compatibility while keeping the bulk properties of the substrate intact. The surface of the treated samples has been characterized and also the surface morphology has been studied. No work on the modification of PDMS with laser to improve blood compatibility has to our knowledge previously been reported.
EXPERIMENTAL

PDMS Vulcanization
Raw polydimethylsiloxane rubber (M 3090 Wacker) was milled with 0.5 phr dicumylperoxide (90%) as curing agent at 80 °C. The rubber was formed into 2.0 mm thick sheets and compression cured at 165 °C for 5 min. Vulcanized films of 0.3 mm thickness and 3.5 x 3.5 cm dimensions were Soxhlet extracted with toluene: methanol (60:40 v/v) for 24 h and then dried in a vacuum oven of ambient temperature to constant weight.

Irradiation Procedure
Laser-induced surface modification was carried out by the simultaneous technique. A belt was made so that the laser beam could be directed vertically onto the surface of PDMS samples on the belt. Both sides of the sample surfaces were treated and the whole surface was scanned by the laser pulses in ambient condition and neither chemical nor photosensitizer were used. The laser used was a line-tunable pulsed CO₂-laser (TEA CO₂ laser Lumonics-103-2) which provides laser beams of wavelengths from 9.1 - 10.6 μm (1098 cm⁻¹ - 943 cm⁻¹). The uniformity of the pulses was checked using a Tectronics oscilloscope (7844) operating at 500 MHz. After each exposure, the samples were removed from the belt and washed first with acetone and then thoroughly extracted with acetone: distilled water (50:50 v/v) at 80 °C for 48 h. The extracted sample was dried in a vacuum oven at 50 °C to constant weight.

Surface characterization and analysis
In order to characterize the laser treated samples the following methods were carried out.
1- Attenuated total reflectance ATR-FTIR (Brucker-88) with KRS-5 prism and an incident angle of 45° was used.
2- Scanning electron microscopy (Cambridge S-360) was performed on gold coated samples using a Polaron sputter coater.
3- Energy dispersive X-ray analysis (AN-10000 EDXA) was used to measure the O/Si ratio of the modified samples.
4- The dynamic mechanical properties of the samples were studied and compared using a Polymer Laboratories DMTA. For each sample, storage modulus (E') and the loss tangent (tan δ) versus temperature were recorded.
5- Water drop contact angle was evaluated by measuring the contact angle formed between water drops and the surface of the samples.
6- Friction coefficients of the untreated and treated PDMS surfaces were measured according to the ASTM D 1894-78 method by using Friction Measuring Apparatus (Davenport).
7- Venous blood from healthy human was collected with a vacuum syringe containing 5% citric acid. The blood was centrifuged at 800 rev min⁻¹ for 10 min at 25 °C and the platelet rich plasma (PRP) was withdrawn with a PE pipette and placed in clean vials. The residue of the blood was centrifuged at 3000 rev min⁻¹ for 10 min to obtain platelet poor plasma (PPP). The platelet count of PRP was determined with Coulter counter (type 4) and adjusted to 150000 platelets mm⁻³. 1 ml of PRP was placed on each of the PDMS films of 1cm² and allowed to stand for 1 hr at 37 °C, rinsed with saline and treated with 2.5% glutaraldehyde in saline at 20 °C overnight. Following critical point drying and gold coating. The polymer surfaces were observed using a scanning electron microscope.

RESULTS AND DISCUSSION

Table 1 show the ATR-FTIR absorbance unit of -Si-O- band of the PDMS samples treated with 1, 5, 10 and 15 pulses of CO₂ laser at the wavelength of 9.58 μm (1043 cm⁻¹) which corresponds to the maximum absorption band of -Si-O- of the PDMS at 1011 cm⁻¹ and compared with the untreated PDMS. The intensity of this group was reduced with increasing of the laser pulses, in comparison
with the unmodified sample. The reduction in the intensity of the 1011 cm⁻¹ band is an obvious manifestation of the intense fragmentation on the surface of PDMS.

Table 1: Experimental data of the modified PDMS in comparison with the unmodified PDMS.

<table>
<thead>
<tr>
<th>Pulse Number</th>
<th>Absorbance unit of -Si-O- band</th>
<th>Contact Angle (degree)</th>
<th>O/Si Ratio</th>
<th>Friction Coefficient (µ)</th>
<th>Platelet Attached (×10⁷/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.303</td>
<td>105</td>
<td>1.06</td>
<td>0.14</td>
<td>9.6</td>
</tr>
<tr>
<td>1</td>
<td>0.604</td>
<td>170</td>
<td>1.11</td>
<td>0.12</td>
<td>1.89</td>
</tr>
<tr>
<td>3</td>
<td>0.516</td>
<td>170</td>
<td>1.25</td>
<td>0.075</td>
<td>1.76</td>
</tr>
<tr>
<td>5</td>
<td>0.395</td>
<td>165</td>
<td>1.262</td>
<td>0.065</td>
<td>1.42</td>
</tr>
<tr>
<td>7</td>
<td>0.306</td>
<td>162</td>
<td>1.264</td>
<td>0.06</td>
<td>1.1</td>
</tr>
<tr>
<td>10</td>
<td>0.217</td>
<td>160</td>
<td>1.268</td>
<td>0.055</td>
<td>1.4</td>
</tr>
<tr>
<td>13</td>
<td>0.211</td>
<td>155</td>
<td>1.271</td>
<td>0.045</td>
<td>2.35</td>
</tr>
<tr>
<td>15</td>
<td>0.205</td>
<td></td>
<td></td>
<td>0.04</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1(a) indicates the modified PDMS exhibited a strong absorption at 1746 cm⁻¹ which was assigned to carbonate groups (-O-COO-) on the surface of laser irradiated PDMS by 3 pulses compared to the unmodified sample, Fig.1(b). This intense peak (1746 cm⁻¹) has not been observed in an oxygen-free atmosphere. This peak gave an evidence of oxidation reactions as a result of the laser irradiation at
9.58 μm wavelength. This is consistent with the EDXA analysis which shows a higher percentage of the oxygen on the surface of the modified PDMS compared to the unmodified sample. It was observed that the induced changes were reproducible. We believe that infrared laser induced surface modification of PDMS by vibrational excitation of -Si-O- band through infrared multiphoton dissociation (IRMPD) mechanism.[10,11] According to this mechanism the produced radicals by laser irradiation may be transferred to the -CH groups on the skeletal chain of the PDMS and these groups converted to the carbonate or other oxidized groups in the presence of oxygen. The schematic reactions of the oxidized pathway of the PDMS surface modification are presented in Scheme 1. Among many possible oxidation schemes tested to explain our experimental observation, that of reactions (I-III), give the most probable mechanism of the CO₂-pulsed laser-induced oxidation onto the PDMS. The schematic reactions of the laser oxidation pathway of the PDMS surface; RH, *, R and H donate PDMS, excited state and radicals respectively.

(I) Initiation:

\[ \text{RH} \rightarrow \text{RH}^* \]
\[ \text{RH}^* \rightarrow \text{R} + \text{H} \text{ (energy transfer)} \]

(II) Propagation:

\[ \text{R} + \text{O}_2 \rightarrow \text{ROO}^- \]
\[ \text{ROO}^- + \text{RH} \rightarrow \text{ROOH} + \text{R} \text{ (radical transfer)} \]
\[ \text{ROOH} \rightarrow \text{ROO}^- + \text{H}^+ \]

(III) Termination:

\[ \text{ROOH} \rightarrow \text{RC}=\text{O} + \text{H}_2\text{O} \text{ (decomposition)} \]
\[ \text{ROOH} + \text{O}_2 \rightarrow \text{R-O-COO}^- + \text{H}_2\text{O} \]

However, we cannot unambiguously conclude that these are the only reactions involved for the oxidation processes, because not all reactions have been identified. The variation of O/Si intensity ratio determined from EDXA analysis is given in Table 1 as a function of the pulse number. As can be seen in this table by increasing of the pulse number, O/Si ratio on the surface of the treated samples is increased up to 5 pulses after which this ratio tends to a plateau state. The increased O/Si intensity ratio is an evidence for oxidized group formation by laser treatment.

The EDXA analysis and ATR-IR spectra show that CO₂-pulsed laser induced reactions on the surface of PDMS when the wavelength of the laser beam corresponds to the strong infrared absorption of PDMS. Water drop contact angle changes versus pulse number is shown in Table 1. As can be seen the contact angle is increased with the increasing of pulse number up to 5 pulses above which the contact angle decreased. It means that the surface property of the treated samples has been changed and a super-hydrophobic surface was obtained compared with the unmodified PDMS. When the surface of the PDMS was treated with CO₂ pulse laser, the surface became super-hydrophobic and very slippery. To quantitatively characterize the surface slipperiness, the friction coefficient of the surface was determined. The observed result is shown in Table 1. As is apparent, the friction coefficient of the untreated PDMS is 0.14 but drastically decreased when the surface is treated with laser. The friction coefficient is 0.05 when the PDMS is treated by 10 pulses. SEM micrographs [Fig.2(a)] show that the no platelet spreading is observed on the laser treated PDMS in comparison with the unmodified sample [Fig.2(b)]. It can be concluded from these studies that the surfaces of treated PDMS up to 10 pulses do not induce platelet activation. The number of platelet adhered on the untreated and treated PDMS films from PRP at different pulses is shown in Table 1. Platelet adhesion is maximum on untreated PDMS while it is minimum on 10 pulses laser treated sample. This can be attributed to the higher carbonate groups which enrich the oxygen and
the uniform porosity onto the PDMS surfaces. It has been reported that the porosity and super-hydrophobicity have a main effect on blood compatibility of the polymer surfaces [12-13]. The weak point in using high energy radiation such as gamma or electron beam as excitation source for surface modification is that the bulk mechanical properties of the substrate may change [14].

Fig. 2. SEM micrographs of the PDMS films exposed to the Platelet Rich Plasma (PRP), (a) unmodified PDMS, (b) CO$_2$-laser treated PDMS.
however, this potential shortcoming can be avoided by using the CO₂ pulsed laser source. To verify this the laser treated PDMS samples were examined by dynamic mechanical thermal analysis (DMTA). It can be seen that the tan δ max and (E) for the treated and untreated PDMS samples appear within the same temperature region. As (E) and tan δ are related to the structural property of the rubber, it can be concluded that the bulk structure and therefore the mechanical properties of the laser-treated samples have remained intact.

CONCLUSION

Our results indicate that the potential of using CO₂-pulsed laser to induce fragmentation and structuring onto the surface of PDMS without photosensitizer. PDMS is surface modified by CO₂-pulsed laser providing it is irradiated by pulses having wavelengths where PDMS has strong absorption. We believe that the CO₂-pulsed laser induced modification on the surface of PDMS at 9.58 μm (1043 cm⁻¹) by vibrational excitation of -Si-O- band through infrared multi-photon dissociation mechanism (IRMPD). Treated samples showed significant variation in hydrophobicity and is found to be depend upon irradiated laser pulses. The bulk structure and therefore the mechanical properties of the laser-treated samples have remained intact. The friction coefficient of the surface drastically decreased when the surface is treated with laser and no platelet spreading and aggregation is observed on the laser treated PDMS in comparison with control.

REFERENCES

SYNTHESIS OF DIPENTAERYTHRITOL HEXAACRYLATE 
AND UV-CURABLE ABRASION RESISTANCE COATINGS

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ABSTRACT

The dipentaerythritol hexaacrylate (DPHA) has been synthesized through the reaction of dipentaerythritol with acrylic acid. Its structure was identified by IR and chemical analysis.

An UV-curable coating was obtained. this hexafunctional monomer was used as a high reactive monomer with low color and medium viscosity when high hardness and high scratch resistance are required.

Key words: UV-curable, monomer, scuff resistance, synthesis.

INTRODUCTION

UV-cure technology is known to be low energy consumption, low pullution, rapid curing and high effiency. Owing to its said advantages, this technology has found a large number of industrial applications, such as wood furniture, paper, inks and the surface protection of many materials. The monomer used as reactive diluent in UV-cure resins plays a key role, for it affects not only the cure speed, the viscosity of coating, but also the polymerization extent. That is to say, it affects the propeties of the final films.

Among monomers acrylic acid esters, 2- ethylhexane acrylate (EHA), cyclohexyl acrylate (CHE), 1, 6- hexanediol diacrylate(HDDA), tripropylene glycol diacrylate (TPGDA), trimethylolpropane triacrylate (TMPTA), pentaerythritol triacrylate(PETA) are widly used.
However, hexaerylates are less discussed in this paper, a method of preparation of dipentaerythritol hexaerylate is described. When it used in UV-curable formulations, this compound was found to be very efficient for achieving fast cure rate and good scuff resistant though it is unable sufficiently to reduce the viscosity.

EXPERIMENTAL

1. Materials

Dipentaerythritol is commercial grade from Heng-Yang Chemical Factory, and the acrylic acid is from Beijing DongFang Chemical Factory. The other chemical regents used in this paper were on the market or self-synthesized.

2. Synthesis method

Using a three-necked flask equipped with an agitator, a reflux condenser with an oil-water separator, there were charged 119g acrylic acid, 63.5g dipentaerythritol, 180g toluene, 3.6g sulfiic acid, 4g cupric sulfate. Agitation was started and the mixture was heated to about 110°C. Temperature was maintained until an acid number 40-50 was obtained. The reaction was stopped and the mixture was cooled, filtered, washed with base and water. Last, 96 g dipentaerythritol hexaerylate was obtained after toluene was removed by distillation (Active Esters: 96.5%) .

3. Coating Formulation

The UV-curable coating formulation is shown in Table I.

**TABLE I. Coating Formulations**

<table>
<thead>
<tr>
<th>Materials</th>
<th>Parts By Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy acrylate</td>
<td>29</td>
</tr>
<tr>
<td>Urethane acrylate</td>
<td>9</td>
</tr>
<tr>
<td>DPHA</td>
<td>12</td>
</tr>
<tr>
<td>Tripropylene glycol diacrylate</td>
<td>28</td>
</tr>
<tr>
<td>Photoinitiator</td>
<td>4</td>
</tr>
<tr>
<td>Flow control agent</td>
<td>0.1</td>
</tr>
</tbody>
</table>
4. Test methods

The acid number were measured with KOH-alcohol solution. Infrared Spectra were obtained from Nicolet spectrophotometers (740 FT-IR).

Using a ultraviolet machine (Model AHDA I), samples are cured with 1Kw lamp suspended 26cm from substrate. Samples are one-passed through machine to obtain a non-tacky film. Cure rate was measured by the speed of transmission belt(m/min). Pencil hardness was determined according to GB6739-86, with Shanghai Zhong Hua 101-A Pencils covering the range 6B—6H. Abrasion resistance is measured by the resistance to tearing of the coating. This is done by running a fingernail at a 90° angle to the film several times.

G=Good—no marking of film
F=Fair—slight marking
P=Poor—penetration and tearing of film

RESULTS AND DISCUSSION

1. Influence of times on the synthesis reaction

Figure 1 shows the relation between acid number and reaction times. It shows the longer reaction times, the lower acid number and the higher yield was obtained. On the other hand, Longer reaction times can darken the colour of product. So we have to seek for some equilibrium between yield and color. In this study the best reaction time is 5 hours.

Infrared spectra for the DPHA is given in Figure 2.

![Fig.1 The relation between acid number and reaction times.](image1)

![Fig.2 Infrared spectra of the DPHA.](image2)
The IR of DPHA shows these characterized absorbance: $810\text{cm}^{-1}$ ($\equiv \text{C-H}$), $1050\sim 1180\text{cm}^{-1}$ ($\equiv \text{C-O}$), $1630\text{cm}^{-1}$ ($\equiv \text{C=C}$), $1730\text{cm}^{-1}$ ($\equiv \text{C-O}$), $3500\text{cm}^{-1}$ ($\equiv \text{-OH}$).

2. Cure speed

Cure speed of various acrylic monomers in the presence of 5% Irgacure 184 are shown in Figure 3. Under air atmosphere film thickness is 25 $\mu$m. Operation was carried out.

![Diagram of Cure Speed](image)

**Fig.3** cure speed of various monomers

Another test method of cure speed is to measure the coating's hardness after each passed through the UV-curing chamber. Curves were generated by plotting pencil hardness versus the number of passed. The results are shown in Figure 4.

![Diagram of Cure Times](image)

**Fig.4** cure times of various monomers (in the presence of 1% Irgacure 184 and 10% Epoxy acrylate)
3. Properties of UV-cured films

It is shown in Table II for the properties of UV-cured coatings whose preparations are described above (Table I). For purpose of comparison, data relating to use of the pentaerythritol triacrylate are included.

Table II. Properties of UV-cured Films

<table>
<thead>
<tr>
<th></th>
<th>UV-1(DPHA)</th>
<th>UV-2(PETA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cure speed (m/min)</td>
<td>8</td>
<td>6</td>
</tr>
<tr>
<td>Pencil hardness(H)</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>Abrasion resistance</td>
<td>G</td>
<td>F</td>
</tr>
<tr>
<td>Adhesion(PVC)</td>
<td>100/100</td>
<td>100/100</td>
</tr>
</tbody>
</table>

Owing to its high degree of crosslinking, we can see from Table II that DPHA cures faster and has high hardness, especially, good abrasion resistance.

CONCLUSIONS

1. The Dipentaerythritol hexaacrylate (DPHA) was synthesized by esterification of acrylic acid and Dipentaerythritol.
2. When PETA is substituted for DPHA in the UV-cured coatings, the coating's cure speed will be faster. It also exhibits an excellent combination of hardness and adhesion, as well as improved abrasion resistance.

REFERENCES

1. USP 4382185
2. JP 03-468127
A Novel UV Curable Adhesive for Plastic Films

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Japan Synthetic Rubber Co., Ltd.
25 Miyukigaoka Tsukuba Ibaragi 305, Japan

ABSTRACT
A new class of UV curable adhesives for lamination of plastic film, polyethyleneterephthalate (PET) and/or polyvinylchloride (PVC), has been developed. It was found that the formulations comprised of soft urethane acrylate oligomers and acrylic monomers having high Tg showed strong adhesion as well as high elongation which is required for the vacuum molding of the laminated film. An optimum Tg of monomers was determined to be 50 ~ 70 °C.

INTRODUCTION
In recent years, UV / EB radiation curing systems are becoming widely used due to their high productivity and environment friendly nature. UV curable adhesives are one of the applications which are drawing strong attention. For example, thermally curable, hot melt, or solvent based adhesives require long periods of treatment at relatively high temperature to proceed thermal reactions, to melt the component, or to evaporate the solvent. The treatment at high temperature is not appropriate for the thermoplastic films for lamination use. Thus, radiation curable adhesives have advantages over conventional thermal adhesives.

In this study, we have developed UV curable adhesives for lamination of PET and/or PVC films, especially suitable to vacuum molding of the laminated film. The laminated film is made as shown in Figure 1. A patterned PVC film is laminated with a transparent PET or PVC film to give a clear surface. The laminated film is applied for decorative furniture, wall, or even surface finish of refrigerator by using vacuum molding technic.

The adhesives suitable to this application need to have the following properties:

a) Adhesion: No delamination. Peel strength is preferable to be larger than 1.0 kg/cm.

b) Viscosity: For easy control of the thickness around 50 μm, the preferable viscosity of
the adhesive should be 500 to 1000 mPa·s

c) Elongation. The laminated film must be vacuum moldable. During the molding, the film could be stretched over 200% at the edge of the mold. The adhesives are required to have large elongation more than 300%.
d) Transparency. Since the base film has patterned surface, the adhesives must be clear and transparent.

EXPERIMENTAL

Synthesis of Urethane Acrylate Oligomers

Urethane acrylate oligomers were synthesized through conventional methods from polyether diol, diisocyanate of non-yellowing type, and hydroxy acrylate. The number-average molecular weight (Mn) of urethane acrylate oligomer was controlled by using polyether diols with Mn ranging from 2200 to 9000 and by changing the molar ratio of diol and diisocyanate. The urethane acrylate oligomers are summarized in Table 1.

Table 1. Urethane acrylate oligomers.

<table>
<thead>
<tr>
<th>Urethane acrylate</th>
<th>Mn of oligomer</th>
</tr>
</thead>
<tbody>
<tr>
<td>UA-1</td>
<td>2700</td>
</tr>
<tr>
<td>UA-2</td>
<td>5200</td>
</tr>
<tr>
<td>UA-3</td>
<td>9200</td>
</tr>
<tr>
<td>UA-4</td>
<td>18800</td>
</tr>
</tbody>
</table>

Selection of Acryl Monomers

Acryl monomers having glass transition temperature (Tg) ranging from -22 to 178 °C were used. The evaluated monomers are listed in Table 2.

Table 2. Various monomers' Tg.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Tg of homopolymer (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomer A</td>
<td>-22</td>
</tr>
<tr>
<td>Monomer B</td>
<td>94</td>
</tr>
<tr>
<td>Monomer C</td>
<td>145</td>
</tr>
<tr>
<td>Monomer D</td>
<td>178</td>
</tr>
</tbody>
</table>

Evaluation of Elongation

A formulated adhesive was coated on a glass plate at about 200 μm thickness, then cured with 1.0 J/cm² of UV dose using a metal halide lamp (275 mW/cm²). The cured adhesive was peeled off from the glass plate and was conditioned for 24 hours at 23 °C, 50% relative humidity (RH). The elongation at break of the cured adhesive was measured at 23 °C, 50% RH by using a tensile tester at an elongation rate of 50 mm/min.

Evaluation of Peel Strength

The adhesion of UV curable adhesives was evaluated by the T-peel test. After UV adhesive was drawn on a patterned PVC film at 20 μm thickness, another
transparent PVC or PET film was placed on the adhesive. Then the specimen was cured with 450 mJ/cm² of UV dose using a high pressure mercury lamp (50 mW/cm²). After being conditioned for 24 hours at 23 °C, 50 % RH, the peel strength was measured at peeling rate of 50 mm/min.

Analysis of Dynamic Mechanical properties

Dynamic mechanical response of the cured adhesive was measured by using a viscoelastometer in the temperature range of -100 to 200 °C at a heating rate of 2 °C/min and at a frequency of 3.5 Hz. Temperature dependence of loss tangent (tan δ) of the cured adhesives were measured. The glass transition temperature, Tg, of cured adhesive was evaluated as the temperature showing peak value of tan δ.

RESULTS AND DISCUSSION

The urethane acrylate oligomer, UA-3, was formulated with the acrylate monomers as shown in Table 3. The dynamic mechanical response of these compositions were measured. The results are also included in Table 3. The most significant observation was that all of the samples showed two peaks of tan δ. This result indicates phase separated structure of the cured film. Figure 2 shows curves of tan δ for AD-1 to AD-7. The lower Tg around -50 °C is attributed to the urethane acrylate oligomer. It seems that the Tg observed at higher temperature region changes in response to the composition of acrylic monomers. Assuming that the Tg observed at high temperature region is correlated to the weight ratio of the monomers and the individual Tgs, the Tg values were calculated and listed in Table 3. Although a certain discrepancy is seen at lower Tg region (AD-1 and AD-2), most of the calculated values are in good accordance with the observed ones indicating that the phase separated films are made of the soft urethane acrylate oligomer phase and high Tg polyacrylate phase.

The T-peel strength of each sample was measured and plotted against the Tg of the polyacrylate phase (Figure 3). The peel strength shows maximum values when the Tg of the adhesive is in the range of 50 to 70 °C. There are several observations that the peel strength of the adhesive exhibits maximum values when the measurements are carried out at Tg of the adhesives. In our case, the temperature for the measurements was kept constant to room temperature and the Tg of the adhesive was varied. If the same thing is happening to our case, the adhesion should have reached its maximum when Tg of the adhesive was at around room temperature. Although the cause of the difference between our observation and former examples is not clear at present stage, there is a close relationship between peel strength and Tg of the adhesives.

The adhesives applicable to the vacuum molding process need to have a large elongation at break. It is expected that the introduction of high molecular weight urethane acrylate oligomer would be effective. In Table 4, elongation and peel strength of several adhesives composed of the urethane acrylate oligomer with various molecular weights are summarized. As expected, samples with high molecular weight oligomer showed high elongation. It was found that the peel strength was also affected by the molecular weight of the urethane acrylate oligomer. In Figure 4, the peel strength is plotted as a function of the molecular weight of the oligomer. The peel strength increases as the increase of the molecular weight and levels off when the molecular weight exceeds 9000. Since the adhesives applicable to the vacuum molding process...
need to have more than 300% of elongation, the adhesives containing urethane acrylate oligomer with molecular weight of more than 9000 are preferable.

One of these adhesives, AD-4, was thoroughly evaluated and the results are summarized in Table 5.

### Table 3. Formulations and properties of adhesives with various monomer compositions.

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>AD-1</th>
<th>AD-2</th>
<th>AD-3</th>
<th>AD-4</th>
<th>AD-5</th>
<th>AD-6</th>
<th>AD-7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formulation (parts)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UA-3</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Monomer A</td>
<td>50</td>
<td>20</td>
<td>35</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>-</td>
</tr>
<tr>
<td>Monomer B</td>
<td>-</td>
<td>30</td>
<td>-</td>
<td>20</td>
<td>10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Monomer C</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>10</td>
<td>20</td>
<td>30</td>
<td>50</td>
</tr>
<tr>
<td>Monomer D</td>
<td>5</td>
<td>5</td>
<td>20</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>HCPK</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Property</th>
<th>First Tg (°C)</th>
<th>Second Tg (°C)</th>
<th>Calculated Tg (°C)</th>
<th>Peel strength (kg/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AD-1</td>
<td>-42</td>
<td>-56</td>
<td>-50</td>
<td>-48</td>
</tr>
<tr>
<td>AD-2</td>
<td>17</td>
<td>39</td>
<td>50</td>
<td>54</td>
</tr>
<tr>
<td>AD-3</td>
<td>-4</td>
<td>59</td>
<td>51</td>
<td>69</td>
</tr>
<tr>
<td>AD-4</td>
<td>0.25</td>
<td>0.53</td>
<td>1.32</td>
<td>1.51</td>
</tr>
</tbody>
</table>

1) 1-Hydroxycyclohexylphenylketone.
2) Calculated Tg based on the composition of monomers and individual Tgs (see text).

### Table 4. Formulations and properties of adhesives with various urethane acrylate oligomers.

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>AD-8</th>
<th>AD-9</th>
<th>AD-3</th>
<th>AD-10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formulation (parts)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UA-1</td>
<td>40</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>UA-2</td>
<td>-</td>
<td>40</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>UA-3</td>
<td>-</td>
<td>-</td>
<td>40</td>
<td>-</td>
</tr>
<tr>
<td>UA-4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>40</td>
</tr>
<tr>
<td>Monomer A</td>
<td>35</td>
<td>35</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>Monomer D</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>HCPK</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Property</th>
<th>Elongation (%)</th>
<th>Peel strength (kg/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AD-8</td>
<td>210</td>
<td>0.60</td>
</tr>
<tr>
<td>AD-9</td>
<td>260</td>
<td>1.10</td>
</tr>
<tr>
<td>AD-3</td>
<td>310</td>
<td>1.32</td>
</tr>
<tr>
<td>AD-10</td>
<td>300</td>
<td>1.40</td>
</tr>
</tbody>
</table>
Figure 2. Tan δ for AD-1 to AD-7.

Figure 3. Peel strength of various Tg of adhesive.

Figure 4. Peel strength of various Mn of urethane acrylate oligomer.
Table 5. Properties of UV curable adhesive AD-4.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity (mPa·s @ 25 °C)</td>
<td>670</td>
</tr>
<tr>
<td>Young's modulus (kg/mm²)</td>
<td>7</td>
</tr>
<tr>
<td>Tensile strength (kg/mm²)</td>
<td>0.9</td>
</tr>
<tr>
<td>Tensile strength (%)</td>
<td>&gt;400</td>
</tr>
<tr>
<td>Peel strength (kg/cm²) PVC</td>
<td>1.5</td>
</tr>
<tr>
<td>Peel strength (kg/cm²) PET/PVC</td>
<td>1.0</td>
</tr>
<tr>
<td>Peel strength (kg/cm²) PVC after 2 hrs in boiling water</td>
<td>0.7</td>
</tr>
<tr>
<td>Peel strength (kg/cm²) PET/PVC after 2 hrs in boiling water</td>
<td>0.6</td>
</tr>
<tr>
<td>Transparency (T% 100 µm)</td>
<td></td>
</tr>
<tr>
<td>@ 400 nm</td>
<td>92</td>
</tr>
<tr>
<td>@ 500 nm</td>
<td>99</td>
</tr>
<tr>
<td>@ 600 nm</td>
<td>100</td>
</tr>
<tr>
<td>@ 700 nm</td>
<td>100</td>
</tr>
<tr>
<td>@ 800 nm</td>
<td>100</td>
</tr>
<tr>
<td>Cure speed peel strength (kg/cm²) PVC</td>
<td></td>
</tr>
<tr>
<td>@ 50 mJ/cm²</td>
<td>0.3</td>
</tr>
<tr>
<td>@ 100 mJ/cm²</td>
<td>1.3</td>
</tr>
<tr>
<td>@ 300 mJ/cm²</td>
<td>1.6</td>
</tr>
<tr>
<td>@ 500 mJ/cm²</td>
<td>1.5</td>
</tr>
<tr>
<td>@ 1000 mJ/cm²</td>
<td>1.6</td>
</tr>
<tr>
<td>Durability of peel strength (kg/cm²) PET / PVC</td>
<td></td>
</tr>
<tr>
<td>80 °C x 24 hrs</td>
<td>0.8</td>
</tr>
<tr>
<td>72 hrs</td>
<td>0.6</td>
</tr>
<tr>
<td>240 hrs</td>
<td>0.6</td>
</tr>
<tr>
<td>720 hrs</td>
<td>0.6</td>
</tr>
</tbody>
</table>

1) Cured at 1.0 J/cm²
2) Cured at 450 mJ/cm²
3) Reflection was canceled

CONCLUSION

The UV curable adhesives comprised of urethane acrylate oligomer and acrylic monomers give two-phase-separated cured materials. The peel strength from PVC film was dependent on the Tg of the acrylic polymer phase showing maximum values at Tgs of 50 – 70 °C. The peel strength and elongation of the cured adhesives were also affected by the molecular weight of the urethane acrylate oligomers. Based on the observations, UV curable adhesives suitable for PVC / PVC or PVC / PET lamination was developed. These adhesives have large enough elongation ( >300 % ) that they are applicable to the vacuum molding process.

REFERENCES

STUDY ON SPECTRAL SENSITIVITY OF RESINS 
FOR STEREOLITHOGRAPHY

Tsuyoshi Watanabe, Ayao Matsumura, and Takashi Ukachi
Tsukuba Research Laboratory, Japan Synthetic Rubber Co., Ltd.
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INTRODUCTION

Optimization of the sensitivity of formulated resins against the light source is one of the most important subject to achieve high accuracy of the cured parts for stereolithography. Recent progress in laser technology enable us to use highly reliable continuous emission from helium-cadmium laser at 325 nm and argon ion laser at 351 and 364 nm for stereolithography. Furthermore, lasers such as Kr, Ne, frequency tripled Nd-YAG, and direct frequency doubled diode lasers are being evaluated. In the most of case, photoinitiators in the resin formulation play a quite important role to enhance the curing sensitivity for the light source employed. Although a number of photoinitiators for UV light have been developed and are available in the market, experimental data of these photoinitiators applicable for the stereolithography are limited. Particularly, information of the spectral sensitivity for cure depth is significantly important to design resins for stereolithography with high accuracy and fast cure speed.

We investigated spectral sensitivity of the several formulations with commercial photoinitiators by using a modified spectral irradiator which gave information of the spectral cure depth. The ability of the modified spectral irradiator and the preliminary results of the spectral sensitivity study of model formulations are discussed.

EXPERIMENTAL

Five different kinds of commercially available photoinitiators were dissolved in ethoxylated bisphenol-A based diacrylate (BPEODA) or tripropyleneglycoldiacrylate (TPGDA) and provided for the experiments. Table 1 summarizes compositions of these model formulations.

The spectral sensitivity of these formulations in the range of 250 to 500 nm was measured by using the modified spectral irradiator CT-25CP developed by Nihon Bunko Keiki Co., Ltd. Schematic diagram of the spectral irradiator is shown in Fig. 1. Since a spectrum band from a Xe lamp was irradiated to the bottom of the sample in 5 mm depth through a quartz plate, it can solidify the resin and give a 3-dimensional cured profile on the quartz plate according to the spectral sensitivity of the resin. The irradiation time and the position can be controlled automatically by a mechanical shutter and a moving stage through a microcomputer. The light intensity at each wavelength was measured by a thermopile photo-detector and was taken into account for the data processing. All experiments were conducted at 23 °C under air or nitrogen atmosphere. A 3-D cured profile shown in Fig. 2 can be obtained by the spectral
irradiator. The spectral sensitivity can be expressed as a function of three parameters, wavelength, cure depth and exposure energy.

UV absorption spectrum was measured for the neat sample in a thin quartz cell with a spectrometer (Hitachi) in order to determine the absorption coefficient. Solid creation system JSC2000 (SONY) was used for the fabrication study.

Table 1. Compositions of model formulations used for this study

<table>
<thead>
<tr>
<th>Code No</th>
<th>Monomer</th>
<th>Conc. (wt%)</th>
<th>Photoinitiator</th>
<th>Conc. (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-1</td>
<td>BPEODA*1</td>
<td>97.0</td>
<td>HCPK*3</td>
<td>3.0</td>
</tr>
<tr>
<td>F-2</td>
<td>TPGDA*2</td>
<td>97.0</td>
<td>HCPK</td>
<td>3.0</td>
</tr>
<tr>
<td>F-3</td>
<td>BPEODA</td>
<td>94.0</td>
<td>HCPK</td>
<td>6.0</td>
</tr>
<tr>
<td>F-4</td>
<td>BPEODA</td>
<td>91.0</td>
<td>HCPK</td>
<td>9.0</td>
</tr>
<tr>
<td>F-5</td>
<td>BPEODA</td>
<td>97.0</td>
<td>DMPA*4</td>
<td>3.0</td>
</tr>
<tr>
<td>F-6</td>
<td>BPEODA</td>
<td>97.0</td>
<td>BDMP*5</td>
<td>3.0</td>
</tr>
<tr>
<td>F-7</td>
<td>BPEODA</td>
<td>97.0</td>
<td>MMMP*6</td>
<td>3.0</td>
</tr>
<tr>
<td>F-8</td>
<td>BPEODA</td>
<td>97.0</td>
<td>TMDPO*7</td>
<td>3.0</td>
</tr>
</tbody>
</table>

*1) BPEODA; 1-hydroxycyclohexylphenylketone  
*2) TPGDA; 2,2-dimethoxy-2-phenylacetophenone  
*3) HCPK; 1-hydroxycyclohexylphenylketone  
*4) DMPA; 2,2-dimethoxy-2-phenylacetophenone  
*5) BDMP; 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butane-1-one  
*6) MMMP; 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinophenyl-butane-1-one  
*7) TMDPO; 2,4,6-trimethylbenzoyldiphenylphosphineoxide

**RESULTS AND DISCUSSION**

1. Critical energy for the solidification (Ec)

Sensitivity of the stereolithographic resin is generally expressed by the critical energy for the solidification, Ec, at the wavelength of the employed light source. Since the resin having smaller Ec value can lead faster laser scanning, one should pay attention to the agreement...
between the sensitivity of the resin and the light source in order to design an effective rapid prototyping system. The values, Ec, of five model formulations measured by the spectral irradiator are plotted against the wavelength in Fig. 3. Formulation, F-6 (BDMB) showed the highest sensitivity in the wide range of wavelength investigated. The Ec value at 351 nm (Ar ion laser output) is less than 0.1 mJ/cm\(^2\) and it is two order of magnitude smaller than that of F-1 (HCPK). It was found that each sensitivity spectrum was similar to the reverse image of the corresponding absorption spectrum and this implies the efficiency of photoinitiator is constant through the investigated wavelength region. Fig. 4 shows the effect of the atmosphere and monomer species on the spectral sensitivity. Under nitrogen atmosphere, Ec of F-1 became several ten \(\mu J/cm^2\) at 351 nm and was about 200 times smaller than that in air through the wavelength region investigated due to the absence of oxygen inhibition. Formulation, F-2 (TPGDA) showed about 2 times larger Ec compared with F-1 (BPEODA) and this indicates that monomer species strongly affect the Ec value as well as photoinitiator species.

![Fig. 3. Spectral sensitivity of 5 different photoinitiators.](image)

![Fig. 4. Spectral sensitivity of F-1 and F-2 in air and F-1 in nitrogen atmosphere.](image)

Since Ec is defined as the minimum energy for the solidification at the zero thickness, it should be inversely proportional to the concentration of initiating radicals at the surface of the resin \(\phi \varepsilon \epsilon \cdot c\) when the quantum yield \(\phi\) of the photoinitiator is assumed to be constant at each wavelength. Thus, Ec at a certain wavelength, \(Ec(\lambda)\), can be expressed as follows:

\[
Ec(\lambda) = K / \epsilon(\lambda) \epsilon c
\]

where \(\epsilon(\lambda)\) is molar extinction coefficient (L/mol·cm) at wavelength \(\lambda\), \(c\) is concentration of photoinitiator (mol/L) and the constant, \(K\) (mJ/cm\(^3\)) is specific energy (amount of energy required to solidify a unit volume of resin) related to solidification speed of the formulation.

The \(K\) value was determined for each formulation at 351 nm and summarized in Table 2. Formulation, F-6 (BDMB) has 4 times smaller \(K\) value than other formulations. This result might reflect the high initiation efficiency of BDMB in the presence of oxygen compared with
other photoinitiators. As shown in Figs. 5(a) and 5(b), experimental results for F-1 and F-8 agree well with the values predicted from absorption spectrum (ε) and K value at 351 nm through the wavelength region investigated. The same results are seen for all other formulations. We can conclude that initiation efficiency of these photoinitiators is constant at the wavelength region, 300 to 500 nm, and the equation (1) is propriety for the prediction of $E_C(\lambda)$ at this wavelength region.

Table 2. The K values of model formulations calculated from $E_C(\lambda)$ and $e(\lambda)$ at 351 nm

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_C(351)$ (mJ/cm²)</th>
<th>$e(351)$ (L/mol·cm)</th>
<th>K (mJ/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-1 (HCPK, 3%, BPEODA)</td>
<td>6.4</td>
<td>63</td>
<td>68</td>
</tr>
<tr>
<td>F-2 (HCPK, 3%, TPGDA)</td>
<td>11.4</td>
<td>63</td>
<td>110</td>
</tr>
<tr>
<td>F-3 (HCPK, 6%, BPEODA)</td>
<td>2.9</td>
<td>65</td>
<td>62</td>
</tr>
<tr>
<td>F-4 (HCPK, 9%, BPEODA)</td>
<td>2.1</td>
<td>53</td>
<td>67</td>
</tr>
<tr>
<td>F-5 (DMPA, 3%, BPEODA)</td>
<td>1.9</td>
<td>233</td>
<td>60</td>
</tr>
<tr>
<td>F-6 (BDMB, 3%, BPEODA)</td>
<td>0.046</td>
<td>3650</td>
<td>16</td>
</tr>
<tr>
<td>F-7 (MMMP, 3%, BPEODA)</td>
<td>1.1</td>
<td>317</td>
<td>43</td>
</tr>
<tr>
<td>F-8 (TMDPO, 3%, BPEODA)</td>
<td>2.0</td>
<td>305</td>
<td>61</td>
</tr>
</tbody>
</table>

Fig. 5(a). Experimental $E_C$ (closed circle) and calculated $E_C$ (line) form absorption spectrum of F-1 (HCPK).

Fig. 5(b). Experimental $E_C$ (closed circle) and calculated $E_C$ (line) from absorption spectrum of F-8 (TMDPO).

2. Cure depth coefficient (Dp)

According to the Lambert-Beer’s law of absorption, cure depth, $C_d(\lambda)$ (cm), can be expressed as follows:

$$C_d(\lambda) = D_p(\lambda) \log(E/E_C(\lambda))$$

(2)

where $D_p(\lambda)$ (cm) is a characteristic constant for the resin and corresponds to $1/e(\lambda)c$ (cm). Fig. 6 shows relationship between logE and Cd, which is so-called working curve, of three formulations with different photoinitiator concentrations. Asterisks in Fig. 6 show the data derived from the experiments with Ar ion laser for F-1. The slopes of Cd vs. logE given by
two different light sources were exactly same. Table 3 summarizes experimentally determined slopes of working curves, \( Dp(\lambda) \), and the predicted slopes from the absorption spectrum for different formulations, respectively. The experimental data well agree with \( 1/\varepsilon(\lambda)c \) at 325 and 351 nm. This agreement was also confirmed at other wavelengths.

Working curves of five different formulations at 351 nm are shown in Fig. 7. It can be said that F-1 (HCPK) is suitable for the fabrication of the models in large size, on the other hand F-6 (BDMB) is rather suitable for the fabrication of models in small size. Notice that F-5 shows sub-logarithmic behavior, and contrary to this, F-6 shows super-logarithmic one at higher exposure energy region. These deviations from the logarithmic behavior were explained by photo-yellowing and photo-bleaching respectively. It is well known that some colored bi-product is produced by the photolysis of DMPA. These phenomena also affect the practical fabrication and will be discussed.

Table 3. Experimentally determined \( Dp \) (cm) and \( 1/\varepsilon(\lambda)c \) (cm) at 325 and 351 nm

<table>
<thead>
<tr>
<th>Sample</th>
<th>( Dp(325) )</th>
<th>( 1/\varepsilon(325)c )</th>
<th>( Dp(351) )</th>
<th>( 1/\varepsilon(351)c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-1 (HCPK, 3%)</td>
<td>0.0649</td>
<td>0.0595</td>
<td>0.1689</td>
<td>0.0940</td>
</tr>
<tr>
<td>F-5 (DMPA, 3%)</td>
<td>0.0309</td>
<td>0.0327</td>
<td>0.0343</td>
<td>0.0319</td>
</tr>
<tr>
<td>F-6 (BDMB, 3%)</td>
<td>0.0010</td>
<td>0.0007</td>
<td>0.0024</td>
<td>0.0029</td>
</tr>
<tr>
<td>F-7 (MMMP, 3%)</td>
<td>0.0013</td>
<td>0.0019</td>
<td>0.0208</td>
<td>0.0255</td>
</tr>
<tr>
<td>F-8 (TMDPO, 3%)</td>
<td>0.0082</td>
<td>0.0069</td>
<td>0.0362</td>
<td>0.0330</td>
</tr>
</tbody>
</table>

Fig. 6. Working curves of F-1, F-3 and F-4 by the spectral irradiator and Ar laser.

Fig. 7. Working curves at 351 nm for the resins formulated with different photoinitiators.

3. Practical fabrication

As previously mentioned, small \( \varepsilon(\lambda)c \) value, like F-1, might be suitable for the fabrication of large-size models. However, too small \( \varepsilon(\lambda)c \) value sometimes causes the lack of the \( Z \)-direction precision. For instance, a hang-over or a small lateral tunnel shape cannot be
fabricated precisely due to the unexpected cure just below the ceiling. Fig. 8 shows micrographs of fabricated parts with four different formulations. The excess cured parts below the ceiling of the lateral tunnel decreased with increasing the number of $\varepsilon_{(351)C}$ and it can be concluded that formulations with larger $\varepsilon_{(351)C}$ has advantage in terms of Z-direction precision. Interestingly, F-5 showed two times better precision compared to F-4, although $\varepsilon_{(351)C}$ value of these formulations are identical. This can be explained as the effect of the photo-yellowing mentioned above.

CONCLUSION

We demonstrated that the modified spectral irradiator was a useful equipment to determine the spectral sensitivity of resins for stereolithography. Characteristic constants Ec and Dp at desired wavelength for the stereolithographic resins were determined by simultaneous measurements without using laser. We found that model formulations obeyed the Lambert-Beer's law well at the low energy exposure region. However, some photoinitiator systems showed the photo-yellowing and the photo-bleaching behaviors which seem to affect the accuracy of the practical fabrication. Photoinitiator, HCPK seems to be suitable for the resin to fabricate large models, on the other hand, BDMB seems to be suitable for the resin to fabricate precise small models with rapid laser scanning at both 325 and 351 nm.

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Radiation Curing for the Automotive Market

Chris Brandl
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RadTech Asia '95
The Fifth International Conference
on
Radiation Curing

Guilin, China
November 20-24, 1995
ABSTRACT

UV curing is in the early stages of penetrating the automotive manufacturing assembly and decorating. There are several reasons the automotive market is considering and beginning to use UV curing processes. VOC reduction continues to be a major driving factor worldwide in all industries. UV cured coatings provide high performance which fit well into the ever increasing performance requirements. Significantly reduced process time, parts in inventory, floor space requirements and capital investment are all features of the UV curing process that interest automotive parts manufacturers. A review of the different types of UV curing equipment, heat management, importance of spectral distribution and its interaction with photo initiators will reveal important factors in a successful UV process. Finally, a look at existing UV automotive applications currently in use and in development will reveal the powerful advantages of UV curing.

WHY UV CURING?

UV curing is growing at a remarkable rate in many manufacturing areas; automotive is no exception. The UV curing process is making its way into many areas of assembly and decorating for automotive trim and body applications. What is driving the interest in UV curables in the worldwide automotive market? One of the main concerns is volatile organic compound reduction. VOC emissions are becoming more tightly regulated worldwide. The economics of UV curing and the continual effort to increase part performance are also playing a big role in the adoption of UV curing processes worldwide.

VOC REDUCTIONS - Many of the UV curable coatings and adhesives on the market are low VOC or zero VOC. 100 percent solids, liquid UV curable coatings are becoming more and more common. An alternative with the use of solvent-based material is to remove any VOCs (volatile organic compounds) from the exhaust. Systems to achieve this can be effective, but quite costly. There is a range of approaches available from incineration with simple afterburner, through energy-recovery heat exchangers, to high efficiency secondary heat recovery systems. These systems still generate a significant amount of CO2 which may eventually be regulated as well. The capital cost and the operating costs of these various systems can be significant, with cost "trade-offs" as illustrated in the following simplified example for a small shop, running one shift (See Table 1 below).

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Annual</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Capital Cost</td>
</tr>
<tr>
<td>Simple Afterburner</td>
<td>$ 50,000</td>
</tr>
<tr>
<td>Burner, with Primary</td>
<td>$200,000</td>
</tr>
<tr>
<td>Heat Exchanger</td>
<td></td>
</tr>
<tr>
<td>High Heat Recovery System</td>
<td>$350,000</td>
</tr>
</tbody>
</table>

The capital cost and operating cost of conversion to UV must be compared to the capital cost and operating cost of incineration and heat recovery.

In the area of coating and decorating, there are some alternative technologies available which are VOC compliant but do not have the application flexibility or performance of UV curable coatings. For example, waferbase coatings are an option for VOC compliance, but these coatings are not solvent free. More importantly, waferbase coatings typically do not provide high performance durability that the automotive manufacturers require for interior and exterior coatings.

Thermally cured powder coatings provide good VOC compliance, but have many application restrictions. Currently, the high-temperature melt points of powder coatings prohibit them from being used on heat sensitive engineered thermoplastics. These heat sensitive plastics represent a growing percentage of the automobiles overall composition. High quality surface finish may also disqualify powder coatings as a decorating option because coating flow out is restricted by the use of heat as the flowing mechanism as well as the curing mechanism. No other coating technology currently available offers the high performance along with process and application flexibility and VOC compliance that UV curable coatings offer.

PROCESS TIME - A second factor advancing the use of UV cured products in automotive markets is the reduction in process time and parts-in-process. Because UV curing provides virtually instantaneous curing, the number of parts in process can be substantially reduced, in some cases by a factor of 10. Adhesive and painting applications using two-part adhesives or RTV types of compounds must allow cure time, usually measured in days. This is because many of the applications are on heat
sensitive circuit boards and can not be exposed to a thermal cure to accelerate the cure. This is most costly in terms of cycle time and tied up work-in-progress inventory.

It is not unusual in a plastic parts manufacturing and decorating operation to have the molding operation operate 24 hours a day, 6 1/2 days a week. Conversely, the decorating operation may only operate 8 to 10 hours per day, 5 to 6 days a week. If a coating and curing process takes 1 hour to 3 hours, it is likely that 8 hours molding time of molded parts are in process at any given time. When a problem with the decorating process is detected at inspection, an entire shift of molded parts is lost, and with the tight scheduling on most molding machines it is very difficult to make up that lost time. Thermally cured adhesives represent similar issues for parts in process.

PERFORMANCE ADVANTAGE - Another driving factor in the change to UV curable coatings is performance. UV curable coatings for interior and exterior automotive applications provide for increased performance over conventionally cured coatings. Interior coatings typically strive for very low gloss especially on the instrument panel near the windshield where minimal reflectance is critical. Very low gloss coatings, whether they are solvent base or waterbase, when thermally cured tend to exhibit poor mar resistance. Waterbase interior coatings also tend to have poor solvent resistance. UV curable interior coatings can achieve a three to five gloss and still have excellent mar resistance and solvent resistance.

Exterior UV curable coatings also exhibit extremely high performance characteristics. The scratch resistant hard coats have far superior abrasion resistance as compared to melamine acrylates or a two component urethane, but still retain good impact resistance on solvent sensitive plastics like polycarbonate. Less rigid scratch resistant hard coats are also available for use as a top coat over pigmented base coats for automotive plastic trim. These UV curable clear coats exhibit excellent long-term exterior weathering, excellent abrasion resistance, chemical and impact resistance. On poorly weathering substrates like extruded vinyl, UV clear coats are used to prevent premature yellowing as well as improve stain and abrasion resistance.

ECONOMICS OF UV CURING

Cost savings is the final driving factor for UV curable coatings and adhesives to be discussed. All manufacturers are continuously looking for ways to reduce cost and increase efficiency. UV curable chemistries can certainly contribute to both of those efforts.

CAPITAL EQUIPMENT COSTS - There are potential cost savings unique to the installation of a new line compared to that of an existing line. In the installation of a new line, there can be significant cost savings related to capital equipment, specifically, the cost of a gas fired thermal cure oven compared to a UV cure oven.

The comparison of capital cost of a thermal system to a UV system is quite direct, as either would be quoted completely by its manufacturer. Installation cost is easily obtained. However, owing to the vast range of equipment size depending on capacity and application, a generalization here is necessary. A small thermal cure unit, such as for small parts, would cost approximately the same as a UV unit - about $10,000 to $15,000. The larger the system, the greater the capital cost difference: UV will represent a smaller cost, in the range of 50% of large capacity thermal system.

SPACE UTILIZATION - A drying oven for a conventional cure may extend for 50 to 100 feet, a space consumption in the neighborhood of 500 to 1000 square feet. At a floor space cost of only $0.50/ft²/mo, that costs $3000-6000 per year. The equivalent UV "dryer" would require 50 to 100 square feet. The instances where floor space carries a premium cost, total indirect operating costs could be significantly sensitive to this element. In some cases, there just isn't physically enough room for a gas fired oven and that profit generating operation would not otherwise be feasible without UV curing.

ENERGY CONSUMPTION - One of the most significant cost factors when comparing thermal cure to UV cure is the energy cost when operating each type of oven. This comparison is equally valid for existing lines as it is for a new installation. A large gas dryer ("oven") consumes 1.50 MBTU/hr (and requires large blowers) for the same production capacity achieved with a UV dryer requiring only 90kW total (See Table 2 below):

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Table 2.

ENERGY CONSUMPTION

Example: Flow coat machine. 420 parts per hour

THERMAL - GAS
1.50 MBTU/hr x $3.60/MBTU = $ 5.40/hr
Blowers 56kW x $0.07/kW-hr = $ 3.92/hr
300 da/yr x 16 da x $9.32/hr = $44.736/yr

UV-ELECTRIC:
5.6 kW/lamp x 12 lamps x $0.07 kW-hr
300 da/yr x 16 da x $4.70/hr = $22.579/yr

Other areas of cost savings can come from reduced parts in process and shorter processing time which directly relates to lower inventories. Quicker cure allows for fewer particles to contaminate the surface finish which directly relates to rework and scrap costs.

SELECTING THE TYPE OF LAMP

One of the first issues to be considered is the type of UV lamp to be used. There are two basic technologies that are available. One type is the electrode type lamp or more commonly referred to as an arc lamp. The second type of lamp is referred to as an electrodeless lamp or microwave powered lamp. These two different types of lamps both produce ultraviolet light as its final output. How they go about generating the output is significantly different.

ARC LAMPS - A well known and widely used type of lamp is the mercury vapor arc lamp. The electrode type lamp uses a quartz tube with a metal electrode on either end. The fused quartz tubing has a wall thickness of about one millimeter and an outer diameter of 20 to 25 millimeters. Inside the quartz tube is generally mercury, a starter gas, as well as several other elements that can be added to alter the spectral distribution. The mercury is vaporized when an arc is struck between the two electrodes. The mercury is vaporized and ultra violet light is produced.

MICROWAVE POWERED LAMPS - With the electrodeless type of lamp, as the name indicates, there are no electrodes incorporated in the quartz tube. The quartz envelope is completely sealed. This bulb is then placed in a chamber where the microwave energy is transmitted directly into the bulb. The microwave energy vaporizes the mercury and once again produces ultra violet light. This design permits relatively simple construction of the bulb because electrodes are not required. This type of design also allows for a small bulb diameter.

TYPE OF SUBSTRATE USED - What issues impact our decision on choosing a particular curing system? One criteria for selecting a UV curing system can be the heat sensitivity of your substrate. If your substrate can tolerate temperatures in excess of 200 degrees Fahrenheit, this criteria is not as critical. However, when working with thin films or polycarbonate, for example, heat sensitivity becomes an issue. The heat generated from the UV lamps is mainly in the form of infrared emitted from the quartz tube. Microwave powered lamps have 9 mm or 13 mm bulbs depending on the power of the lamp. Arc lamps typically have 20 mm - 25 mm bulbs; some arc lamp suppliers now offer smaller diameter bulbs as well. Typically, the smaller diameter of the bulb the less infrared heat that must be managed in the system. There are varying ways to manage the heat generated which will be discussed in the next section of this presentation.

HEAT MANAGEMENT - Heat management is an important part of UV curing on plastic substrates. Many heat sensitive plastics are currently in use. Through proper management of infrared produced in the UV process, even the most heat sensitive thin filmed plastics can be used in the UV curing process. There are several techniques for managing heat in both electrode and electrodeless systems. I will first discuss the techniques that are available to both lamp types.

Positive air cooling is using filtered air and blowing it through the reflector, across the bulb and down onto the part. In the case of microwave lamps, this air is also used to cool the magnetrons. The level of cleanliness of the air used will greatly impact the life of the bulb and reflector. In some cases this same air is expelled on to the part and must be clean enough as to not contaminate the part.

A second technique used in heat management by both lamp types is a dichroic reflector. The dichroic reflector has good reflectance to UV and intentionally poor reflectance of IR. This reduces the amount of infrared irradiance at the surface while providing focused UV. There is, however, some diminished UV at the surface. For example, a cure speed of 21.1 meters per minute produced a temperature of 54 degrees Celsius using a standard reflector. To achieve the same cure with dichroic reflector, a line speed of 19.7 meters per minute was used and the part temperature rose to 43 degrees Celsius. This is a 7 percent loss in cure speed and a 21 percent reduction in temperature.
A third method of reducing the heat in the curing process available to both lamp types is to circulate chilled water immediately below the parts being cured. Arc lamps also have the capability of employing water cooled reflectors as well as water cooled filters. However, a water cooled filter can significantly diminish the amount of UV energy available for curing. Arc lamps can also use negative air flow cooling which is not available for the microwave powered lamp. Negative air flow cooling is drawing the cooling air in through the bottom of the lamp, over the bulb, and expelled out through the back of the reflector.

**PEAK IRRADIANCE** - In addition to the dosage level that will be generated by a given power level of a lamp, an additional consideration is the intensity or peak irradiance that is required. Irradiance in watts/cm, is the measure of light "intensity" at the surface. It has been found that many UV inks and coatings respond more efficiently to higher peak irradiance, rather than to exposure to a lower level of energy for a longer period of time. Higher peak irradiance also allows for a more complete conversion of the reaction. Generally, the more complete the reaction the higher performance characteristics of a given coating. Higher bulb power, smaller diameter bulb, and high efficiency reflector will yield the highest peak irradiance.

**SELECTION OF THE PROPER SPECTRAL OUTPUT** - The selection of proper spectral output is extremely important. Most equipment suppliers produce several different spectral output bulbs. The standard bulb is a mercury vapor bulb which typically has a majority of its energy in the 210 nm to 285 nm range. Also, generally available are metal halide doped lamps which provide a majority of their energy in the 350 nm to 390 nm range. Other bulbs that are typically available can provide significant energy in the 400 nm to 430 nm range. Each chemistry will use a photo initiator package that will respond to a particular wave length or group of wave lengths. It is important that your chemistry supplier inform you which spectral output his chemistry will respond to.

There are several other issues that can change your spectral output requirements. The first is whether the coating, ink or adhesive is pigmented or clear. Products which are clear, obviously, can be the most easily penetrated with short wave length UV which is typically provided by the mercury vapor bulb. Typically, pigmented systems require a slightly longer wave length to penetrate through the coating to achieve total cure. Many of the pigmented systems available respond very well to the spectral output of the metal halide bulb. However, certain pigments such as titanium dioxide pose unique requirements for UV curing. The titanium dioxide reflects or absorbs most UV light below 400 nm so the use of a bulb which has a majority of its energy above 400 nm is required. When curing through a substrate like polycarbonate or acrylic, it is important to know what wave lengths will not penetrate or be absorbed. In the case of polycarbonate it has been found when curing through it down into an adhesive track, it absorbs or reflects most energy below 400 nm, but acts like a light tube efficiently transmitting wavelengths above 400 nm directly into the adhesive track. The thickness of a coating or adhesive can also dictate the type of spectral output being used for curing. Extremely thick coatings require the initial dose of UV light to be a long wave length to penetrate through the coating to get adequate cure at the interface of the coating and the substrate which will allow for good adhesion. A second bulb of shorter wave length can then be used to achieve cure at the shallower depths and on the surface. In some cases, we may want to apply multiple coats of clear over pigmented. Again, in this case, you would want a two stage curing, first the pigmented with a metal halide and then the clear coat with a mercury vapor bulb.

One additional item that may impact your selection of a spectral output can be the physical properties required of the final product. If high abrasion resistance is required, generally, a short wave length bulb such as the mercury vapor bulb would be recommended. The short wave lengths produce high density cross linking on the surface of most chemistries. It is possible to further increase the cross link density and hence the abrasion and staining resistance properties of a top coat by curing in an inert environment.

In the remainder of my paper, I would like to discuss specific applications of UV curing in the automotive industry. In the examples that are already commercial, I will note the advantages or reasoning for switching to a UV cure process. In the examples that are still in the development stage, I will try to note some advantages over to existing technology.

**APPLICATIONS**

**HEAD LAMP LENSES** - One of the applications that has been in production the longest and has been most commercially successful is the UV cured, scratch resistant hard coat on polycarbonate head
lamp lenses. This process was taken commercial first by the Japanese auto makers some eight years ago and is now wide spread in the US and is beginning to be utilized in Europe. The benefits of the UV cured hard coat were significant as compared to the thermally cured silicone hard coats. First, it created drastic reduction in process time. The original thermal cure process required heat annealing, primer coat, bake, cool down, top coat, bake, cool down. This complete process could take up to three and one half hours. The comparable UV curing process took only 6 to 8 minutes from start to finish. A drastic reduction in parts-in-process was achieved. It also allowed for a more responsive production environment by allowing much quicker part changes. The instantaneous cure allowed for a reduction in rejected/dirt contaminated parts as well as significant energy cost savings and floor space savings. Equally important was the ability to coat very complex shapes produced by the use of plastic head lamp lenses and aerodynamic body designs.

HEAD LAMP REFLECTOR HOUSING - The lens is not the only UV application on the head lamp assembly. In all five, UV applications are currently in production in the United States and Japan on head lamp assemblies. The next two applications are the base coat and top coat applied to the plastic reflector housing. The base coat is applied to the plastic reflector housing to provide the smoothest possible surface for a thin coat of vaporized aluminum to be deposited on the reflector in a vacuum chamber. This extremely smooth and uniform surface allows the vaporized aluminum to produce a mirror-like finish. After the base coat is applied, UV cured and the vaporized aluminum is deposited, a very soft surface exists susceptible to scratching and hazing. A protective UV cured clear top coat is then applied to preserve the mirror-like finish on the reflector housing. In the past, this process is done using high bake varnish coatings needing up to one and one half hours of baking to achieve cure. A three hour base coat/top coat process is achieved in seconds with the UV curable base coat/top coat. Again, parts in process, parts inventory, floor space and energy costs were all reduced with an even or slight increase in performance.

ASSEMBLY OF THE HEAD LAMP - The third process on a head lamp assembly to utilize UV curing is the assembly process. A UV curable adhesive is applied to the reflector in an adhesive channel, then the hard coated lens is placed in the channel for assembly. The polycarbonate lens and UV cured coating absorbs much of the short wave UV used in UV curing which provide excellent long term weatherability. So the chemistry formulator utilized a special fill, long wave length UV bulb from Fusion which the polycarbonate actually conducts efficiently directly down into the adhesive channel and cures in seconds. The thermal process takes as much as thirty minutes for a complete cure. As for the performance of the adhesive, no failure point was detectable because the plastic incurred a structural failure before the adhesive failed.

EXTERIOR PLASTIC TRIM - Plastic wheel covers are a high volume and high performance product for the automobile industry. The painted plastic wheel cover must have high impact retention and excellent abrasion resistance. Current coating technology utilized is a two component urethane base coat and clear coat. This system provides good long term weathering, impact retention and abrasion resistance. The draw backs are 30 minute bake time, costly raw materials and 4.8 to 5.2 VOC pounds/gal as applied. One alternative nearing commercialization is a water base color coat with a UV cured clear coat. This system allows for significantly reduced VOC content with excellent performance in weathering abrasion resistance and impact resistant. A zero VOC wheel cover decoration process is in the early stages of development. This consists of a color matched vinyl laminate applied in-mold to the wheel cover. The laminate is placed in the mold, the mold is closed and the plastic is injected. The end product out of the mold is a color matched wheel cover. To meet the abrasion resistance, staining resistance, and weathering requirements, a UV cured liquid clear coat or UV cured powder can be applied. The vinyl color laminate combined with the UV cured powder clear coat produce the lowest VOC and the highest performance product. All of the above technology can apply to other molded plastic auto trim such as mirror housings, grills and others.

INTERIOR VINYL - On the interior of the vehicle, water base UV clear coats are being applied to vinyl wrapped parts. The UV cured clear coat provides excellent mar resistance and chemical resistance at a very low gloss. This coating provides much higher performance than solvent base and water base thermally cured coatings and very low VOC content. Process time is also reduced. This product is currently being evaluated on pre-formed vinyl wrapped instrument panels and on vinyl sheets which are pre-coated and vacuum formed around a structural skeleton. The performance of the coating under 200 to 300 percent elongation is critical.
Some chemical suppliers are also evaluating UV cured pigmented coating for these same applications.

GASKETING - A recently commercialized UV automotive application is the use of a UV solid or foamed gasketing material. The material is applied by robot to create any shape gasket needed. The bead of gasket material is then irradiated and becomes a solid gasket held firmly in place through its natural adhesion to the substrate. A variety of cost savings are realized utilizing this process. No adhesive is required to bond a urethane foam gasket in place. It is no longer necessary to inventory a variety of shapes of gaskets. One manufacturing line can apply a gasket to many different sizes and shapes of parts. Even more impressive is the gasket's performance. In tests on an electrical connector harness between the engine compartment and the interior of the vehicle, a urethane foam gasket with RTV adhesive was utilized. After being assembled for three days the gasket was permanently compressed and provided no sealing properties for the electrical connector. In some cases, the RTV failed before assembly. The UV cured foam gasket was still firmly in place and fully resilient after 30 days of testing. Reduction in material cost and an increase in performance resulted. This process is commercial in Japan, Europe and the United States.

ELECTRONICS - UV curable materials for processing electronic circuit boards are readily available for a variety of processes. They can be used for potting, marking, masking and conformal coating. For potting and masking, the speed of the cure is very important. In many cases, with thermal or ambient cure testing of the part was not able to be done for hours or even days. If a problem arose in testing, the parts could have already been assembled into other components, packaged or even shipped out of the plant. With the heat sensitivity of most circuit boards thermal curing of potting, marking or conformal coating was very difficult and heat damage was common, while ambient cure added a significant amount of processing time. Many of the UV cured products employ a secondary cure mechanism such as moisture cure for the non-line-of-sight area that may need to be cured. Here again, processing time and performance were driving factors in the use of UV cured products in electronics.

AUTO GLASS - I have by no means touched on all the UV applications currently utilized by the automotive industry, but I will conclude with one final application. An application that has been commercial for many years is the process of applying a combination of carbon black ink and glass frit to the border of automotive glass. This combination of carbon black, glass frit and a UV curable resin is silk screened on to a flat piece of glass and immediately run through a UV oven. This keeps the ink from being smeared or contaminated. The glass is then fired in a sag mold to produce the proper shape of the glass. The high temperature of the sag mold also burns off the UV resin and melts the carbon black in glass frit onto the glass so the glass and silk screen become one. The UV process is time and space efficient.

CONCLUSION

The recent past has been full of hurdles for UV chemistry suppliers to overcome. Through diligent and creative work, many of these hurdles have been overcome. The UV chemistries of today are environmentally safe, as well as much safer for human contact. The chemistries are extremely process efficient and increases in the use of raw materials and more efficient manufacturing methods have made them cost competitive. So what are the barriers to wide spread implementation of UV processes in automotive or any other area of manufacturing? I believe it is only our imagination that is between us and our next UV application. Don't accept old ways of processing only because it is the way it has always been done. Push your chemistry and equipment suppliers to develop faster, better, less expensive methods of processing. Your pursuit of a faster, better, less costly process will naturally lead you to a UV process.
EFFECT OF UV PRE-IRRADIATION ON OPTICAL FIBER TO ENHANCE THE ADHESION WITH UV INK LAYER

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ABSTRACT

Enhancement of adhesion between the outer-primary coating of optical fiber and the UV ink was studied. The UV pre-irradiation of the cured coating and curing the coating under oxygen-rich atmosphere were found to be effective to obtain better adhesion properties. The mechanism of the enhancement was discussed in terms of cure degree of the coating determined by using ATR-ir method.

INTRODUCTION

As a rapid growth of optical fiber telecommunication networks, four- or eight-fiber count ribbon structure has been widely employed because of advantages in down-sizing the cable and mass splicing. In ribbon structure, ultra violet (UV) curable ribbon matrix material bundles four or eight optical fibers which are individually colored by UV curable ink for the purpose of identification. When a single fiber is spliced from the ribbon to make a connection, the ribbon matrix material must be removed off easily. The UV ink should have good adhesive property with the coated fiber as well as the better releasability with the matrix material. Poor adhesion of UV ink against the coated fiber may cause the delamination of the UV ink layer, and resulting from this, one can not identify each optical fiber.

Several approaches have been proposed for UV ink to achieve better performance in the adhesive property and the releasability between the fiber coating and the ribbon matrix material. In order to increase the releasability of ribbon matrix material with UV ink layer, many kinds of silicone release agents are added to UV inks or matrix materials. Certain release agents can give rather better releasability, however, addition of a considerable amount of release agents may decrease cure rate of the UV ink or the matrix materials, and in some cases may reduce storage stability of UV ink due to the incompatibility of the silicone release.
agents to the ink vehicle. In addition, the compatibility of the silicone release agents strongly depends on the components of UV inks or matrix materials, it is thus needed an entangled work to choose an appropriate combination of UV inks, silicone release agents and matrix materials. On the other hand, corona discharge, UV pre-irradiation of the surface of the coated fiber, or curing the fiber coatings under atmosphere containing certain amount of oxygen has been known to enhance the adhesion between UV ink and coated fiber surface because of the generation of active species, such as peroxy radicals on the surface of coated fibers.\(^{(1)}\) These methods to enhance the adhesion of the UV ink with the coatings are versatile because these will not depend on the kinds of coatings and UV inks.

This paper demonstrates the effect of UV pre-irradiation and curing under oxygen-containing atmosphere to enhance the adhesion with the coated fibers for obtaining the better break-out performance of the ribbon fibers.

**EXPERIMENTAL**

In order to simulate the adhesion property between UV ink layer and outer-primary coatings, we evaluated the adhesion strength by preparing the UV ink layer on the cured outer-primary coating film. As for the outer-primary coating and the UV ink, DeSolite R3104 manufactured by Japan Synthetic Rubber Co., Ltd. and Bestcure FI manufactured by T&K TOKA Co., Ltd. were used respectively. The outer-primary coating was drawn on a glass plate as a thickness of 200 µm and cured by using high-pressure mercury lamp with desired UV dose ranging from 20 mJ/cm\(^2\) to 1000 mJ/cm\(^2\). Oxygen content during curing was controlled at desired value between 0 % to 21 %. After conditioning the cured outer-primary coating film for 12 hours at 23 °C x 50 % RH, UV pre-irradiation was made by exposing the film to the UV lamp with a dose of 10 to 500 mJ/cm\(^2\). On the cured and/or the UV pre-irradiated outer-primary coating film, the UV ink was spin-coated as a thickness of 12 nm. Immediately after being coated the UV ink, the sample was exposed by the UV lamp with a dose of 10 mJ/cm\(^2\) to 300 mJ/cm\(^2\) under oxygen-free atmosphere.

The double layered specimen was cut into a strip in size of 1 cm x 10 cm. The adhesion strength between the UV ink layer and the outer-primary coating was evaluated by measuring the 90°-peel strength at a peeling rate of 50 mm/min. In case that the UV ink layer fractured before being peeled off, the peel strength was regarded as to be larger than 100 g/cm. In order to analyze change in the surface of the outer-primary coating before and after the UV pre-irradiation, infrared (ir) spectrum was measured by using the ATR method. For this analysis we employed model JASCO MFT-2000 which can focus an ir beam to 2 µm in diameter at the surface of coatings.

**RESULTS AND DISCUSSION**

Figure 1 shows UV dose dependence of the 90°-peel strength of the UV ink layer. The outer-primary coating was cured under oxygen-free atmosphere with the UV dose of 100 mJ/cm\(^2\). When the UV ink layer was cured at the dose above 300 mJ/cm\(^2\), the adhesion
between two layers was sufficient because the UV ink layer fractured when it was peeled. However, smaller UV dose is preferable for obtaining higher productivity of colored optical fiber. Thus the UV ink must show the sufficient adhesion even at the lower UV.

The effect of UV pre-irradiation was evaluated by using a specimen of which UV ink layer was cured at relatively lower UV dose, 10, 20, and 50 mJ/cm\(^2\) on the outer-primary coating which was cured at 100 mJ/cm\(^2\) and UV pre-irradiated with the dose ranging from 10 to 500 mJ/cm\(^2\). The results of 90°-peel strength are shown in Figure 2. Enhancement of the adhesion between the UV ink layer and the outer-primary coating is seen even in the case that the UV ink layer was cured at relatively lower UV dose, 10 mJ/cm\(^2\). The enhancement on the adhesion by the UV pre-irradiation appears above the UV dose larger than 100 mJ/cm\(^2\). These results were obtained on the specimen of which UV ink layer was coated and cured on the outer-primary coating immediately after UV pre-irradiation.

It was supposed that certain active species generated on the surface of outer-primary coating would be inactivated under ambient atmosphere with the passage of time. We thus examined the durability of the UV pre-irradiation. The outer-primary coating film which was UV pre-irradiated with 500 mJ/cm\(^2\) dose was kept at the 23 °C x 50 % RH for several days and then the UV ink was coated and cured at 50 mJ/cm\(^2\) dose. As shown in Figure 3, the adhesion strength drastically decreases within only three days. Thus, an in-line UV pre-irradiation is preferable for obtaining better adhesion performance.

On the other hand, it was known to enhance the adhesion that a substrate was cured under atmosphere containing certain amount of oxygen. In order to examine the effect of oxygen for the adhesion enhancement, UV ink was coated and cured at the UV dose of 10, 20, 50 mJ/cm\(^2\) on the outer-primary coating which was cured under atmosphere containing desired concentration of oxygen ranging from 0.2 % to 21 %. As shown in Figure 4, even at the lowest dose, 10 mJ/cm\(^2\) for curing UV ink, only 1.5 % of oxygen in the curing atmosphere is effective for curing the outer-primary coating to enhance the adhesion. We also examined the durability of oxygen effect for the enhancement of the adhesion properties of the outer-primary coating. Each outer-primary coating cured at UV dose of 100 mJ/cm\(^2\) under the atmosphere containing 1.0 % or 2.0 % of oxygen was kept at ambient atmosphere for several ten days and then the UV ink was coated and cured at 10 mJ/cm\(^2\). The results are shown in Figure 5. The adhesion strength was maintained at the highest level more than 30 days when
the outer-primary was cured at the oxygen content of 2.0 %. Even at the oxygen content of 1.0 %, relatively high adhesion strength was observed more than 30 days.

**Figure 2.** The effect of the UV pre-irradiation on the adhesion strength of the UV ink layer. The outer-primary coating is cured at 100 mJ/cm^2 of UV dose under oxygen-free atmosphere.

**Figure 3.** Durability of the effect of UV pre-irradiation. The outer-primary coating pre-irradiated with the UV dose of 500 mJ/cm^2. The UV ink was cured at the dose of 50 mJ/cm^2.

Each surface of the coating cured at 100 mJ/cm^2 of UV dose under the atmosphere containing 0 % or 21 % of oxygen was analyzed by using the ATR-ir method. Excepting absorbance at around 810 cm^-1 assigned to the out-of-plane vibration of the C-H bond in acrylic double bonds, no significant difference was seen between these two coatings. For the ATR-ir analysis, the penetration depth of ir beam is limited only a few micrometer, thus the information obtained by this method reflects only the surface of the coating. As shown in Figures 6(a) and 6(b), the absorbance at around 810 cm^-1 obtained from the coatings cured under oxygen-rich atmosphere (b) is larger than that cured under oxygen-free atmosphere (a). From the quantitative analysis of the absorbance change at 810 cm^-1, the content of the un-reacted acrylic double bonds was found to be only 8 % for the coating cured at oxygen-free atmosphere. In comparison, content of the un-reacted acrylic double bond of the outer-primary coating cured at oxygen-rich atmosphere was estimated to be 30 %. These suggest that polymerization or cross-linking reaction of acrylic double bonds is inhibited at the surface of the outer-primary coating cured under the oxygen-rich atmosphere, and resulting from this the cross-linking density of the surface is relatively lower than that cured under the oxygen-free atmosphere. The UV ink coated on the outer-primary coating of which cross-linking density is low can easily penetrate into the outer-primary coating and tends to give interpenetrating networks between the UV ink and the outer-primary coating. Consequently, the higher adhesion strength was achieved. The un-reacted acrylic double bonds at the surface of the outer-primary coating is stable, thus the oxygen effect for the enhancement of adhesion can last longer than 30 days.
Figure 4. Effect of oxygen in the curing atmosphere for enhancement of adhesion between the UV ink and the outer-primary coating. The UV ink was cured at the dose of 10 (●), 20 (△), or 50 mJ/cm² (○).

Figure 5. Durability of the effect of the oxygen in the curing atmosphere for the outer-primary coating. Closed and open circles represent the 1 % and 2 % of the oxygen content, respectively.

Figure 6. ATR-ir spectra of the outer-primary coatings cured at 100 mJ/cm² of UV dose; (a) under oxygen-free atmosphere, (b) under oxygen-rich atmosphere, and (c) under oxygen-free atmosphere followed by the UV pre-irradiation done by the UV dose of 100 mJ/cm².

The change in the surface of the coating before and after UV pre-irradiation was also analyzed by the ATR-ir. Figure 6(c) shows the ATR-ir spectrum of the coating cured at 100 mJ/cm² under oxygen-free atmosphere followed by the UV pre-irradiation done by the UV dose of 100 mJ/cm². Certain active species such as peroxy radicals were supposed to be generated on the surface of the coating, however no detectable change excepting the absorbance change in 810 cm⁻¹ was seen between Figures 6(a) and 6(c). The content of un-reacted acrylic double bounds decreased from 8 % to 4 % by the UV pre-irradiation. The
active species such as peroxy radicals generated on the surface can be easily quenched by atmospheric oxygen and/or radical scavengers in the coating, thus the effect of the enhancement of the adhesion lasts only one to three days. The UV pre-irradiation and curing under oxygen-rich atmosphere enhance the adhesion of the outer-primary coating to the UV ink, however the mechanism of the enhancement can be different from each other.

Considering an optical fiber manufacturing process, fiber runs through reels immediately after being cured. When the outer-primary coating is cured under oxygen-rich atmosphere, the coating tends to give tacky surface due to the lower reaction conversion of acrylic double bonds. This tacky surface is preferable for the purpose of enhancement of the adhesion. However, the tacky surface of the outer-primary coating may stick to the reel and resulting rough surface which leads the attenuation loss of the optical fibers. Thus the UV pre-irradiation is preferable to enhance the adhesion with the UV ink.

CONCLUSION

Enhancement of adhesion between the outer-primary coating and the UV ink was studied. The UV pre-irradiation of the cured outer-primary coating was found to be effective to enhance the adhesion even when the UV ink was cured at relatively lower dose, 10 mJ/cm². Curing the outer-primary coating under oxygen-rich atmosphere was also effective to obtain better adhesion properties and this effect lasted more than 30 days after curing. The ATR-ir analysis revealed that the considerable amount of un-reacted acrylic double bonds was found on the surface of the coating cured under oxygen-rich atmosphere and these remaining acrylic double bonds might play an important roll to enhance the adhesion. However, the coating containing un-reacted acrylic double bonds tends to give a tacky surface and resulting attenuation loss increase of the optical fiber. On the other hand, only a few percent of un-reacted acrylic double bonds was observed on the UV pre-irradiated coating. Thus the better surface of the coating will be obtained by the UV pre-treatment comparing to the curing under oxygen-rich atmosphere, and resulting from this, one can expect the better performance of the optical fibers. Since the effect of adhesion enhancement by the UV pre-irradiation disappears within a few days under ambient atmosphere, an in-line UV pre-irradiation is strongly recommended to obtain better adhesion performance between the outer-primary coating and the UV ink layer.

REFERENCES

A UV-CURING SYSTEM USED IN HOLOGRAM COPY

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ABSTRACT

Epoxy acrylate was synthesized by reacting epoxy resin with acrylic acid in the presence of quaternary ammonium salt. The effects of photoinitiators and crosslinking agents on the curing rate and polymer property have been studied. The UV-curing system which is available for use in the productive equipment has been selected.

INTRODUCTION

Since early in 1990s, the industrialization of holographic embossing technology has been developing rapidly in China. The laser holography industry is the best means of combining high technology with art. The mark of laser holography and the laser glass which is a kind of decorative material have entered into people's daily life. In accord with the case mentioned above, the material industry has been developed. Increasing attention has been paid towards the synthesis of epoxy acrylate as epoxy acrylate pre-polymer characterized by its higher viscosity, better softness, lower yellowing and better chemical corrosion resistance. In the recent twenty years epoxy acrylates which contain active polyfunctional groups and many initiators have been commercialized. The sculpture is characteristic of the hologram micro-structure. Based on the two reasons above, a new type of hologram copy technology—the UV-curing copy technology was developed.

EXPERIMENT

1. Chief Chemical Reagent

EP6101; acrylic acid; TMBAC(trimethyl benzyl ammonium chloride); hydroquinone; benzoin dimethyl ether; TMPTA(trimethylolpropane triacrylate); TEGDA(triethylene glycol diacrylate); DEGDA(diethylene glycol diacrylate); NPGDA(neopentylene glycol diacrylate); MOEA(methyloxymethane acrylate).

2. Synthesis of Epoxy Acrylate

UV-curing epoxy acrylate was synthesized by reacting epoxy resin with acrylic acid in the presence of quaternary ammonium salt. The reaction was performed in a 2000ml four-necked, round-bottomed flask fitted with a reflux condenser, a thermometer, a dropping funnel, a nitrogen gas inlet port and a turning. In the flask 966g of EP6101 were placed,
when the temperature rose to 80°c the stirrer was started, under N\textsubscript{2} to this a mixture involved 7.6g of TMBAC, 1.99g of hydroquinone and 308g of acrylic acid were dripped. Temperature automatically rose. Addition was finished within two hours. Reaction continued 5 hours at 90-110°c. When acid value decreased below 7, the boiling was stopped. The mixture was stirred continuously until the system was cold. Then, epoxy acrylate pre-polymer was obtained.

Synthetic reaction between epoxy resin and acrylic acid in the presence of TMBAC can be shown as the following:

\[
2 \text{CH}_2=\text{CHCOH} + \text{CH}_2=\text{CHCH}_2-\text{OR}-\text{O}-\text{CH}_2\text{CH}_2-\text{CH}_2
\]

\[
\left[\text{C_6H_5CH}_2\text{N}^+\text{(CH}_3)_2\right]Cl^- \rightarrow \text{CH}_2=\text{CHCH}_2\text{CH}_3\text{O}R\text{OCH}_2\text{CH}_2\text{OCCH}=\text{CH}_2
\]

Reaction endpoint was judged by the acid value of the system. Some of the reaction mixture were taken and dissolved in benzene. To it two drops of phenolphthalein indicator were added. The reaction mixture titrated with the alcoholic solution of potassium hydroxide.

The acid value was calculated by the volume of potassium hydroxide:

\[
\text{acid value} = \frac{\text{mole number of acid} \times \text{mole weight of potassium hydroxide} \times 1000}{\text{total weight of reaction mass}}.
\]

3. Infrared Spectrometry Analysis

Perkin-Elmer 783 Infrared spectrometer was used to study the structure of epoxy resin and epoxy acrylate.

4. Component of the UV-curing System

The component of the UV-curing system shown in table involves the different kinds and different amounts of photoinitiators and the raw materials. They were coated on the glass. After the hologram film had been covered on the coating it was put under UV light which power and exposure distance were 40W and 12cm. The photoinitiators were chosen by this means.

Gelation rate was measured by weight method. It was consistent with the conversion of the double bond and epoxy group that expressed curing degree by infrared spectrometry.

5. The Influence of Crosslinking Agent on Curing Hologram Film

TMPTA, TEGDA, DEGDA, NPGDA and MOEA were put separately as shown in Table 1. It was cured by UV light. The sequence of the diffractive efficiency about these crosslinking agents is shown as follows: NPGDA > DEGDA > TEGDA > TMPTA > MOEA

RESULTS AND DISCUSSION

1. Infrared Spectrometry of Epoxy Acrylate
Infrared spectrum of epoxy acrylate was given below:

![Infrared spectrum of epoxy resin and epoxy acrylate](image)

It can be seen from the spectrum that the peaks at 915 cm\(^{-1}\) and 866 cm\(^{-1}\) are assigned to epoxy bond. The peaks at 1040 cm\(^{-1}\), about 1720 cm\(^{-1}\) and 1640 cm\(^{-1}\) separately are assigned to ether bond, carbonyl of epoxy acrylate and non-saturation double bond of epoxy acrylate. Because of the addition reaction of acrylic acid and EP6101, the peaks of epoxy group at 915 cm\(^{-1}\) and 866 cm\(^{-1}\) disappeared. Absorption peak of hydroxy at about 3340 cm\(^{-1}\) is widened. Along with photoinitiative curing process of epoxy acrylate, absorption peak of non-saturation double bond gradually disappeared.

2. Component of the UV-curing System

The component of the UV-curing system is filled in table 1.

<table>
<thead>
<tr>
<th>raw material</th>
<th>grade</th>
<th>weight(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>acrylic acid epoxy acrylate</td>
<td>self-made</td>
<td>100</td>
</tr>
<tr>
<td>crosslinking agent</td>
<td>CP</td>
<td>15</td>
</tr>
<tr>
<td>di-n-butyl phthalate</td>
<td>CP</td>
<td>9.0</td>
</tr>
<tr>
<td>diluent 1</td>
<td>CP</td>
<td>9.0</td>
</tr>
<tr>
<td>diluent 2</td>
<td>CP</td>
<td>9.5</td>
</tr>
<tr>
<td>diphenylamine</td>
<td>CP</td>
<td>0.3</td>
</tr>
</tbody>
</table>

The crosslinking agents are vinylic compounds which involve polyfunctional groups and are the high boiling points compounds, it can make good use of UV-light quantum energy that is absorbed by photoinitiator, at the same time it improves velocity and depth of crosslinking. But the consumption of it should be suitable because too little of it can lengthen the time of curing, on the other hand too much of it not only makes the curing film become brittle but also increases the cost. So we generally control weight within 15~20.

3. Effect of Photoinitiators on Curing Rate
Effect of photoinitiators on curing rate is shown in Table 2.

Table 2. Effect of photoinitiators on curing rate

<table>
<thead>
<tr>
<th>Photoinitiator</th>
<th>Content (%)</th>
<th>Curing Rate (% min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bensoin dimethyl ether</td>
<td>0.8 1.0 1.2 1.5 3.0 3.5</td>
<td>66 68 50 35 27 20</td>
</tr>
<tr>
<td>Bensoin n-butyl ether</td>
<td>3.0 3.5 4.0</td>
<td>36 27 25</td>
</tr>
<tr>
<td>Benzophenone</td>
<td>3.5 4.0</td>
<td>40 37</td>
</tr>
</tbody>
</table>

According to Table 2, we know the different curing rates with different photoinitiators. The sequence is shown as follows: bensoin dimethyl ether > bensoin n-butyl ether > benzophenone. As the content of bensoin dimethyl ether is 2%, the curing rate is suitable for use in the productive equipment selected.

4. Polymerization Rate

Relationship of the gelatinization rate to the curing time is shown in Fig.2.

Fig. 2. Relationship of gelatinization rate to time
- System: component 1, contain 1.2% bensoin dimethyl ether
- UV light power: 40W
- Exposure distance: 12cm
- Immersed time: 10 days

The effect of the time on gelatinization rate is shown in Fig.2. The slope of curve is the curing rate. We may see that initial curing rate is faster than the later curing rate.

5. The kinetic of the Synthetic Reaction

The kinetic equation of the synthetic reaction is shown below:

\[ \text{epoxy group} + \text{quaternary ammonium salt} \rightarrow \text{oxygenium ion} \]

\[ t = t (a-x) \quad (b-x) \quad x \]
\[ K(x)/(a-x)(b-x) \]

\[ \text{oxygennium ion + acrylic acid—ester + quaternary ammonium salt} \]

\[ t = t \quad x = (c-x) \quad x \]

\[ -d(c-x)/dt = k\times(a-x)(b-x)(c-x) \]

\[ t = t, \text{ [quaternary ammonium salt] = b-x+x = b} \]

\[ -d(c-x)/dt = K'(a-x)(c-x) \]

\[ K' = k\times b, \text{ when } a = c, \quad -d(c-x)/dt = K'(c-x)^2, \]

\[ \text{it can be obtained by integration:} \]

\[ 1/(c-x)-1/a=K'\times t, \text{ then } 1/x = t \text{ is a straight line.} \]

In Fig.3. acid value—time is a straight line, so above kinetic equation is right.

![Fig.3. Dependence of the 1/(acid value) on time](image)

**Temp.110° c; Mole number of epoxy group is equal to mole number of acrylic acid; Content of TMBAC is 0.6 percent.**

**CONCLUSION**

The viscosity of UV-curing system is 1.8Pa-sec(25°c), transmittance is 95 percent, refractive index \( n = 1.54 \). Under UV light of power 40W, the content of benzen dimethyl ether is 2 percent, exposure distance is 12cm, this system cures about 50 min. Both diffractive efficiency and utilization time of hologram film are higher and more than other products.

**REFERENCES**

( omission )
Pressure sensitive adhesives (PSA's) have become a ubiquitous element in our society. Solvent-borne PSA formulations traditionally based upon modified rubber chemistry are now being challenged by low VOC, fast curing systems such as UV and EB cured PSA's. This paper describes both water-based and 100% solids UV curable PSA's and their properties. A new acrylate monomer, ethoxylated nonyl phenol acrylate, has great utility in the formulation of water-based PSA's.

UV PSA systems are formulated to contain three major components: tackifier resins for peel strength and tack, monomers for Tg modification and viscosity control, and oligomers for shear performance. Two minor components are additives such as antioxidants and photoinitiators.

PSA's described in this work have been evaluated by three test methods: rolling ball tack (RBT), 180 degree peel, and shear. Each of these test methods will be described in the results section. PSA's were prepared by a procedure developed in order to minimize premature polymerization.

While test methods described previously are sufficient for evaluating PSA performance, the formulator is well served to quantify adhesive properties during the conception and preparation of the particular adhesive. To this end, we have found the Fox equation to be useful where:

\[ \frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} + \frac{W_3}{T_{g3}} \ldots \]

and \( W_1 + W_2 + W_3 = 1 \) (W=weight fraction, T in degrees K)
The Tg of a multicomponent system can be determined via the Fox equation and subsequently related to adhesive performance (see Fig. 1). One can argue as to the accuracy of the Tg values derived via the Fox equation based upon empirically derived data, functionality of acrylate used, and the Tg of the non-reactive tackifying resin, nevertheless it was shown that the Tg is related to the performance of the adhesive formulation.

Figure 1
Adhesive Performance versus Tg

Peel Strength
as a Function of Tackifier and Tg

Table 1 describes the monomers evaluated and the compatibility of the monomer with the rest of the PSA formulation.
Table 1
Monomer Compatibility with PSA Formulation

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Description/Tg</th>
<th>Compatibility</th>
</tr>
</thead>
<tbody>
<tr>
<td>isodecyl acrylate</td>
<td>non-polar/-45</td>
<td>no</td>
</tr>
<tr>
<td>ethoxylated nonyl phenol acrylate</td>
<td>polar/non-polar/15</td>
<td>yes</td>
</tr>
<tr>
<td>tridecyl acrylate</td>
<td>non-polar/-75</td>
<td>no</td>
</tr>
<tr>
<td>isoocytyl acrylate</td>
<td>non-polar/-100</td>
<td>no</td>
</tr>
<tr>
<td>2 (2-ethoxyethoxy) ethyl acrylate</td>
<td>polar/-50</td>
<td>yes</td>
</tr>
<tr>
<td>aromatic epoxy acrylate</td>
<td>non-polar/?</td>
<td>no</td>
</tr>
<tr>
<td>aliphatic epoxy acrylate</td>
<td>polar/?</td>
<td>no</td>
</tr>
</tbody>
</table>

The polarity of the monomer played a large role in the relative compatibility within the PSA formulation, though it was surprising that the aromatic epoxy acrylate was not compatible.

PSA formulation 6 (see appendix i) was developed using 2 (2-ethoxyethoxy) ethyl acrylate and ethoxylated nonyl phenol acrylate as the monomer components.

**SAMPLE PREPARATION AND TEST METHODS**

**100% Solids UV PSA’s**

Adhesive films were drawn down on 1 mil Mylar at a nominal thickness of 2 mils. The films were then cured at 7.6 mpm while being exposed to a single 300 W/inch Hg-arc medium pressure "D" type lamp. After curing, the films were allowed to equilibrate 24 hours in a 75 F, 50% R.H. atmosphere before testing.

**Water-based UV PSA’s**

Adhesive films were drawn down on 1 mil Mylar at a nominal thickness of 2 mils. The films were then dried at 90 C for 5 minutes before UV curing. The films were UV cured by exposure to a single 300 W/in Hg-arc lamp on a conveyor running at 7.6 mpm. After curing, the films were allowed to equilibrate 24 hours in a 75 F, 50% R.H. atmosphere before testing.

Rolling ball tack testing was done using a stainless steel ball rolled down an inclined plane and onto the surface of the adhesive film. Test procedures were as per PSTC specifications.
The distance the ball travelled was recorded and compared to other readings. The test was carried out in triplicate and the average value reported.

Peel testing (180 degree) was performed using a peel/slip tester which was used to pull a 2.54 cm wide strip of adhesive coated Mylar from a stainless steel panel. The force in Newtons was recorded for triplicate runs and the average value in Newtons/100 mm was reported. All test procedures were carried out according to PSTC specifications.

Shear testing was performed by placing a one square inch section of a 7.5 cm long adhesive strip onto a stainless steel plate and suspending a 1 kilogram weight form the opposite end. The time required for the weight to be pulled away from the plate was recorded. Test procedures were as per PSTC specifications. Cheminstruments equipment was used for all testing.

Values for rolling ball tack are listed in centimeters. Values for peel strength are listed in Newtons/100mm. Shear values are listed as time to failure.

RESULTS

Several new UV PSA formulations were prepared based upon conclusions drawn from work presented at Radtech '94. Specifically, studies were done to assess the relative performance of photoinitiator systems, to assess the influence of monomer ratios, and to assess the performance of water-based UV PSA’s. All UV PSA formulations are listed in Appendix i.

100% Solids UV PSA Formulations

Table 2 lists UV PSA formulations having varying ratios of 2 (2-ethoxyethoxy) ethyl acrylate to ethoxylated nonyl phenol acrylate. All other components and total monomer concentration were as reported for Formulation 6 in appendix i. The results reported are for 50 micron samples cured at 7.6 mpm using one 300 W/in Hg-arc lamp.
Table 2

UV PSA’s with Varying Monomer Ratios

<table>
<thead>
<tr>
<th>Formulation</th>
<th>ethoxylated nonyl phenol acrylate: 2 (2-ethoxyethoxy) ethyl acrylate</th>
<th>Rolling Ball Tack (cm)</th>
<th>Peel (N/100 mm)</th>
<th>Appearance after cure</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>1:1</td>
<td>30.5</td>
<td>96</td>
<td>clear</td>
</tr>
<tr>
<td>6-A</td>
<td>0.77:1</td>
<td>19.1</td>
<td>97</td>
<td>clear</td>
</tr>
<tr>
<td>6-B</td>
<td>0.35:1</td>
<td>3.2</td>
<td>75</td>
<td>cloudy</td>
</tr>
<tr>
<td>6-C</td>
<td>100% 2 (2-ethoxyethoxy) ethyl acrylate</td>
<td>10.16</td>
<td>85</td>
<td>sl. cloudy</td>
</tr>
</tbody>
</table>

Small changes in monomer ratio had little effect on peel strength but showed decreasing RBT values with decreasing concentration of ethoxylated nonyl phenol acrylate. Peel strength had a minimum value in formulation 6-B but recovered to near control values in formulation 6-C. A reduction in clarity was observed with decreasing content of ethoxylated nonyl phenol acrylate.

Table 3 lists adhesive properties for formulations having various photoinitiators. Commercial names for photoinitiators are listed in the interest of brevity. Photoinitiator concentrations were held constant as in Formulation 6. All samples were cured at 7.6 mpm using one pass under a single 300 W/in Hg-arc lamp.

Table 3

Effect of Photoinitiator on Adhesive Properties

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Photoinitiator</th>
<th>Rolling Ball Tack (cm)</th>
<th>Peel Strength (N/100 mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>Esacure KIP100F</td>
<td>30.5</td>
<td>96</td>
</tr>
<tr>
<td>6-D</td>
<td>Esacure KB1/Irgacure 651</td>
<td>14.6</td>
<td>79</td>
</tr>
<tr>
<td>6-E</td>
<td>Darocur 1173</td>
<td>11.4</td>
<td>93</td>
</tr>
<tr>
<td>6-F</td>
<td>Benzophenone/methyl diethanolamine</td>
<td>Did not cure properly</td>
<td></td>
</tr>
</tbody>
</table>

329
Water-based UV PSA Formulations

New monomers such as ethoxylated nonyl phenol acrylate which are self-emulsifying have been integral in the development of water based UV PSA’s. Table 4 lists the properties for water based UV PSA’s that have been tested.

Table 4
Water-Based UV PSA Properties

<table>
<thead>
<tr>
<th>Formulation</th>
<th>% Trifunctional</th>
<th>Rolling Ball Tack (cm)</th>
<th>Peel (N/100 mm)</th>
<th>Shear</th>
</tr>
</thead>
<tbody>
<tr>
<td>W-3</td>
<td>5.0</td>
<td>30.5</td>
<td>27</td>
<td>1 hour</td>
</tr>
<tr>
<td>W-1</td>
<td>5.8</td>
<td>27.2</td>
<td>14</td>
<td>&gt;550 hrs.</td>
</tr>
<tr>
<td>W-6</td>
<td>9.5</td>
<td>30.5</td>
<td>18</td>
<td>&gt;550 hrs.</td>
</tr>
</tbody>
</table>

Overall performance of the water-based UV PSA’s was not as good as the 100% solids formulations. However, there are factors such as other tackifiers and water dispersible oligomers yet to be evaluated. There is, as expected, a clear correlation between the amount of crosslinker, i.e. ethoxylated TMPTA, and the shear strength with shear strength increasing with increasing crosslinker. Generally speaking the relative proportions of the oligomer (crosslinker), monomers, and tackifier resin in the 100% solids UV PSA does not translate to the water-based UV PSA’s.

EXPERIMENTAL

100% Solids PSA Preparation

To an appropriate sized resin kettle equipped with thermometer, condenser, air sparge, and mechanical stirrer were added the oligomer, monomer, inhibitor, and antioxidant. The mixture was heated with stirring and air flow to about 60 C after which the tackifier resin was added over a period of about 15 minutes. The tackifier was added in this manner to prevent clumping. The speed of stirring was increased as the tackifier was added. After the tackifier resin was added, the temperature was raised to about 80 C and maintained there until the tackifier resin was completely dissolved. Formulations containing higher amounts of tackifier resin may take up to 3 hours at 80 C to ensure solution of the tackifier resin. It is not recommended to raise the temperature of the PSA formulation over 80 C or to maintain the temperature at 80 C for longer than 4 hours. After the tackifier resin is dissolved, the temperature was lowered to 40 C and the photoinitiator was added. The PSA formulation was
mixed 15 minutes after the addition of photoinitiator, then bottled, making certain to leave a headspace equivalent to 1/4 the volume of the container.

**Water-Based PSA Preparation**

To an appropriate sized Erlenmeyer flask were added the ethoxylated nonyl phenol acrylate, aqueous tackifier, ethoxylated TMPTA and photoinitiator. The Erlenmeyer was stoppered and the contents were shaken vigorously for two minutes. The water was added and the contents were shaken vigorously for an additional two minutes. The resulting creamy emulsion was stable and able to be coated onto substrates.

**CONCLUSIONS**

1. Changing monomer ratios in 100% solids UV PSA’s affects RBT values and coating clarity.

2. Peel strengths increase with tackifier content so long as Tg’s are adjusted with monomers.

3. Shear durations increase with increasing cure and crosslinking and decrease with tackifier content in 100% solids PSA’s. Shear values increase with ethoxylated TMPTA content in water-based UV PSA’s.

4. Water-based UV PSA’s generally do not perform as well as 100% solids formulations, but are continuously developing.

**BIBLIOGRAPHY AND REFERENCES**


2. Cheminstruments, 510 Commercial Drive, Fairfield, OH, 45014, Tel. 513-860-1597

**ACKNOWLEDGEMENTS**

My utmost appreciation is extended to the entire Sartomer technical staff without whom this work would have been far the poorer.
## APPENDIX 1

### 100% Solids UV PSA Formulations

<table>
<thead>
<tr>
<th>Component</th>
<th>6</th>
<th>6-A</th>
<th>6-B</th>
<th>6-C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urethane Oligomer</td>
<td>15.8</td>
<td>19</td>
<td>15.8</td>
<td>15.8</td>
</tr>
<tr>
<td>Tackifier resin</td>
<td>31.6</td>
<td>31.6</td>
<td>31.6</td>
<td>31.6</td>
</tr>
<tr>
<td>2 (2-ethoxyethoxy) ethyl acrylate</td>
<td>21.0</td>
<td>21.0</td>
<td>32.4</td>
<td>43.9</td>
</tr>
<tr>
<td>Ethoxylated nonyl phenol acrylate</td>
<td>22.9</td>
<td>19.7</td>
<td>11.5</td>
<td>-</td>
</tr>
<tr>
<td>MEHQ</td>
<td>0.08</td>
<td>0.08</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>Antioxidant</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Photoinitiator</td>
<td>7.82</td>
<td>7.82</td>
<td>7.82</td>
<td>7.82</td>
</tr>
<tr>
<td>Peel Strength, lbs/in</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Appearance, postcure</td>
<td>clear</td>
<td>clear</td>
<td>cloudy</td>
<td>sl. cloudy</td>
</tr>
</tbody>
</table>

### Water-based UV PSA's

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>W-1</th>
<th>W-3</th>
<th>W-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethoxylated nonyl phenol acrylate</td>
<td>55/63.7%</td>
<td>55/55%</td>
<td>55/52%</td>
</tr>
<tr>
<td>Aqueous Tackifier (57% solids)</td>
<td>32/21.2%</td>
<td>56/32%</td>
<td>56/30.5%</td>
</tr>
<tr>
<td>Ethoxylated trimethylolpropane triacrylate</td>
<td>5/5.8%</td>
<td>5/5%</td>
<td>10/9.5%</td>
</tr>
<tr>
<td>Photoinitiator</td>
<td>8/9.3%</td>
<td>8/8%</td>
<td>8/7.5%</td>
</tr>
<tr>
<td>Water</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
</tbody>
</table>
STUDY ON HIGH SENSITIVITY DIAZOTYPE MATERIAL

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ABSTRACT

The present paper reports a new class of superfast diazonium salt—pyrrolidinyl benzene diazonium salt. The method of synthesizing these compounds has been described. Their behaviors have been measured such as UV—Vis spectra, the rate of photodecomposition and the temperature of thermal decomposition. The diazonium salts are applied in a blue line diazotype paper. The results show that they have good photosensitivity and thermal stability. When comparing the photochemical decomposition of diazo compound in photosensitive paper, the photosensitivity of the diazonium salt paper is higher than that of conventional diazotyper paper.

INTRODUCTION

Diazo systems are one of the oldest photochemical non—silver process and are still widely used. The success of the diazotype process is due to its simplicity economy and high resolution.

Basically, diazotype processes rely upon the light—sensitivity of diazo salts and the fact that such salts undergo two different types of reactions.

one is that diazo compound is decomposed by radiation between 300 to 450 nanometers. During decomposition, the nitrogen is lost as nitrogen gas

\[ \text{ArN}_2\text{Cl}^- \xrightarrow{\text{hv}} \text{ArOH} + \text{N}_2 + \text{HCl} \]

The second is that diazo compound reacts with certain coupling component to form azo dye

\[ \text{ArN}_2\text{Cl}^- + \text{Ar'OH} \xrightarrow{\text{NH}_3 \text{ or alkali}} \text{Ar} - \text{N} = \text{N} - \text{Ar'OH} \]

The basic component of the diazotype process is a diazonium salt. This compound has two fundamental properties essential for photoimaging—the photosensitivity and the thermal stability.

In order to increase the speed of the diazo process, we investigated a new class of superfast diazonium salt—pyrrolidinyl benzene diazonium salt.
In this paper some pyrrolidinyl benzene diazonium salts were synthesized and the influence of substituents on the visible spectra, rate of photodecomposition as well as on the thermal stabilities were studied. The diazonium salts were applied in a blue diazotype paper to obtain good results.

EXPERIMENTAL

1. Syntheses of pyrrolidinyl benzene diazonium salts.

The pyrrolidinyl benzene diazonium salts can be synthesized according to the following reactions:

1) Cycloalkylation of aromatic amine

\[
\text{NH}_2 + \text{BrC}_6\text{H}_5\text{Br} \rightarrow \text{N} \text{C}_6\text{H}_5 \rightarrow 2\text{HBr}
\]

Aromatic amine was heated under reflux with dibromo butane

2) Diazotization of p- amino benzene sulfonic acid

\[
\text{SO}_3\text{H} \cdot \text{NH}_2 \cdot \text{H}_2\text{SO}_4 + \text{HNO}_2 \rightarrow \text{SO}_3\text{H} \cdot \text{N}_2\text{HSO}_4 + 2\text{H}_2\text{O}
\]

p-aminobenzene sulfonic acid was diazotized by nitrous acid.

3) Coupling reaction

\[
\text{N} \text{N} + \text{SO}_3\text{H} \cdot \text{NH}_2 \rightarrow \text{N}_2\text{HSO}_4 + \text{H}_2\text{SO}_4
\]

Diazonium salt was coupled with amine to form azodye.

4) Reducing reaction

\[
\text{N} \text{N} \text{NH}_2 + \text{NH}_2 \rightarrow \text{SO}_3\text{H} + \text{Na}_2\text{S}_2\text{O}_4 \rightarrow 3\text{H}_2\text{O}
\]

Azo dye was reduced by sodium dithionite to form pyrrolidinyl benzene amine.

5) Diazotization of pyrrolidinyl benzene amine

\[
\text{NH}_2 \cdot \text{HCl} + \text{HNO}_2 \rightarrow \text{N}_2\text{Cl} \rightarrow 2\text{H}_2\text{O}
\]

Pyrrolidinyl benzene amine was diazotized by nitrous acid.

2. Performance measurement

1) Absorption spectra
Pyrrolidinyl benzene diazonium salts studied were dissolved in water, and their ultraviolet and visible spectra were measured with UV—260 UV—visible recording spectro photometer.

(2) The rate of photodecomposition
Pyrrolidinyl benzene diazonium salts studied were dissolved in mixed solvent and coated on polyester base to form diazo film and the rate of photodecomposition was measured

(3) The temperature of thermal decomposition.
The temperature of thermal decomposition of pyrrolidinyl benzene diazonium salts were measured by DSC method.

RESULTS AND DISCUSSION

The absorption spectrum ($\lambda_{max}$), rate of photodecomposition and the temperature of thermal decomposition are reported in Table 1.

Table 1. Some Characteristics of Diazonium Salts

<table>
<thead>
<tr>
<th>No.</th>
<th>Diazonium salt</th>
<th>absorption spectrum ($\lambda_{max}$ nm)</th>
<th>rate of photodecomposition ($k$.sec$^{-1}$)</th>
<th>temperature of thermal decomposition (T.°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\text{N}^+\text{PF}_6^-\text{N}^+\text{PF}_6$</td>
<td>380</td>
<td>$1.8 \times 10^{-2}$</td>
<td>153.64</td>
</tr>
<tr>
<td>2</td>
<td>$\text{CH}_3\text{N}^+\text{PF}_6^-\text{N}^+\text{PF}_6$</td>
<td>393</td>
<td>$2.43 \times 10^{-2}$</td>
<td>139.78</td>
</tr>
<tr>
<td>3</td>
<td>$\text{OCH}_3\text{N}^+\text{PF}_6^-\text{N}^+\text{PF}_6$</td>
<td>408</td>
<td>$4.94 \times 10^{-2}$</td>
<td>116.78</td>
</tr>
<tr>
<td>4</td>
<td>$\text{CH}_3\text{N}^+\text{PF}_6^-\text{N}^+\text{PF}_6$</td>
<td>379</td>
<td>$1.29 \times 10^{-2}$</td>
<td>159.74</td>
</tr>
<tr>
<td>5</td>
<td>$\text{OCH}_3\text{N}^+\text{PF}_6^-\text{N}^+\text{PF}_6$</td>
<td>387</td>
<td>$2.65 \times 10^{-2}$</td>
<td>133.47</td>
</tr>
</tbody>
</table>

The results in table 1 showed:
1) Substitution of these diazonium salts by electron donating groups $\text{CH}_3, \text{OCH}_3$, meta to the diazo group results in a bathochromic shift of $13-28$nm. 3–methoxy 4–pyrro-
Iidino benzene diazonium salt has an absorption peak at 408nm and the rate of photodecomposition increases. This compound is one of the superfast photosensitive diazonium salt.

(2) Substitution of this diazonium salt by an electro donating group CH₃ ortho to the diazo group results in a hypsochromic shift. 2- methyl 4-pyrrolidino benzene diazonium salt has an absorption peak at 379nm and the rate of photodecomposition decreases. However the temperature of thermal decomposition increases and this diazonium salt has good thermal stability.

(3) When there is di-substitution of electron donating groups ortho and meta to the diazo group, the overall shift of absorption peak is toward longer wavelength. 2,5-dimethoxy 4-pyrrolidino benzene diazonium salt has an absorption peak at 387nm. This diazonium salt has good photosensitivity and thermal stability.

The application of two pyrrolidinyl benzene diazonium salts to diazotype paper achieves good results. Other conditions being equal, the density of the image obtained and the fog of the background upon exposure of four diazotype papers depend to a considerable extent on the photosensitivity of four diazonium salts. The higher the sensitivity of diazotype paper becomes, the shorter the exposure do. The duration of exposure is listed in Table 2.

<table>
<thead>
<tr>
<th>Diazotype paper No.</th>
<th>Diazonium salt</th>
<th>Exposure (sec)</th>
<th>Diazotype paper No.</th>
<th>Diazonium salt</th>
<th>Exposure (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>OCH₃</td>
<td>10</td>
<td>3</td>
<td>OCH₃</td>
<td>45</td>
</tr>
<tr>
<td>2</td>
<td>OCH₃</td>
<td>15-20</td>
<td>4</td>
<td>OCH₃</td>
<td>20-25</td>
</tr>
</tbody>
</table>

The results in Table 2 showed:

(1) Most significant in these data are the markedly superior photosensitivity of the pyrrolidinyl benzene diazotype papers over the conventional one.

(2) Compared with conventional diazotype paper, the photosensitivity of 2,5-dimethoxy 4-pyrrolidino benzene diazonium salts paper is roughly 1.3 times greater than that of 2,5-dimethoxy 4-diazo-N-phenyl morpholine paper and is 3 times higher than that of BG salt paper.

(3) 3-methoxy-4-pyrrolidino benzene diazonium salt paper has the highest photosensitivity.
CONCLUSION

2.5-dimthoxy-4-pyrrolidino benzene diazonium salt has higher photosensitivity and good thermal stability. Thus the diazo salt can be used in superfast diazotype paper.

REFERENCES

Investigation on Modification of Printing Material by Means of Plasma

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Abstract
Some investigated results on surface modification of printing materials in plasma were reported. The results showed that under plasma condition the physical and chemical construction, and the corresponding behaviors of surface were changed.

1. Introduction
The surface characteristics of printing materials were very important for printing quality. However, some original printing materials such as paper, plastic, printing plate, ink etc were lack of necessary related behaviors. This is a key problem to obtain high printing quality. However this problem has not solved yet up to now.

On the other hand, plasma is a special medium consisted of free elections, ions, atoms and photons. Therefore it is a source of ion, electron and photons. Under the irradiation of them the plasma-physical and plasma- chemical reactions will happen on the interface of plasma and material.

In order to look for a new way to improve the printability of printing materials, base on the understanding of plasma, an investigation on modification of printing materials in plasma had been done in our laboratory in recent years. In this paper some experimental results will be reported.

2. Experimental results
1> Surface modification of paper.
During recent years advanced devices were equipped in many printing houses of our country. However, these devices have not yet approached their potential in printing and it was difficult to obtain high printing quality. One of the major reasons is that paper quality can not meet the requirement of advanced printing machines. As mention above, this problem had been a project studied by several institutions during the past decade. But the results were not satisfactory. According to this situation the research on plasma modification of paper has been done in our laboratory. The main results include:

(a) Under plasma condition the physical and chemical construction of paper surface were changed. This conclusion was obtained from SEM photo and IR tested results. They were shown in Fig.1 and Fig.2 respectively.

From Fig.1 we can see that many fine capillaries produced on the treated surface. These capillaries would promote the absorption of printing ink and speed up ink drying on paper surface.

Fig.2 show the variation of chemical construction of paper surface. It was found that many small peaks appeared on the infrared absorption spectrum for treated sample at wave-number of 1200cm⁻¹ - 1800cm⁻¹ as compared with untreated sample. This corresponded to the presence of carboxyl group(-OH).

There was also a marked peak appeared at 441cm⁻¹ for treated sample.
maybe due to the presence of carboxide groups[1].

![SEM photo of treated (left) and untreated (right) samples](image)

Fig.1 SEM photo of treated (left) and untreated (right) samples

All of SEM photos and IR spectrum indicated that after irradiation of plasma both of physical and chemical construction of paper surface varied.

(b) The variation of surface behaviors of treated paper:

A way to represent the variation of surface characteristics was to measure the contact-angle of water with paper. The measured results were shown in fig.3

![Infrared absorption spectrum of paper](image)

Fig.2 Infrared absorption spectrum of paper.

![Contact-angle varies with treating power](image)

Fig.3 Contact-angle varies with treating power.

The variation of surface free energy before and after treatment were given in table 1.

Table 1. Surface free energy of treated and untreated paper.

<table>
<thead>
<tr>
<th></th>
<th>$r_d$</th>
<th>$r_p$</th>
<th>$r_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>untreated</td>
<td>685.9</td>
<td>74.6</td>
<td>760.5</td>
</tr>
<tr>
<td>treated</td>
<td>852.0</td>
<td>93.2</td>
<td>945.3</td>
</tr>
</tbody>
</table>

Here $r_d$, $r_p$, and $r_s$ were polar and dispersion components of surface energy respectively. $r'_s$ was
surface free energy of paper. It is clear that after treated in plasma the surface polar energy increased obviously, and therefore the free energy increased too.

(c) Improvement of printability
For a treated paper the printability improved obviously. The main results were given in table 2 and table 3.

Table 2. Surface absorbance results

<table>
<thead>
<tr>
<th>paper grade</th>
<th>untreated (sec.)</th>
<th>treated (sec.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>285.0</td>
<td>72.0</td>
</tr>
<tr>
<td>2</td>
<td>375.0</td>
<td>66.0</td>
</tr>
</tbody>
</table>

Table 3. Print density of treated and untreated paper

<table>
<thead>
<tr>
<th>color grade</th>
<th>untreated</th>
<th>treated</th>
<th>increment (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.029</td>
<td>1.037</td>
<td>0.8</td>
</tr>
<tr>
<td>B</td>
<td>0.600</td>
<td>0.650</td>
<td>7.4</td>
</tr>
<tr>
<td>C</td>
<td>0.289</td>
<td>0.339</td>
<td>17.3</td>
</tr>
<tr>
<td>D</td>
<td>0.060</td>
<td>0.097</td>
<td>61.6</td>
</tr>
</tbody>
</table>

From table 2 and table 3 we can see that after irradiation the absorbability of paper increased and printing density increased obviously.

(d) The increment of surface energy and wettability of paper was very useful in paper making industry. Treating the original paper before pasting the surface strength of finished paper will increased obviously. The experiment results were given in Fig.4(a) and Fig.4(b).

Fig.4(a) Relation of surface strength of paper with treating time.

Fig.4(b) Relation of surface strength of paper with treating power.
It is clear that when the technique of plasma modification was used in processing of making paper, the surface strength will increased obviously.

2> Plastic surface modification

Plastic is one of main printing materials. But the surface of original plastic such as PP and PET products were often difficult to wet and bond by ink when they were printed. Because of low surface energy, chemical inertness or the presence of contaminants and weak boundary layers.

It was similar to the results of paper modification. Under plasma condition the PP and PET surface can be modified. A lot of active groups appeared on the modified surface[2]. The wettability and printability improved obviously. These results were given in Fig.5 and table 4

![Fig.5 The relation between treated power and contact-angle of PET(a) and PP(b) with water.](image)

![Table 4](image)

<table>
<thead>
<tr>
<th>No.</th>
<th>Material</th>
<th>Treatment parameter</th>
<th>Average density</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PET</td>
<td>untreated</td>
<td>1.163</td>
</tr>
<tr>
<td>2</td>
<td>PET</td>
<td>8kv, 9A</td>
<td>1.204</td>
</tr>
<tr>
<td>3</td>
<td>PET</td>
<td>10kv, 11.5A</td>
<td>1.183</td>
</tr>
<tr>
<td>4</td>
<td>PET</td>
<td>11kv, 15.5A</td>
<td>1.175</td>
</tr>
<tr>
<td>5</td>
<td>PP</td>
<td>untreated</td>
<td>1.157</td>
</tr>
<tr>
<td>6</td>
<td>PP</td>
<td>6kv, 7A</td>
<td>1.166</td>
</tr>
<tr>
<td>7</td>
<td>PP</td>
<td>8kv, 9A</td>
<td>1.170</td>
</tr>
<tr>
<td>8</td>
<td>PP</td>
<td>10kv, 15A</td>
<td>1.135</td>
</tr>
</tbody>
</table>

From fig.5 and table 4 we can find that there was an agreement between contact-angle and
increment of printing density, and there was a best treatment dose under which the contact angle was smaller and the printing density was higher.

3> Modification of carbon powder

Carbon powder with diameter of several microns is a special material with fine size, deep black color and conductivity. It was an important row material for making ink and rubber. In order to get product with higher quality, the carbon powder must be adhesive with binder and could be easily dispersed in binder. However, the raw carbon black was lack of these behaviors. It must be treated before used in processing in ink. The traditional ways to treated them were some chemical methods, but the results were not satisfied. In order to look for a better way to modify the carbon powder an investigation on carbon black in plasma has been done in our lab. The results were as showing as following.

a) The ability to adsorb water increased. The tested equipment was designed as shown in Fig.6. The tested results were shown in Fig.7.

![Fig.6 Tested system of wettability. 1.testing tube, 2.carbon powder 3.web, 4.water.](image)

![Fig.7 The h²-t pattern under different plasma 1.DBD plasma in O₂, 2.DBD plasma in air, 3.glow plasma in air, 4.untreated.](image)

Here t and h were rising time and rising higher. From fig.7 we can see that after treated in plasma the wet part of carbon column increased, and the longer treating time the higher height. Oxygen played an important role in plasma modification.

b) After treatment in plasma the PH value of carbon changed. The results were given in tables 5 and 6.

Table 5. The variation of PH value of different sort carbon powder

<table>
<thead>
<tr>
<th></th>
<th>sample 1</th>
<th>sample 2</th>
<th>sample 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>untreated</td>
<td>5.67</td>
<td>8.43</td>
<td>6.0</td>
</tr>
<tr>
<td>treated</td>
<td>3.22</td>
<td>4.44</td>
<td>2.51</td>
</tr>
</tbody>
</table>

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Table 6. The variation of PH value of same sample with different power

<table>
<thead>
<tr>
<th>treating power</th>
<th>0</th>
<th>lower</th>
<th>middle</th>
<th>high</th>
</tr>
</thead>
<tbody>
<tr>
<td>PH value</td>
<td>6.03</td>
<td>5.35</td>
<td>4.61</td>
<td>2.51</td>
</tr>
</tbody>
</table>

It was clear that after treated in plasma the PH value decreased and the higher treating power the larger decrement.

c) The chemical construction of carbon powder changed under plasma condition. This conclusion was obtained from XPS measurement results. The XPS patterns were shown in Fig.8.

From fig.8 we can see that the strength of XPS signals on energy range of 535.5 - 537.0 ev increased after treated in plasma. As we know this range of energy on XPS pattern corresponded to the groups of hydroxyl, carbonyl and carboxyl. It means that after treatment in plasma the content of active groups containing oxygen increased in the surface of powder. This conclusion was agreeable to the testing results about PH value.

3. Conclusion

From the experimental results mentioned above we can get a conclusion as following:

(1) Under plasma condition the physical and chemical construction of surface can be changed. A lot of small holes and active groups appeared on the treated surface.

(2) The wettability, printability and surface free energy, in special polar energy increased obviously. All of these were very useful for improvement of printing quality.

(3) As a new method to improve the surface of material, plasma technique will have a wide use in printing, ink making and paper making industry.

Conference


PREPARATION OF SUPER ABSORBENT BY IRRADIATION POLYMERIZATION

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Hua-Kai Science and Trade Company, Shanghai, 200237

ABSTRACT

A kind of absorbent is prepared by gamma-rays irradiated by reversed-phase suspension polymerization. Drying particals have 1400 (g/g) absorbency in deionic water.

Effects of reactive conditions, e.g.: dose-rate, dose, monomer concentration, degree of monomer neutralization and crosslinking agents on absorbency in deionic water are discussed. The cause of absorbing deionic water by polymer is related to its network structure and ionic equilibrium in partical. Accordingly, a suit reactive condition is chosen for preparation of hydro gel spheres.

INTRODUCTION

The polyacrylate has been used as super absorbent in the napkin paper and paper diaper widely. We have reported its preparation method initiated by heating. The polymerization reaction may be carried out at room temperature by irradiation initiation, and this method has been used to prepare the super absorbent in many reports. In this paper, the hydro gel microsphere is prepared by gamma rays irradiation using reversed-phase suspension way. Drying particals have 1400 (g/g) absorbency in deionic water.

EXPERIMENTS

1. Reagents
   Acrylic acid (Industrial grade); Tween 20 (C.P); N,N-Methylene bisacrylamide (C.P); Span 60 (C.P); Sodium dodecyl sulfate (C.P); 732# Resin (Industrial grade); Triethylene glycol diacrylate (C.P).

2. Experiment Process
   The Acrylic acid is added into the solution of sodium of hydroxide slowly, then the solution is put into a flask containing crosslinking agent, surface active agent and organic solvent. The reaction system is protected by Nitrogen and irradiated by Cobalt-60 gamma rays at room temperature. The hydro gel microsphere is obtained by filter.
3. Analysis Methods

3.1 Determining of the Absorbency

The ability of absorbency ($Q$) can be calculated by formula (1):

$$Q = \frac{(W_t - W_o)}{W_o}$$  \hspace{1cm} (1)

$W_o$ is the weight of the dry absorbent; $W_t$ is the weight of absorbent absorbed solution (such as deionic water, 0.1 mol/L NaCl or Urine) saturated.

3.2 Determining of the Sol-fraction

The sol-fraction ($S$) can be obtained in the Solex extractor, and can be calculated by formula (2):

$$S = 1 - \frac{(W_t - W_o)}{W_o}$$  \hspace{1cm} (2)

$W_o$ is the weight of the dry absorbent; $W_t$ is the weight of absorbent having been extracted.

3.3 Determining of the Remaining Concentration of Monomer

The remaining concentration of monomer can be titrated by Bromide[2].

RESULTS AND DISCUSSION

1. Effect of Irradiation Dose on Absorbency (Fig. 1)

In the system of reversed-phase suspension, the monomer containing water is dispersed in the organic solvent. Its diameter is between 10 μm and 100 μm. There are a lot of surface active agents between the two phases. The water loving end groups stretch into the liquid drop of water, otherwise, the oleophylic end groups stretch out, so that the metastable electric structure forms in the drop of water, and the drop of water are dispersed among the organic solvent stably. When the system is irradiated by gamma rays, the polymerization will
happen on free radical mechanism. The absorbency of the polymeric compound increases, then, decreases along with the increasing of irradiation dose because the irradiation crosslinking and irradiation splitting decomposition exit at the same time in the course of irradiation[4]. When the irradiation dose is lower, the crosslinking is in the dominant position, the absorbency increases along with the increasing of the irradiation dose; When the irradiation dose is higher, the splitting decomposition is in the dominant position, the absorbency decreases.

2. Effect of Irradiation Dose Rate on Absorbency (Fig. 2)

![Figure 2](image)

Figure 2: Effect of irradiation dose rate on absorbency of deionized water, 10°C, Dose: 0-300Gy

There is an extreme value of absorbency along with the dose-rate. When the dose-rate is lower, the reaction rate is lower, a lot of oligomers are produced, so the solubility of the absorbent becomes larger, the absorbency becomes lower. The initiating rate and reaction rate are faster along with the increasing of dose-rate, meanwhile, the gel-effect becomes notable, so the molecular weight and the absorbency become larger. If the dose-rate becomes enough large that the crosslinking points become more, the molecular weight of the segments in the crosslinking network becomes smaller, the absorbency becomes lower.

3. Effect of Monomer Concentration on Absorbency (Fig. 3)

![Figure 3](image)

Figure 3: Effect of monomer concentration on absorbency of deionized water, 10°C, dose rate is 0.3395Gy/h, dose is 2.7Kgy, degree of neutralization is 98.9%
At the same conditions of irradiation, the reaction rate becomes faster with the increasing of monomer concentration, so the gel-effect becomes notable, the molecular weight becomes larger, the absorbency becomes higher.

4. Effect of Neutralization Degree of the Monomer on Absorbency (Fig. 4)

The absorbency of the absorbent increases with the increasing of the neutralization degree of the monomer. Because neutralization degree being higher, the viscosity of the solution is lower, the spreading rate of the monomer is faster, the molecular weight of the polymer is bigger. On the other hand, the ions concentration in gel-sphere becomes higher, its osmotic pressure increases at the theory of Dannan equilibrium.

5. Radiation Gelation-dose and Irradiation Yield

At the range of irradiation dose in experiments, the relation of irradiation crosslinking dose and gel-fraction is shown as formula (3) at the theory of Charlesby-Pinner:

\[ S + S^{1/2} = \frac{p_o}{q_o} + \frac{1}{q_o u r} \]  

\( S \) is the sol-fraction of the polymer; \( p_o \) is the density of splitting decomposition; \( q_o \) is density of crosslinking; \( u \) is the number-average molecular weight; \( r \) is the irradiation dose.

The gel-dose can be obtained (Dg=0.526Kgy) from the relation of \((S+S^{1/2})\) and \(1/r\) (Fig. 5). The radiation yield of the solution can be calculated by the formula of Rosick (G=24.6).
6. The Absorption Mechanism of the Absorbent

A lot of anions (COO\textsuperscript{-}) and cation (Na\textsuperscript{+}) are fixed on the network of hydrogel. That is the reason for osmotic pressure. The structure model of hydrogel absorbing deionic water is shown in Fig. 6. The gel spheres expand immersed in water, the foiled molecular of the polymer will extend, and water can be contained in the network of it. When osmotic pressure equals to molecular elastic force, the system reaches absorbing equilibrium.

![Diagram of hydrogel absorbing deionic water]

**Figure 6: Model of hydrogel absorbing deionic water**

7. The Relativity of Quality between Heating Initiation Polymerization and Irradiation Initiation Polymerization
The relative results is shown in table below:

<table>
<thead>
<tr>
<th></th>
<th>Initiation of heating</th>
<th>Initiation of irradiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorbency in deionic water (g/g)</td>
<td>1286</td>
<td>1427</td>
</tr>
<tr>
<td>Yield(%)</td>
<td>98.7</td>
<td>99.8</td>
</tr>
<tr>
<td>Left of monomer(%)</td>
<td>0.3</td>
<td>0.0</td>
</tr>
<tr>
<td>Initiation temperature(°C)</td>
<td>59</td>
<td>21</td>
</tr>
<tr>
<td>Rate of lose in press(30g/cm2,%)</td>
<td>40</td>
<td>8.7</td>
</tr>
<tr>
<td>0.1mol/LNaCl(g/g)</td>
<td>165</td>
<td>167</td>
</tr>
<tr>
<td>Urine(g/g)</td>
<td>74</td>
<td>67</td>
</tr>
</tbody>
</table>

CONCLUSIONS

1. The super absorbent is prepared at suitable dose, dose-rate, concentration and degree of neutralization of the monomer.
2. The absorbing mechanism of the absorbent is discussed, the irradiation yield is calculated.
3. The properties of the hydro gel prepared using irradiation initiation polymerization is better than that of using heating initiation polymerization.

REFERENCES

3. Li Qian, Irradiation Research and Technology, 1992:12-16.
PRODUCTION AND APPLICATION OF CATION / ANION EXCHANGE MEMBRANES OF HIGH PERFORMANCE

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East China University of Science and Technology
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ABSTRACT

A third affiliated factory of our university has been established for the production in batches of cation/anion exchange membranes of high performance, trade marks of which are HF-1 and HF-2. Membrane products have been applied in various fields (including industries and research institutions) with great success.

INTRODUCTION

Homogeneous cation/anion exchange membranes are the main part of electrolyzers and electrodialyzers, but their successful application depends upon the quality of ion exchange membranes.

Ion exchange membranes of high performance can be produced by different ways, among them the radiation grafting and crosslinking of perfluorinated films has been proved to be an effective method for this purpose.

We have carried out radiation induced grafting of various monomers into Teflon FEP films to obtain different sorts of homogeneous cation and anion exchange membranes, which exhibit good electrochemical properties, excellent thermo- and corrosion resistance, high mechanical strength, and long service life. So they have found a wide range of application.

In order to improve the uniform distribution of grafted chains through membrane substrate of large dimension, Prof. Xu Zhili had designed and worked out special devices for irradiation and reactions.

EXPERIMENTAL

1. Materials:
   Teflon FEP films, commercially available.
   Styrene, commercially available, distilled before use.
   Divinylbenzene, commercially available, inhibitor was extracted by 2N NaOH aq. sol. before use.
   Chlorosulfonic acid and concentrated sulfuric acid, (c.p.).
   Chloromethyl methyl ether, commercially available.
Trimethyl amine, commercially available.

2. Apparatus:
Van de Graaff electron accelerator, 2 Mev; 150 microampere.
Co-60 Radiation source, 3 x 10^14 Bq.

RESULTS AND DISCUSSION

1. The Uniformity of Irradiated Teflon FEP Films
Dimension of irradiated Teflon FEP films – 400 x 800 mm.
Samples (20 x 40 mm) were cut off randomly through the whole area. Then, the percentage graft of samples after reaction was detected as shown in Tab. 1.

2. The Stability of Grafting Process
Samples were cut off from the irradiated films, and their corresponding percentage graft was detected after certain pre-set reaction time. The typical grafting curve is shown in Figure 1. All points were plotted on a curve with 1.0 % standard deviation.

<table>
<thead>
<tr>
<th>No.</th>
<th>Relative G(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>51</td>
<td>102.0</td>
</tr>
<tr>
<td>52</td>
<td>100.3</td>
</tr>
<tr>
<td>53</td>
<td>100.1</td>
</tr>
<tr>
<td>54</td>
<td>98.7</td>
</tr>
<tr>
<td>55</td>
<td>98.3</td>
</tr>
</tbody>
</table>

\[ G = (100 \pm 0.7) \% \]

Fig. 1. Percentage graft vs. reaction time
3. Major Characteristics of Ion-exchange Membranes

Major characteristics of ion-exchange membranes, made from Teflon FEP films by means of radiation induced grafting, are listed in Table 2.

<table>
<thead>
<tr>
<th>Ion-exchange capacity (meq/g)</th>
<th>0.8-1.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selectivity (0.1NKCL/0.2NKCL)</td>
<td>&gt; 96%</td>
</tr>
<tr>
<td>Specific resistance (ohm*cm)</td>
<td>100-200</td>
</tr>
<tr>
<td>Tensile strength (Kg/CM²)</td>
<td>140-180</td>
</tr>
<tr>
<td>Bursting strength (Kg/CM²)</td>
<td>5-7</td>
</tr>
</tbody>
</table>

4. Results of Accelerated (Enhanced) Oxidation Test

Accelerated (enhanced) oxidation test of produced ion-exchange membranes was carried out at room temperature in a solution, containing 10% H₂O₂ + 0.05M NaOH + 1.85x10⁻⁴ g-ion of Fe/L. Experimental results are compared with some published data as shown in Table 3.

<table>
<thead>
<tr>
<th>Trade mark</th>
<th>Substrate</th>
<th>Monomer</th>
<th>Time for doubled resistance (H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnC-26</td>
<td>P(VF+HFP)</td>
<td>St</td>
<td>0.025</td>
</tr>
<tr>
<td>MPO-26</td>
<td>ibid</td>
<td>TFS</td>
<td>1.8</td>
</tr>
<tr>
<td>MPO-4ME</td>
<td>P(TFE+HFP)</td>
<td>TFS</td>
<td>2.0</td>
</tr>
<tr>
<td>[HF]</td>
<td>ibid</td>
<td>St+DVB</td>
<td>» 4.0</td>
</tr>
</tbody>
</table>

5. Results of Extra-corrosion Test

Extra-corrosion test of produced ion-exchange membranes was conducted at ambient temperature in a mixture of 16N HNO₃ + 23N HF (2:1 by volume) and the experimental results are listed in Table 4.
IEC / (IEC)₀ – Remaining portion of ion exchange capacity
L / L₀ – Remaining portion of specific conductivity

Tab. 4. Experimental results of extra-corrosion test

<table>
<thead>
<tr>
<th>Time(H)</th>
<th>IEC/(IEC)₀ (%)</th>
<th>L/L₀ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cation</td>
<td>anion</td>
</tr>
<tr>
<td>48</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>480</td>
<td>100</td>
<td>94</td>
</tr>
<tr>
<td>3600</td>
<td>68</td>
<td>61</td>
</tr>
</tbody>
</table>

6. Examples of Membrane Application

Ion exchange membranes of [HF] series have been successfully applied at various factories and research institutions. Some interesting examples are described as follows.

1) Regeneration of Chromine-plating Solution

Waste chromine-plating solution, concentration of which may reach as high as 250-300 g/L [CrO₃], containing impurity exceeded 12 g/L of Fe, Cu and Ni, was treated with [HF-1] cation exchange membranes by means of electrolytical separation. Regenerated plating solution can be adopted as fresh one.

2) Direct Preparation of Pure Magnesium Hydroxide

Direct preparation of pure magnesium hydroxide via electrolysis of magnesium chloride using single cation exchange membrane electrolyzer. Current efficiency exceeded 95% and purity of Mg(OH)₂ is close to 99%.

3) Electrochemical Synthesis of p-Aminophenol from Nitrobenzene

Ion exchange membranes of [HF] series are operated in such a corrosive and contaminating medium with noticeable service time.

4) Electrodialytical Desalination of Mixed Amino-acids

When desalting percentage varies from 90% to 95%, the current efficiency and recovery of amino acids consists of 90% and 80% respectively.
STUDY ON UV CURABLE MATERIAL FOR OPTICAL FIBRE RIBBON

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Huainan, Anhui 232001, P. R. China

ABSTRACT

The material researched is used as a bonding agent for optical fibre ribbon, which consists of prepolymer of epoxy acrylates, combined active diluents, photosensitizers, and modifiers, and is cured by UV (ultraviolet) radiation, with Young's modulus of the cured films among 750—810 MPa, and its mechanical properties up to IEC 794—3. This paper is mainly concerned with the effects of the material components on curing rate and the properties of the cured films.

INTRODUCTION

With the development of optical fibre communication, more and more special requirements are demanded for the construction of optical cables: (a) containing more fibres, (b) smaller diameter, (c) being light and easy to splice and (d) compatible with ordinary cables. The multicore ribbon cables have all of the above properties. In this case, 4—12 parallel fibres are assembled in a composite linear array by UV curable bonding agents. There are two typical ribbon structures: edge—bonded (Fig. 1) and encapsulated (Fig. 2). The later is more often used, which is just what we've researched.

Figure 1—Cross-section of a typical edge-bonded ribbon

Figure 2—Cross-section of a typical encapsulated ribbon
The agent we report here can be cured at the rate of 80m per minute. The ribbons obtained have little additional transmission loss, no colour bar migration and are easy to be separated. And the mechanical properties are up to IEC 794—3.

EXPERIMENTAL

1. Preparation of the Bonding Material

Stoichiometric quantities of epoxy resin E—51, 1,6—hexandiol glycerol ether, and castor oil acid were added to a reactor. The reaction was carried out with stirring at 115—120°C until the acid value was less than 3. In the process of heating, nonane diacid was added at 60°C, and acrylic acid was added in drops at 100°C. The quantity of the E—51 should exceed by 5% (wt) in order to limit the residual toxic monomer.

When the prepolymer was cooled around 70°C after reaction, combined active diluents, in which combined photosensitizers and different dyes were dissolved, were added. Finally, the termination product was obtained after purification by vacuum filtration.

2. Property Test

The results of test are shown in Table 1

<table>
<thead>
<tr>
<th>(Curing rate*)</th>
<th>Young’s modulus (MPa)</th>
<th>glass temperature (Tg/°C)</th>
<th>separability up to IEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>(m/min)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>≥80</td>
<td>750—810</td>
<td>≤—10</td>
<td>794—3</td>
</tr>
</tbody>
</table>

note: exposed to the air in the light of high or middle pressure mercury lamps.

RESULTS AND DISCUSSION

As we know, the properties of the bonding material are mainly determined by its components together with curing techniques. These major influential factors are as follows:

1. Curing Rate

Compared with UV curable coatings for optical fibres, the bonding layer of ribbons is thicker, therefore more favourable curing properties are required. In order to perform a satisfactory curing without the preservation of nitrogen, we’ve undertaken some experimental studies to obtain information about combined photosensitizers as well as prepolymer and modifiers.

It is well known that oxygen in air will substantially decrease UV curing rate. Although the use of nitrogen atmosphere is an effective measure, it needs extra equipment. In our work we find that benzophenone/Michler’s ketone combined photosensitizers system makes the bonding material be cured in air in either high or middle pressure mercury lamps. More recent experiments in this area lead us to suggest that the reasons are as follows:

a. The system can use UV energy more efficiently. In UV spectra of a high pressure mer-
cury lamp. The intensity of light of 365 nm is the strongest among that of 250—310 nm and others. While for a mid-pressure mercury lamp, the UV spectra is ranging from 254 nm to 355 nm. Bonzoin ethers of photosensitizers absorb UV at about 360 nm easily, which is approximately equal to the maximum peak of the high pressure mercury lamp, but the rest of the spectra cannot be used effectively. The absorption peak of benzophenone is at 257 nm, and that for Michler's ketone is at 366 nm. The combination of both improves not only the utilization ratio of the UV energy but also the adaptability to the UV lamps.

b. The adding of Michler’s ketone helps hold back the inhibiting action of oxygen in polymerization. Berner indicates that tert-amine derivatives can absorb oxygen dissolved in liquid materials. The mechanism is outlined below.

\[
\begin{align*}
\text{C}_6\text{H}_5\text{C}_6\text{H}_5 & \xrightarrow{hv} \left[ \begin{array}{c}
\text{C}_6\text{H}_5 \\
\text{C}_6\text{H}_5
\end{array} \right] \\
\text{C}_6\text{H}_5 & \xrightarrow{(\text{RCH}_2)_N} \left[ \begin{array}{c}
\text{C}_6\text{H}_5 \\
\text{C}_6\text{H}_5
\end{array} \right]
\end{align*}
\]

Absorption of 257 nm UV results in the formation of triplets of excited benzophenone, which encounter with tert-amine molecules to form charge transfer complexes. Hydrogen transfer occurs subsequently in the complexes, yielding two types of radicals; semi-benzopinacol radicals and tert-amine radicals. The former is easy to recombine and disappear; the latter is capable of initiating polymerization (equation a) or forming peroxide radicals (equation b) which are stable but can further react with tert-amine molecules giving tert-amine radicals. As a result, polymerization is initiated while oxygen is consumed. Michler’s ketone ([(CH₃)₂NC₆H₄]₂CO) acts as both tert-amine and photosensitizer. Therefore, considering high rate curing and applicability of UV resources the benzophenone/Michler’s ketone combined photosensitizers system is ideal.

2. The Role of Nonane Diacid

Wang and our previous studies showed that if curing rate was the only factor considered, besides the monomer reactivity, in general, the higher the functionality and the smaller the molecular weight of the monomer is, the faster the curing rate is. Our recent work indicates that when nonane diacid is partly substituted for acrylic acid to enlarge the molecular weight and reduce the
double—bond density of the prepolymer, the shrinkage and transmission loss caused by side pressure of the cured film is reduced after curing.

3. The Role of 1,6—Hexandiol Glycerol Ether and Castor Oil Acid

Generally, as for acrylates there exists strong interaction between the interface of bonding material and primary coating, whether they are cured or not. However, it is necessary that optical fibres be separated completely from the ribbon construction with neither permanently detriment to the fibre performance or the destruction of colour coding of the fibres. Therefore the bonding agent based on epoxy acrylates must be modified for this purpose. Inspired by the idea of drawing of patterns and considering both curing rate and mechanical properties, we synthesized 1,6—hexandiol glycerol ether and castor oil acid, which resulted in the fruitful development of ribbon bonding materials. Besides good mechanical properties and high curing rate, another requirement for UV curable bonding agent is that the transmission properties of the fibres in the ribbons not be deteriorated, and thus the cured material must be of enough low glass temperature Tg. The basic component studied is bisphenol A type of epoxy resin, which bears higher Tg as well as high mechanical strength and stable chemical performances. Therefore modification of the prepolymer is necessary. The synthesis and application of the castor oil acid \[ \text{CH}_2(\text{CH}_2)_{5}—\text{CH}—\text{CH}—(\text{CH}_2)_{6}\text{COOH} \] (a) and 1,6—hexandiol glycerol ether (b) not only greatly improved separability of individual fibres from a ribbon but also contributed definitively to the successful modification. There is only one double bond in compound (a), and the prepolymer containing (a), therefore, bears only isolated double bonds. On the other hand, macromolecular chains with isolated double bonds are flexible and have lower Tg. So the introduction of (a) provides perfect low—temperature performance of the fibres and separability of the ribbon but slowed curing rate. In the case of (b), the introduction not only reduces density of the benzene rings but also decreases Tg because of ether bond introduced, which permits more easily spin of the chain. What is more, combination with active diluents improves curing rate greatly. Thus the problem of obtaining great curing rate with better low—temperature performance is completely solved.

CONCLUSIONS

The bonding agent studied has a satisfactory curing rate and the cured material bears good temperature performances and separability.

REFERENCES

Introduction

The last decade is characterised by a profound evolution in radiation curing (RC) technologies. For this reason, it has become a widely used technique in numerous industrial processes such as wood-finishing, metal coating and the embedding of electronic materials. Additionally, radiation curing gained success in the field of silicone release coating-manufacturing and is nowadays well established and rapidly growing. In the following text we aim to summarise our developments in this field within Goldschmidt.

CHART 1

Silicone based release coatings have been used in the market for over 30 years up to now. This results from the special properties of silicones in providing an unique combination of surface activity, low modulus, moisture resistance and low glass temperature. Solvent based condensation products were the first and soon the most important and proven systems introduced. In order to meet public demands for environmental friendlier products with a considerably lower emission of volatile organic compounds, the use of organic solvents has to be reduced. Therefore, 100% solvent-free, transition metal catalysed, thermal curing products were introduced into the market some years ago. Water based emulsions were also developed for some special applications.

CHART 2

Silicone Acrylates

Parallel to ongoing developments in the field of solventless silicone release systems Goldschmidt started its own activities and in 1983, radiation curable 100% solvent-free silicone acrylates were introduced into the market. Compared to other radiation curing silicone systems, silicone acrylate based products provide the opportunity to be cured by either ultraviolet light (UV) or electron beam (EB).

In the chemists view, these substances are liquid polydimethylsiloxane prepolymers. Radiation curable groups are introduced into the molecule via modification with acrylic acid. Reactivity and degree of crosslinking are adjustable over a wide range by varying the functionality (i.e. concentration of reactive groups) and constitution (i.e. steric arrangements of reactive groups within the polymer chain). Due to the numerous possibilities of variations there results a large spectrum of products with different characteristics.

CHART 3

358
The cure is based on the polymerisation of the acrylic C=C double bond via a radical chain reaction. In the EB curing process a sufficient number of radicals for spontaneous polymerisation is produced due to the high radiation energy whereas with UV light the energy is not as intensive thus a photoinitiator is required for a UV process. The required high local radical concentration is provided by its decay.

**CHART 4**

The radical generation and immediate chain-growing leads to rapid and efficient crosslinking even at room temperature. It is for this reason that silicone acrylates cure immediately, i.e. in less than one second.

**Application**

For the production of radiation cured silicone release liners essentially the same equipment is needed as for thermally cured coatings; with the exception of the dryer, which is replaced by an EB- or UV-unit. Unwind, coating head, and rewind station can be identical. Since the radiation unit required takes up considerably less space than curing ovens, in a number of cases it is possible to insert such an unit into an existing conventional production line without extensive changes.

**CHART 5**

However, since TEGO RC Silicones are 100% solventless products, consideration must be given to the coating head. A good control of the coat weight is required for obvious cost considerations. Pinhole free films must be applied to prevent migration of the adhesive to the substrate. All coaters capable of handling 100% thermally curing silicones are suitable for the use with Goldschmidt's RC Systems.

Most of our experience lays in the field of multi-roll smooth roll coaters. We find that this equipment will give excellent results at high production speeds. Even with coat weights of approximately 0.9-1.2 g/sqm on paper or 0.6 g/sqm on plastic films uniform pinhole-free silicone coatings can be reliably achieved. Extensive work is being done in the industry using other types of equipment; including: differential offset gravure, porous roll, and reversed roll coaters.

In contrast to other silicone release products, the thermal stability of TEGO RC Silicones offers the possibility of using a novel process technique. Coating at elevated temperatures up to 60°C leads to improved surface coverage due to reduced viscosity and better rheological properties of the warm silicones. Even formulations containing photoinitiators can be applied in this way without gelation on the equipment.

**Inerting**

A basic effect in the radical polymerisation is its inhibition in an air containing atmosphere. Molecular oxygen as a stable diradical is not able to initiate polymerisation, but readily reacts with other radicals. Therefore the growing radical chain is effectively terminated by contact with oxygen. Because of the large O₂ excess, the reaction of free radicals with oxygen is approx. 10⁵ times faster than with another acrylate molecule. The limited chain growth leads only to short, still liquid polymers and results in a wet or tacky substrate surface, which is unfit for further use.
These undesirable effects are eliminated by curing in an inerted atmosphere. The most efficient way is by the use of nitrogen blanketing. By flooding the reaction chamber with nitrogen the concentration of oxygen can be reduced to some ppm. Goldschmidt has done active research and development on the optimal constructional design for inerting radiation curing lines. We have worked out the significant parameters for effective and efficient inerting, which are summarised in our inerting concept. Due to this improved know-how in inerting technique the consumption of nitrogen can be drastically reduced while still obtaining the necessary low oxygen levels. The preconditions for effective inerting and minimum inert gas consumption include an effective barrier nozzle at the entry side, since the boundary layer of oxygen on the coated side of the substrate has to be completely replaced. This can be done effectively with an adjustable slit nozzle with laminar gas flow. The opening of the barrier nozzle should be maximum three times the distance between nozzle and web and the angle between web plane and nozzle should be in the range of 3-10°.

**CHART 6**

In order to guarantee rapid safe purging, the reaction chamber should be designed to have a volume as small as possible and a simple geometrical shape. To ensure that nitrogen loss through leakage is kept to a minimum, careful sealing of the chamber and on the exit sides is recommended. It is also useful to add a blade, to guide the rolls at the entry and exit sides. The ideal way to uniform nitrogen distribution in the chamber is done by means of a perforated manifold tube. Purging should take place against the web direction. Accurate monitoring of the oxygen level at multiple points is another important factor to guarantee accurate inerting.

In case you have further questions, we have a brochure with more detailed information on this subject and, of course, we are also prepared to give practical assistance to those, who want to install a new line or retrofit their existing one.

In our mobile UV units, theory was turned into practise. Their inerting technology were tailor-made for the requirements of TEGO RC Products.

**Pilot Plants**

To work out the properties of radiation curing silicone acrylates, we installed in cooperation with Pagendarm and RPC a pilot electron beam unit located at Pagendarm’s technical center in Hamburg, Germany with a working width of 1.25 m (49 inch) and line speeds up to 600 m/min (2000 ft/min). It is running since mid of 1991.

**CHART 7**

For the practical demonstration of UV-curing, in summer 1992 we introduced a mobile UV facility with a working width of max. 1.60 m (63 inch) and two 100 W/cm medium pressure Mercury UV-lamps from Eltosch. The base plate was manufactured by GTU (Hamburg/Germany). The mobile UV-unit can be integrated into existing solvent-free siliconising lines for industrial testing. Up to now this mobile UV-unit has proven its usefulness, since numerous successful trials with different customers all over Europe were made and the waiting list for interested parties is growing. Apart from customer trials we also installed the UV-unit at the Kroenert technicum in Hamburg/Germany for some time and used it for basic research on new development products.
In order to serve the needs of US-customers a second mobile UV-unit from Convertech (UK) was constructed with a working width of max. 1.07 m (42 inch), equipped with a 240 W/cm (600 W/inch) UV-lamp from Aetek (Illinois/USA).

Apart from that, it is also worth mentioning that due to the growing interest in radiation curing technology nowadays more and more equipment suppliers, e.g. Polytype (Switzerland), Kroenert (Germany), Prime (USA), Faustel (USA) and Fusion (USA, Europe, Japan) have the technical background to manufacture state of the art inerted UV machines.

Examples

Depending on a number of factors (e.g. adhesive, substrate, final product), there is a need of proper adjusting different release levels. TEGO RC Products offer the complete range from easy via controlled to supertight.

**CHART 9**

By mixing different components of our RC Products, release levels can be fine-tuned to meet the customer requirements. A typical example is shown in the following chart.

**CHART 10**

Some of our work has been focused on the question of the compatibility of RC Silicone Acrylate release coatings with common adhesives. Different types of adhesives with thermally cured release liners (solvent containing and solventless), provided by several well known European producers of self adhesive materials, were included in the study. The tested adhesives belong to the categories of rubber based systems and acrylic dispersions.

In order to compare the original laminates and the same adhesives on RC materials different substrates (glassine paper, clay coated paper and polypropylene film) were first coated with an easy release product and then cured by UV. The adhesives have been laminated onto these release liners and afterwards stored under defined conditions, together with the original materials. After certain periods, the release values are evaluated and compared to those of the original materials.

**CHART 11**

Some of our results from the group of acrylic dispersions are shown in chart 11. In this graph, the data blocks on the left side represent the values of the original laminates whereas the results for the RC Products are shown by the right rows. The release values are determined according to FINAT #3 (i.e. a constant stripping speed of 30 cm/min (12 inch/min) and an angle of 180°). Although the types of adhesives differ in their specific properties, it is clearly shown that there are no major differences between thermally and radiation cured silicone acrylates. RC Silicones meet the technological trends in the industry and fit into customer requirements.

Advantages of Radiation Curing

The radiation curing technology leads to a number of advantages, resulting from the absence of heat and the different curing mechanism.
Resulting from the absence of a catalyst, the danger of catalyst poisoning is not given. This may be of importance if you are looking at special paper qualities like e.g. recycling papers. Due to the complete curing, there is no postcuring after the product leaves the UV chamber or the electron beam zone. Therefore, release values are immediately stable, so that in-line processing such as siliconising, adhesive coating and laminating in one run is possible.

As a result of the ability to cure at room temperature, the use of a large palette of substrates, even heat sensitive ones, is possible. Additionally, no paper shrinking occurs and the remoisturing unit is no longer necessary. In cases of double sided coated papers, problems like blistering are also eliminated.

In the area of process engineering, there are also new opportunities. The compact construction of a radiation unit takes up considerably less space than curing ovens, and in a number of cases it is possible to insert such an unit into an existing conventional production line without extensive changes (this was successfully done at Pagendarm's technical center). In addition, high line speeds - without misting - and lower energy consumption are further economical benefits.

Conclusion

The concept of radiation curable siloxanes has proven to be extremely promising. Of course we will continue our work in upgrading, expanding and improving the Goldschmidt product range. Present market reactions and the intensive use of our pilot facilities indicate that we and our customers are already well on the right way to success.

Acknowledgements

The authors gratefully acknowledge Mr. Hardi Döhler for creating the charts.

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AN OVERVIEW OF ULTRAVIOLET CURABLE COATINGS FOR THE WOOD INDUSTRY.

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ABSTRACT
Ultraviolet cured coatings have been utilized on a limited basis for almost 25 years. The use of UV was restrained to roll applications of very viscous fillers, sealers and fillers for particle board and other porous substrates. Due to technological advances, it is now conceivable to augment the application of UV onto, not only roll coat, but curtain coat as well as spray coat. An overview of the application methods and resins that have been applied in the UV curable wood industry will be discussed.

INTRODUCTION
Ultraviolet-curable coatings in the wood industry have been in existence for numerous years. This coating technology was first applied as 100% non volatile coatings applied by roller coaters. The composition of these coatings were based on an unsaturated polyester, styrene and photoinitiator. This composition was then activated with a thin coat via roller coater and cured instantaneously with exposure to an elevated intensity UV source. The UV source was from a low pressure mercury vapor lamp within a defined wavelength. The UV inception allows the photoinitiator to be stimulated to a free radical stage to initiate the polymerization, thus, generating a highly crosslinked polymer possessing exceptional chemical and physical properties.

Manufacturers of finished wood products soon realized the usefulness of UV curable coatings. The realizations is that flat sections could be finished faster, which in turn increases production output hence lowering the labor and machinery costs. However at this point, the enduser was unable to spray coat onto uneven surfaces with 100% non-volatile UV material.

In the late 80's, coatings manufacturers and raw material suppliers started developments for low viscosity type UV resins to accommodate to viscosity restrictions for spray, curtain coating and other viscosity restricted applications. There were then numerous furniture manufacturers who accepted the technique and have been continuing to support this technique till the present day. Nevertheless, endusers must investigate and perform feasibility studies to implement this technique to a conventional coating line.

SUBSTRATES
There are many different types of wood accessible in the marketplace. The variation of the pores, rosin and texture of the wood provides the coating formulator with a challenge to ensure that adhesion along with all the other properties are maintained. The other less expensive alternative to using solid wood is wood veneer over different substrates. Another domain that has been of conversation, due to environmental restriction and the perpetual increasing cost of pure wood is melamine impregnated MDF. The application is usually by curtain coat or roller coat, since majority times these products are flat stocks. The coating weight in these areas can range from 10 - 150g/m2, which, at an elevated film weight, the formulator is faced with an immense challenge of adhesion and cure.

EQUIPMENT
The commonly used application methods are

(a) Roller Coater
(b) Curtain Coater
(c) Spray Coater
Roller Coater

Roller coater (Figure -1) by far has been the most widely used technique in the wood industry. The spray and curtain coat techniques are gaining world wide acceptability with the low viscosity resins available in the market today.

There are numerous types of roller coaters available in the market. The choice of a roller coater for the UV industry is crucial as we are dealing with a 100% solids material. The differential roller coater can consistently apply a precise amount of coating material in a very thin film range. UV curable coatings are generally high quality coatings, so a heavy film thickness is not as critical as with conventional coatings. A 0.5 to 0.75 mil final thickness is often adequate.

When applying two or three coats of UV product, several roller coaters are used. Roller coaters can be used for the filler, sealer and topcoat stages. There can be a minimum curing that occurs at each stage, when sanding is not required. This is to ensure that intercoat adhesion is maintained with a higher film build which is desirable in the finished product.

Temperature can play an important part with the flow out of the coating. It is possible to have the liquid at a mildly elevated temperature or the rolls occasionally can have heating capacities. The heating of these liquids are usually only between 30°C - 45°C and usually no more, to prevent instability of the liquid coating over time.

A typical roller coat UV line will have the following configurations

1. Sanding
2. Direct roller coat
   for stain application / or spray
3. Brush and wipe stain
4. Hot air forced oven
5. Differential direct
   roller coater - UV sealer
6. UV sealer gel

---

Curtain Coater

Curtain coater (Figure -2) is a method that is primarily used for topcoat application with a film thickness of 4 - 6 mils. The ink is pumped from a reservoir up to a coating head. From there it falls through a narrow gap forming a liquid curtain and into a collector duct which feed it back into the reservoir. The board to be coated is placed on a conveyor in the horizontal position and then it rapidly passes through the falling curtain of liquid. The coating completely covers the board on one side. The application viscosity of a curtain coater is very low. A typical curtain coater line with a usual line speed of 15m/min to 20 m/min. will have the following configuration

1. Mild Sanding
2. Roller Coat Filler
3. Dry Filler(IR)/UV
4. Roller Coat Sealer
5. UV Gel Sealer
6. Curtain Coat Sealer
7. UV cure sealer
8. Sanding
9. Curtain Coat UV topcoat
   (pigmented or clear)
10. Flash Topcoat (IR)-if required
11. Low Intensity UV
12. UV cure topcoat
13. Stack
Spray application of UV curable coatings are best qualified for usage on automated spray lines. The automation refers to electrostatic disk, automatic reciprocating spray guns, automatic carousel spray and fixed guns. Automatic allows for more consistent sprays, efficient usage and a decrease in the employees exposure. These coatings can also be handsprayed. The choice of a spray gun and equipment is crucial. One can conclude that if the optimal coating performance is required, an in-depth evaluation of the type of wood finishing and liquid properties are very important in establishing the appropriate equipment.

A typical spray UV line will have the following configuration:

1. Sand
2. Clean panel
3. Automatic spray machine
   (apply Stain)
4. Stain Wipe
5. IR.
6. Automatic Spray machine
   (UV Clearcoat)
7. UV semicure
8. Automatic Spray Machine
   (UV Clearcoat)
9. UV full cure
10. Stack

**FORMULATION GUIDELINES**

Radiation curing involves the polymerization of monomers and oligomers directly onto the substrate. This polymerization occurs at a very high rate when the coating is exposed to radiation. The polymerization is dependent upon the intensity of the radiation used. This ability to control or time the cure process enables one to have a shelf stable, one package, high solids system at room temperature. There are several components that define a UV curable coating and the components are:

(i) Oligomers
(ii) Monomers
(iii) Additives
(iv) Photoinitiators
(v) Fillers/pigments

In order for the coating to perform to the full expectation of the individual, the balance of the components are crucial and optimization will be of utmost importance to increase product performance without additional costs. An in-depth discussion will be performed on the oligomers and monomers. The possibilities of photoinitiator, additives and fillers will not be covered in this paper at this stage.

(i) Oligomers

The oligomers will impart most of the basic properties to the final cured products. The oligomers commonly used in the wood industry are as follows:

(a) Aromatic and Aliphatic Urethane Acrylates
(b) Epoxy Acrylates
(c) Polyester Acrylates

Since abrasion and stain resistance is important to a great many finishes in the wood industry, a study of abrasion resistance has been performed to evaluate a variety of oligomers with varying backbones and family. However, due to extravagant information and text restrictions, the discussion of the effects of stain resistance will be covered in another presentation in the near future. A standard formulation was prepared and evaluated for abrasion resistance listed as the following:

<table>
<thead>
<tr>
<th>Standard Formulation</th>
<th>Description</th>
<th>parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oligomer</td>
<td>HDDA*</td>
<td>30</td>
</tr>
<tr>
<td>benzophenone*</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Irgacure® 651*</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Ebecryl® P104*</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Baysilon® OL*</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

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The coating was applied at 40g/m² and cured with a medium pressure mercury lamp at 20m/min. at 6 passes. The taber abrader meter following ASTM D4060-84 was used to perform the abrasion tests and the results recorded as follows:

Table 1: Study of oligomers on abrasion resistance

<table>
<thead>
<tr>
<th>OLIGOMER</th>
<th>WEIGHT LOSS IN MG</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>200 cycles</td>
</tr>
<tr>
<td>1. URETHANE</td>
<td></td>
</tr>
<tr>
<td>Aliphatic</td>
<td></td>
</tr>
<tr>
<td>Ebecryl® 220*</td>
<td>69.5</td>
</tr>
<tr>
<td>Ebecryl® 270</td>
<td>6.6</td>
</tr>
<tr>
<td>Ebecryl® 260</td>
<td>2.9</td>
</tr>
<tr>
<td>Ebecryl® 250</td>
<td>-</td>
</tr>
<tr>
<td>Aromatic</td>
<td></td>
</tr>
<tr>
<td>Ebecryl® 210</td>
<td>9.6</td>
</tr>
<tr>
<td>Ebecryl® 200</td>
<td>1.6</td>
</tr>
<tr>
<td>Ebecryl® 220</td>
<td>1.7</td>
</tr>
<tr>
<td>2. EPOXY</td>
<td></td>
</tr>
<tr>
<td>Ebecryl® 860</td>
<td>16</td>
</tr>
<tr>
<td>Ebecryl® 600</td>
<td>1.6</td>
</tr>
<tr>
<td>3. POLYESTER</td>
<td></td>
</tr>
<tr>
<td>Ebecryl® 810</td>
<td>3.5</td>
</tr>
<tr>
<td>Ebecryl® 830</td>
<td>3.3</td>
</tr>
<tr>
<td>Ebecryl® 450</td>
<td>4.8</td>
</tr>
</tbody>
</table>

From the test results attained above, a conclusion can be made where the use of urethane acrylates are advised for the topcoats of most wood furnishings and floorings. The use of epoxy acrylates and polyester acrylates are recommended for sealers and fillers because of the excellent sanding capabilities offered by these oligomers. It is however, very widely practiced to use a combination of epoxy - urethane acrylated oligomer mixture, polyester - urethane acrylated oligomer and epoxy - polyester acrylated oligomer in the formulation to balance the cost and the performance of the product. There are also a wide variety of epoxies, urethanes and polyester acrylated oligomers available today to cater to the formulator needs and further investigations need to be made to decide if a unique epoxy acrylate oligomer can be used as a topcoat because of the backbone nature which allows flexibility, abrasion resistance coupled with excellent cost savings.

(ii) Monomers

Monomers are well noted for their effectiveness as diluents in the UV curable technology, but are also vital in the physical and chemical performance of the coating. The specific chemical structure of these monomers will govern their ability to promote adhesion, to flexibilize or to add some other unique properties to the finished product. Because one is dealing with monomeric material or relatively low molecular weight, care must be exercised to see that the quantity and type of monomer chosen for the formulation do not pose worker exposure problems. It has been mentioned before that in the wood industry that the abrasion evaluation is important for an effective sanding sealer or a topcoat for obvious reasons. A study has been performed to evaluate the abrasion resistance of monomers. A standard formulation was prepared listed as the following:

<table>
<thead>
<tr>
<th>Standard Formulation</th>
<th>Description</th>
<th>parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomer *</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>Benzophenone *</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Irgacure® 651 b</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Ebecryl® PI04 *</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Baysilon® OL c</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>
The coating was applied at 40g/m² and cured with a medium pressure mercury lamp at 40m/min at 10 passes. The taber abrader meter following ASTM D4060-84 was used to perform the abrasion tests and the results recorded as follows.

Table -2 Study of monomers on abrasion resistance

<table>
<thead>
<tr>
<th>MONOMER</th>
<th>WEIGHT LOSS IN MG</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>200 cycles</td>
</tr>
<tr>
<td>TMPTA</td>
<td>-</td>
</tr>
<tr>
<td>BUDA</td>
<td>1.2</td>
</tr>
<tr>
<td>NPGDA</td>
<td>1.4</td>
</tr>
<tr>
<td>HDDA</td>
<td>0.6</td>
</tr>
<tr>
<td>DEGDA</td>
<td>4.1</td>
</tr>
<tr>
<td>TPGDA</td>
<td>12.3</td>
</tr>
<tr>
<td>OTA 480</td>
<td>33</td>
</tr>
<tr>
<td>50% OTA 480 / 50% TPGDA</td>
<td>-</td>
</tr>
<tr>
<td>50% HDDA / 5% HBA</td>
<td>57</td>
</tr>
<tr>
<td>50% HDDA / 50% NVP</td>
<td>15.5</td>
</tr>
<tr>
<td>50% TMPTA / 50% HEA</td>
<td>-</td>
</tr>
<tr>
<td>50% TMPTA / 50% NVP</td>
<td>-</td>
</tr>
</tbody>
</table>

From the tests results attained above, a conclusion can be made, if abrasion resistance is required for a topcoat, the ideal monomer of choice would be HDDA and TMPTA, the latter being used for a more severe resistance requirement. A blend of the two components can be used to optimize cure speed and hardness. The higher the acrylated functionality, usually contributes to a harder, faster cured coating but the diluting factor will be decreased. This, by no means states that the other monomers cannot be applied. In fact, most of the monomers listed above are commonly used for the wood industry. One has to review the overall package of the coating as opposed to a single component. The above tabulations are only a helpful guideline into the proper choice of monomers for a specific requirement without balancing all other physical and chemical requirements.

STARTING POINT FORMULATION

There are many approaches to formulating for different type coatings. The considerations must be weighed to the choice of resin, pigments/fillers, additives and photoinitiator package used. A guideline on the basic formulations for different stages of wood preparation are listed for the beginners in the industry.

1. Sealer/Fillers
2. Topcoat - Flat / high gloss

(1) **Sealer/fillers**

The sealers have a lower viscosity compared to the fillers, but both are similar in function and are applied directly onto the substrate with a full cure. The effect of the sealer is to fill the chipboard so that the pores of the substrate are filled to give a smooth surface. An open grain effect is obtained by the sealers on wood and wood veneers. Since sealers are required to proceed through a sanding process, it is clear that in most cases an epoxy acrylate oligomer will be used. This has also been shown in Table-1, that the epoxy acrylates are recommended for effective sandability. Recommended fillers are usually precipitated Calcium Carbonate, Barium Sulphate, Calcium Sulphate, Talc and Zinc Oxide. The lists in Table-3 are the basic starting point formulations for the sealers and fillers which balance the oligomers and monomers effectively.

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Table-3 - Formulations

<table>
<thead>
<tr>
<th>Sealer 1 Description</th>
<th>parts</th>
<th>Sealer 2 Description</th>
<th>parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ebecryl® 6040 *</td>
<td>60</td>
<td>Ebecryl® 6040 *</td>
<td>45</td>
</tr>
<tr>
<td>OTA 480 *</td>
<td>20</td>
<td>TPGDA *</td>
<td>11</td>
</tr>
<tr>
<td>Fillers</td>
<td>5</td>
<td>Fillers</td>
<td>37</td>
</tr>
<tr>
<td>Benzophenone *</td>
<td>2</td>
<td>Benzophenone *</td>
<td>2</td>
</tr>
<tr>
<td>Irgacure® 651 b</td>
<td>5</td>
<td>Irgacure® 651 b</td>
<td>2</td>
</tr>
</tbody>
</table>

(2) Topcoat

There are comprehensive varieties of topcoat formulations conceivable. High gloss achievement has not at all been an uncertainty in the UV industry. It is more challenging to obtain a matt finish. A study has been performed to contemplate the effects of oligomers, matting agents and photoinitiators on matting efficiency.

Table -4 - A study of matting efficiency

<table>
<thead>
<tr>
<th>Description</th>
<th>1</th>
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<th>3</th>
<th>4</th>
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<th>6</th>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>21</td>
<td>21</td>
</tr>
<tr>
<td>Ebecryl® 6040</td>
<td>-</td>
<td>-</td>
<td>34</td>
<td>34</td>
<td>-</td>
<td>-</td>
</tr>
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<td>Ebecryl® 810</td>
<td>21</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>21</td>
<td>21</td>
</tr>
<tr>
<td>Ebecryl® 210</td>
<td>-</td>
<td>34</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HDDA *</td>
<td>42</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>42</td>
<td>42</td>
</tr>
<tr>
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<td>52</td>
<td>26</td>
<td>26</td>
<td>-</td>
<td>-</td>
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<td>OTA 480 *</td>
<td>-</td>
<td>-</td>
<td>26</td>
<td>26</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Benzophenone *</td>
<td>4</td>
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<td>3</td>
<td>3</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Irgacure® 651 b</td>
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<td>2</td>
<td>2</td>
<td>-</td>
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<tr>
<td>Ebecryl® P115</td>
<td>-</td>
<td>-</td>
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<td>Syloid® 821 d</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>9</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Syloid® 166 d</td>
<td>11</td>
<td>9</td>
<td>9</td>
<td>-</td>
<td>10</td>
<td>10</td>
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<tr>
<td>Gloss at 60 10g/m2</td>
<td>8</td>
<td>14</td>
<td>45</td>
<td>34</td>
<td>73</td>
<td>8</td>
</tr>
<tr>
<td>20g/m2</td>
<td>12</td>
<td>14</td>
<td>52</td>
<td>55</td>
<td>80</td>
<td>12</td>
</tr>
<tr>
<td>60g/m2</td>
<td>11</td>
<td>11</td>
<td>38</td>
<td>80</td>
<td>85</td>
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</table>

It is apparent from the results attained, that in order to achieve a low gloss coating, the film thickness is of great importance. The application of an epoxy acrylate, high functionality monomer and amine additives are not recommended. The oligomer of choice for ease of matting will be a polyester which in this case is Ebecryl 810. Unfortunately, other properties are essential such that other oligomers have to be used in conjunction with the polyester acrylate.
CONCLUSION
Wood coatings formulation requires extensive investigation into the equipment and coating formulation in order for a successful end product. The possibilities of choosing oligomers and monomers are endless but from the results compiled here it is more obvious that formulation of a sealer is ideal with an epoxy acrylate due to the ease of sanding. The success of a matt topcoat is a function of the film thickness, photoinitiator package, matting agent and resin of choice. The polyester acrylates will give the best matting efficiency, then followed by the urethane acrylates. The monomers with high functionality will contribute to difficulties in matting due to the elevated crosslinking and cure speed of the film.

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SUPPLIERS INFORMATION

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d Grace GmbH, Postfach 449, 6520 Worms Germany
EPOXY-ENR HYBRID SYSTEM FOR ULTRA-VIOLET CATIONIC CURING OF SURFACE COATINGS

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ABSTRACT

Preliminary studies on the Cyclo-aliphatic di-epoxide-ENR hybrid system were carried out employing glycidyl methacrylate as the reactive diluent for the cationic UV curable surface coatings. Tri-aryl sulphonium salts were used as the cationic photo-initiator. Effect of operating variables on the coating hardness and toughness was determined with a view to optimize the formulations for maximum performance. The role of ENR as a toughening agent and a suitable oligomer capable of substituting partially the expensive epoxy systems currently employed is discussed.

INTRODUCTION

Cationic photopolymerization of epoxy systems is becoming increasingly popular in the surface coating industry. They offer several advantages over the acrylic compositions in having low order and exhibiting less sensitivity to oxygen inhibition. The cured films display good adhesion to a number of substrates. However the cationic systems suffer from serious limitations to their development by virtue of limited number of reactive oligomers and diluents and their relatively high costs compared with their free radical counterparts. Obviously there has been so far a great reluctance on the part of the coating industry to change over to the cationic systems from the currently popular acrylic based formulations. There has however been a renewed interest recently in cationic systems as a result of availability of new reactive diluents such as vinyl ethers of high reactivity. Besides the epoxy functional bisphenols and novolacs, epoxy functionalised polysiloxanes have become popular. Polyurethanes with vinyl ether end groups and compositions based on epoxidized polybutadiene in combination with the conventional reactive diluents have been reported recently.

The objective of the present work was to evaluate epoxidized natural rubber (ENR) as a partial substitute of cycloaliphatic diepoxide in the cationically curable systems. ENR provides a strong economic incentive to be used in the UV curable systems because of its availability in sufficient abundance to be considered as potential renewable resource at significant cost advantages. This is particularly relevant to Malaysia which is a rubber producing country. Acrylated ENR has been employed as the oligomer in the free radical curing system by Dahlan et al and the results are encouraging. This however requires an additional acrylation step before it can be cured in coating formulations.

Besides economic advantages, ENR is non-toxic and can impart toughness to the conventional photocurable epoxides. It is well known that small amounts of elastomer can greatly improve the fracture toughness of epoxy resins by forming discrete rubbery domains that are chemically bonded to the matrix. Opening of the oxirane ring enables participation of ENR in cross linking reactions with the matrix epoxy resin assisted by the difunctional glycidyl methacrylate. There has been no published literature to the best knowledge of the authors on this system.

This paper reports the preliminary investigation on UV curable systems formulated from cycloaliphatic diepoxide, ENR and glycidyl methacrylate under different operating conditions. The effect of operating variables and their treatment combinations to produce the optimum compromise of properties are also reported.
EXPERIMENTAL

(a) Materials:
Cycloaliphatic diepoxide and cationic photoinitiator, Bis[4-(diphenyl sulfonio)-phenyl]sulfide-bis hexafluophosphate, were obtained from M/S Degusa AG, Hanau, Germany. ENR-50 was obtained from Guthrie Research Chemara, Malaysia. Glycidyl methacrylate was of BDH grade.

(b) Methods:
The following factors were identified as the process variables affecting the cure of the coatings.
1. ENR concentration in the coating formulations
2. Photoinitiator concentration
3. Time of pre-exposure to UV radiation
4. Time of post cure
5. Temperature of post cure.

As non-linear trends in at least some of these variables were considered likely, a central composite rotatable second order design was used in the present study. A half-replicate of $2^5$ factorial design was used as the core of the design. The design matrix arranged in random order adapted in the present studies is given in Table 1 in coded variables and Table II contains the relationship between the coded variables and the real variables.

Experimental data was systematically collected in accordance with the experimental design. A coating thickness of 60 mm on a 120mm by 70 mm steel plates was used in all the experiments. The coatings were irradiated by UV radiation from a Portacure 1000 UV light (American Ultraviolet) at an intensity of 200 W/inch.

After the irradiation for a definite time interval the coatings were post cured. The exact conditions of exposure and post cure (time and temperature) were adapted again in accordance with the design of Table 1. The completely cured coatings were tested for hardness (Konig Pendulum Hardness), Gardner impact strength and solvent resistance. The cured films were examined by the light microscope.

Table 1. Experimental Design Matrix

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* Konig Hardness
Table 2. Coded and real variables

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</table>

RESULTS AND DISCUSSION

1. Effect of ENR on the Impact strength:
The results of the Gardner Dart impact test on the UV cured surface coatings at four different concentrations of ENR are given in Table 2. It is clear from the Table that the impact strength steadily increases as the ENR content increases thus acting as a toughening agent.

2. Effect of Process variables on the Konig Pendulum Hardness:
The results of the various treatment combinations on the Konig Pendulum hardness are given in Table 1. These results are fitted to the following response function by known methods (3):

\[ y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ij} X_i X_j \]  

(1)

The values of the regression coefficients are given below: Constant = 98.8889; \( \beta_1 = -17.4167 \);
\( \beta_2 = 25.6667; \beta_3 = 5.25; \beta_4 = 1.16667; \beta_5 = 0.5; \beta_6 = 4.25; \beta_7 = 1.75; \beta_8 = 3.5; \beta_9 = 1.625; \beta_{10} = 11.25; \)
\( \beta_{11} = -2; \beta_{12} = -4.375; \beta_{13} = 1.5; \beta_{14} = -1.625; \beta_{15} = -0.625; \beta_{16} = -9.0833; \)
\( \beta_{17} = -17.7083; \beta_{18} = 1.16667; \beta_{19} = -4.20833; \beta_{20} = -4.08333; \)

Table 3 Effect of ENR Concentration on Impact Resistance
Epoxide K126 = 100 parts; Photoinitiator K1 85 = 3 parts; UV radiation 200 W/inch

<table>
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<th>% ENR</th>
<th>Time of cure (Min)</th>
<th>Gardner Impact</th>
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<td>25</td>
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</tr>
<tr>
<td>30</td>
<td>3</td>
<td>O</td>
</tr>
</tbody>
</table>

O is >25; A is 21 to 25; B is 16 to 20; C is 6 to 10

Fig. 1. Effect of Time of UV Pre-exposure and Temperature of Post-cure on Hardness
The adequacy of the fit of the second degree polynomial was tested by residual analysis and the plot of normal probability for the residuals was found to be a straight line thus establishing that the second degree model adequately describes the experimental findings. The three dimensional representations of the second degree model are given in Figs 1 to 3. The effects of time of pre-exposure to UV radiation and the temperature of post cure are given in Fig 2.

The value of hardness increases as the pre-exposure time to UV radiation increases at constant post cure temperature. On the other hand the post cure temperature has a positive effect initially on the hardness which reaches maxima and levels off later. As the slight reduction in the hardness beyond a post cure temperature of 125°C was suspected to happen due to thermal degradation of ENR, higher post cure temperature was not employed. Polybutadiene and its derivatives are reported to be susceptible to degradation upon heating. Poh and Lee reported recently that ENR undergoes oxidative degradation both in the double bond region and in the epoxide ring at temperatures around 120°C. Thus post polymerization under moderate thermal treatment not exceeding 120°C is perhaps ideal for the system. Another point of noteworthy significance is the reduction in the pre-exposure time as the post cure temperature increases.

The effects of photo-initiator concentration and the post cure temperature on the hardness are depicted in Fig 3. As the photoinitiator concentration increases at constant post cure temperature, the hardness values first increase and later fall. This is an interesting observation and these results could be attributed to the plasticizing effect of the initiator fragments remaining with the coating. Atusushi et al. have reported from the dynamic mechanical testing that the T<sub>c</sub> values of the cycloaliphatic epoxides cured with the sulphonium salts decrease as the photoinitiator concentration increases. This was attributed to the plasticizing action of the photoinitiator fragments. Post cure temperature has a positive effect on the hardness. No maxima could be observed to be present in the set of curves with respect to the post cure temperature since the responses correspond to the central points of the other factor particularly the pre-exposure time and time of post cure. Similar trends are indicated in the effects of percentage photoinitiators and time of exposure of the coatings to the UV radiation. The reasons for the response is in accordance with the explanations offered earlier.
The effect of percentage of ENR is given in Fig 4. As the ENR percentage increases the hardness falls as expected since an elastomer has been incorporated in the system. Here one must aim at the compromise between the hardness and toughness of the film. As has been already given in Table 3 the toughness increases with the increase of ENR in the formulations. It is thus possible to formulate coating systems with the right combination of hardness, flexibility and toughness by appropriate adjustment the percentage of the rigid and elastomeric components.

The statistical analysis of the experiments also provided information on the nature of response surface and the optimum conditions for the desired performance characteristic. The Konig pendulum hardness which is directly related to the degree of cure of the coating has been chosen as the response parameter in the analysis. Similar analysis with respect to other properties such as impact strength, chemical resistance, flexibility, aging properties etc. is in progress.

The nature of response surface generated by the second degree polynomial was analysed by transforming the equation (1) to its "canonical form" (equation 2) and examining the eigenvalues

\[ y = y_0 - B_{11}x_1^2 - B_{22}x_2^2 + B_{33}x_3^2 + B_{44}x_4^2 + B_{55}x_5^2 \]  

where the X's are the eigenvectors. The eigenvalues are \( B_{11} = -18.1, B_{22} = -7.2, B_{33} = -25.9, B_{44} = 0.49, B_{55} = -25.9 \). Thus the stationary points with respect to all variables other than \( x_5 \) are maxima since the eigenvalues are negative. Stationary points with respect to \( x_5 \) are saddle points. The optimum conditions were obtained by partially differentiating the equation (1) with respect to the individual variables and solving the resulting normal equations. The optimum conditions in the coded variable are \( x_1 = -0.8331, x_2 = 0.2456, x_3 = -1.75, x_4 = -0.7158, x_5 = 1.104 \).

From these results it appears that up to 17% of ENR can be incorporated with the cycloaliphatic di-epoxide with good compromise of toughness and hardness. Higher levels of ENR produces good toughness but the hardness values are impaired.

**MICROSCOPIC EXAMINATION OF THE CURED FILM**

The cured films of both control and those containing ENR were examined by light microscope and the microphoto graphs are given in Fig 5. It was interesting to examine the size and distribution of the elastomeric domains at two levels of ENR concentration. The sizes of the particles of elastomeric domain appear to be uninfluenced by the concentration since at both 12 phr and 30 phr, the particles appear to have undergone no change in size as shown in the figure. These results are suggestive of two phase system comprising of cycloaliphatic diepoxide and ENR. Irregular shape must be considered as the manifestation of rubbery nature and they become distorted in shape during the mixing and coating operation just prior to curing. The UV curing causes solidification in a very short duration and the time is insufficient to allow the rubbery particles to relax from the distorted state.

There is an unique and important feature of compositional toughening by means of incorporating small rubber domains into the brittle resin matrix. By this means the brittle resin still remains external phase of the rubber-resin mixture. Thus the basic mechanical properties such as hardness is still controlled predominantly by the resin domain. This unique arrangement of the rubber phase internal to the resin phase is believed to provide the necessary ductility to the coating compositions without lowering the mechanical properties to an unacceptable level.

For an effective toughening of brittle resins the following requirements are to be fulfilled:

1. It must be immiscible with the matrix to allow the dispersions with a well controlled morphology.
2. Interphase adhesion between the elastomer and the glassy phase must be strong enough to allow significant energy dissipation.
3. The micro domain morphology must be preserved by cross linking.
In the present system it is believed that the preservation of the microdomain morphology is effected by UV radiation by compositional and morphological quenching. The interphase adhesion between the ENR and epoxide system can be promoted by the participation of glycidyl methacrylate which can provide covalent bridge between the cycloaliphatic diepoxide and the ENR through the opening of the oxirane ring. It is also likely that the unsaturation of the glycidyl methacrylate can participate in the cross linking reaction with the unsaturation of the ENR initiated by the free radicals generated along with the cations during the photolytic reaction of the cationic initiator. It has also been found that the incorporation of ENR in the coating compositions reduces significantly the shrinkage and produces a smoother and wrinkle free surface compared with the control. It is believed that the ENR could function as a low profile additive in the same manner as thermoplastic components do in moulding compounds based on unsaturated polyesters.

**CONCLUSIONS**

The incorporation of ENR in the Epoxide based coating formulations enhanced the toughness of the coatings without seriously affecting the hardness and by partially substituting the epoxy resin can reduce the cost.

**ACKNOWLEDGMENTS**

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UV PHOTOPOLYMER MATERIALS AND TECHNIQUE
FOR MAKING LASER GLASS
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ABSTRACT
In this paper, we describe a technique and materials for making laser glass. The technique includes cleaning glass plates, coating UV photopolymer materials onto glass plates, attaching a master hologram to the plates, giving an UV light exposure to cure, screen printing, vacuum film deposition, and covering a protective coating. The UV photopolymer material is composed of photoinitiator, monomer, oligomer and other additives. The experimental results show that the laser glass products have high resistance to alkali, acid, heating and UV irradiation.

INTRODUCTION
What is a laser glass? Laser holograms are replicated onto a glass plate, the glass plate is called a laser glass. It becomes colorful when it's lighted. On the same surface, with the change of ray's angle and visual perspectives, spectrum of seven colors will appear, which makes the ornament splendid, elegant and gives people a feeling of mystery. The laser glass is a new decorative building material.

There are several replicating techniques, such as reconstructing record technique[1,2], contact printing technique[1], molding or embossing technique[3,4,5,6].

Mass embossed holograms are commonplace, appearing on credit cards, consumer packaging, and the like. They typically serve as security devices as well as decorations. Four processes are involved in completing embossed holographic product. They are: (1) The holographic process of producing a photoresist master. (2) Electroplating or casting of the above to produce metal shims. (3) Embossing of an appropriate plastic sheet material (PVC or mylar) with the metal shim, replicating holograms on the plastic sheet material. (4) Preparation of the embossed material for final use, which includes sizing, cutting, hot stamping, etc. This presentation will focus on replicating holograms on a glass plate and making up photopolymer materials for the laser glass.

PROCESSES AND MATERIALS
1. Processes for Making Laser Glass

The eight-step process for making laser glass is shown in Fig. 1. In the first step, a laser glass master is made by embossed holography as follows: holograms are made by interfering two beams of coherent light at a finite angle with each other on a photoresist medium. The resulting master hologram is made to be of surface relief type; that is, the image information is stored in surface variations.

The fragile photoresist hologram master is then used to make a rigid embossing master plate in order to emboss replicas. Such a rigid master is formed in an electrolytic bath on the surface of the photoresist master. Multiple masters are then made from this first rigid master, for use in embossing holograms on
substrate material. The metal masters are generally made of nickel.

The most common substrate materials into which holograms are embossed by metal masters include PVC, mylar or similar sheet plastic materials. The substrate materials of our application are glass plates.

A laser glass master can use a metal or a sheet of plastic material product in which the surface relief pattern is imprinted.

In the second step, glass plates are cleaned with cleaning machine for increasing the adhesion of UV photopolymer materials to the glass plates.

In the third step, liquid photopolymer materials are applied on glass plates. Fig. 2 illustrates the coating process: a cylindrical roller 3 rotates about its axis through the liquid bath 1. The roller 3 has a very large number of small holes in its very smooth cylindrical outside surface. These holes pick up liquid when passing through the bath 1, a blade 2 removing any excess liquid not retained by the holes. A second cylindrical roller 4 picks up on their surface liquid photopolymer materials from the holes of the roller 3 and then transfers the liquid to the glass plate surface 5.

In the fourth step, a laser glass master 8 is attached to the surface of glass plates 6, in the nature of liquid photopolymer materials 7, as shown in Fig. 3. The laser glass master is a sheet plastic material. The roller 9 is a master guide roll. The roller 11 is a drive roll. The roller 10, combining with roller 11, attaches the laser glass master to the surface of glass plates and removes gas bubbles from the liquid photopolymer material.
In the fifth step, the coated glass plate is given an UV light exposure as shown in Fig. 4. The liquid photopolymer material is hardened by curing. The UV-light passes through the glass plate to the photopolymer material.

In the sixth step, the laser glass master is removed from the glass plate after the liquid photopolymer material hardened. Then, ordinary screen printing is applied. Printing can be performed on the glass plate, after the hologram is formed, and before reflective metal is applied.

In the seventh step, the aluminum is vacuum deposited onto the glass plate to provide reflective properties to the glass plate, in order to result in a reflective hologram. Finally, the metallized surface relief pattern is coated with a protective layer.

2. Materials

The liquid photopolymer material refers to a substantially solvent-free composite. Photocurable composition is comprised of (a) a epoxy acrylate, a mono- or multi-functional acrylate monomer, and

A vinyl ether monomer; (b) a photoinitiator should be capable of producing free radicals upon irradiation by ultraviolet light. A wide variety of photoinitiators can be used for the purpose, for example benzophenone, benzoin ethyl ether, Irgacure 651, Irgacure 184, Irgacure 500, Irgacure 907, Irgacure 369, and Darocur 1173. The preferable photoinitiators are Irgacure 500 and Darocure 1173 because they are liquid and mixed with other ingredients easily; (c) additives, for example couplers, surface active agents, and leveling agents. A coupler serves to increase the adhesion of the cured compositions to the glass plates. The cured compositions should have greater adhesion to the glass plates than to the laser glass master since the laser master must be removed from the cured compositions. The compositions also include
a surface active agent and leveling agent for modifying the rheological properties of the compositions to have good film-forming properties and form a good layer on glass plates.

Amounts of ingredients in the compositions will generally be within the following percentage by weight:

(a) oligomer (epoxyacrylate) 10 - 60%
(b) monomer 20 - 80%
(c) photoinitiator 0.5 - 10%
(d) other additives 0 - 10%

3. Sample Preparation

A liquid photopolymer material is prepared by mixing the following ingredients:

- bis-phenol A epoxy diacrylate 35 parts
- 2-hydroxyethyl methacrylate 45 parts
- diethylene glycol diacrylate 10 parts
- photoinitiator (Darocure 1173) 5 parts
- surface active agent 2 parts
- leveling agent 3 parts

The mono- and/or multi-functional acrylate monomer generally serves to reduce the viscosity of the compositions imparted by the presence of the epoxy acrylate.

The liquid photopolymer material was coated onto a cleaned glass plate as shown in Fig. 2, attached a laser glass master as shown in Fig. 3, given an UV light curing as shown in Fig. 4. The intensity of the UV lamp is 80w/cm². The time required for irradiation was about one second. The photocured layer was firmly adhered to the glass surface where the hologram was transferred from the laser glass master to the glass plate. A laser glass was made after screen printing, vacuum reflective film deposition, and protective coating. A reflective metal film also can be titanium, stainless steel and so on. A laser glass can be transparent with above reflective metals, like curtain wall glass.

RESULTS AND DISCUSSION

Under UV initiation, photoinitiator decomposes to produce radicals which initiate polymerization of monomer and oligomer. By the method, the relief hologram of master was transferred to the glass plate. The polymerization process of monomer and oligomer can be seen from IR spectrum as shown in Fig. 5. The characteristics absorb peak of double bond lies in 1628 cm⁻¹ and 810 cm⁻¹ that disappeared apparently after exposure, indicating the polymerization of oligomer and monomer.

The cured photopolymer material was assessed by scratching and scotch tape peeling tests immediately after cured, and by immersion in ethanol, 4 percent aqueous sodium hydroxide, household bleach, water, and domestic detergent. The results of the tests follow, no visual physical changes (no breaking, gas bubbles generating, color changing) and no visual decrease of diffraction efficiency. The results show that the cured photopolymer materials had a good adhesion to the glass plates and resistance to attack by a variety of fluids, for example alcohol, acid and alkaline solution.

Several qualification tests have been performed on a laser glass after coating protective on the reflective film surface. Results from these accelerated life tests are summarized in Table 1.
Table 1  Accelerated Life Tests of the Laser Glass

It was found that no visual physical changes (no gas bubbles generating, no breaking, and no color changing) and no losses in optical performance (no diffraction efficiency decreasing) at following accelerated test.

- **resistance to alkali**: after 72 hours of immersing in 1 mol/L aqueous sodium hydroxide solution at 23 ± 2 °C.
- **resistance to acid**: after 48 hours of immersing in 1 mol/L aqueous chlorhydric acid solution at 23 ± 2 °C.
- **resistance to cold**: after 2 hours of placing vertically in a thermostat at -40 ± 2 °C, the distance between samples and wall of the thermostat was more than 5 mm.
- **resistance to heat**: after 2 hours of immersing vertically in boiling water, samples were pulled out when water cooled to room temperature.
- **resistance to weathering**: after 500 hours of the accelerated sun test with xenon lamps. One cycle was 2 hours. It took 102 min. to expose only and 18 min. to expose and spray water simultaneously in one cycle.

Fig. 5  IR spectrum change after exposure

"—" before exposure, "・・・" after exposure, UV intensity: 80 w/cm², exposure time: 1 s
CONCLUSIONS

The technique and materials have been given for making laser glass. The cured photopolymer materials have a high fidelity to transfer the holograms from masters onto glass plates, a good adhesion to glass plates, and a good resistance to alcohol, acids and alkaline solutions. Several qualification tests have been performed on the laser glass. The results show that the laser glass products have no visual physical changes and no losses in optical performance after accelerated life tests. The laser glass can be as a new decorative building material.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China.

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PHOTOCROSSLINKING OF HYPERBRANCHED POLYESTER LAMINATES

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ABSTRACT

Hyperbranched methacrylated polyesters with high number of functional groups on each molecule (about 8, 12 and 16), have been photocrosslinked with UV light as glass fiber-reinforced laminates (laminates) in a rapid process (0.02 to 0.10 seconds). The cured laminates from hyperbranched polyesters with 35 wt% glass fiber mats have excellent mechanical properties. Addition of 10 to 40 wt% comonomer (TMPTA) has only small effects on tensile modulus, flexural strength and impact strength but decreases tensile strength with 15%.

Keywords: hyperbranched polyester, starburst polymer, radiation-curable polyester, photocrosslinking, glass fiber-reinforced plastic composite, laminate.

INTRODUCTION

The recently developed hyperbranched polyester, or termed dendrimer may open a new line of radiation-curable products. They may be modified to meet particular application requirements for coating, lamination and adhesive systems.\(^1\)\(^2\)\(^3\)\(^4\) Compared with conventional linear oligomers dendrimers have unique molecular structure with many branches, a high number of functional groups on each molecule, and some degree of three-dimensional molecular architecture.\(^3\)\(^4\) Consequently, the expected performance of these materials are lower viscosity, better adhesion to substrates, and higher reaction rate.

Lamination materials based on glass fiber-reinforced polyester resins have replaced metals for many applications, such as, vehicle, furniture and construction industries, due to their mechanical strength, low weight, high corrosion resistance, and low fabrication cost.\(^5\) The advantages of photochemical crosslinking, mainly short curing time, energy saving, complete automation, and strong reduction of pollution, compared with thermal processes are presently studied for the manufacture of glass fiber reinforced polyester laminates. However, there is growing concern about the health risks of the volatile compounds used in the maleate-styrene or maleate-acrylate-based photopolymer systems. Allylic or vinyl ether monomers are preferred to replace or reduce the amount of styrene or acrylate monomers. However, slow polymerization rate or high price can be obtained with above systems. Therefore, development of a thermosetting oligomer which would both decrease the viscosity of the resin formulation and increase the cure speed, while also improving the physicochemical properties of radiation cured materials, has thus become a real challenge.
In two previous articles,\textsuperscript{1,2} we have synthesized hyperbranched methacrylated polyesters in a divergent preparation and investigated the structure and properties of these hyperbranched polyesters including the photopolymerization characteristics in UV curing process. These modified hyperbranched polyesters containing about 8, 12 and 16 double bonds per oligomer molecule, designated as D-1, D-2 and D-3, respectively, have low viscosity, high curing rate, and high degree of curing and the final product has excellent mechanical properties.

We now report the use of the methacrylated hyperbranched polyesters as reactive oligomers in glass fiber-reinforced laminates instead of the traditional maleate-based unsaturated polyester compositions. The effects of radiation time and comonomer content, as well as the functionality of the hyperbranched polyester on the tensile and flexural properties, and the impact strength of the UV crosslinked laminates have been investigated.

**EXPERIMENTAL**

**Materials**

The laminates in this investigation are made of modified hyperbranched polyesters with multifunctional comonomer added and cured with mat of chopped E-glass fibers. The hyperbranched polyester was prepared from pentaerythritol and 1,2,4-benzenetricarboxylic anhydride, end-capped by glycidyl methacrylate and methacrylic anhydride in a stepwise divergent preparation (Figure 1).\textsuperscript{2}

![Fig. 1. Reaction scheme for the synthesis of the hyperbranched polyester.](image)

Three hyperbranched methacrylated oligomers with about 8, 12 and 16 of terminal methacrylic double bonds were numbered D-1, D-2 and D-3, respectively. The idealized formula scheme of the hyperbranched methacrylated polyester with 16 double bonds at the ends of molecular chains is given in Figure 2.

The multifunctional comonomer added to all formulations was trimethylolpropane triacrylate (TMPTA) (Aldrich, Germany). As photoinitiator, benzildimethylketal (BDK, Irgacure 651, Ciba Geigy). The glass fiber mats were of randomly oriented chopped fibers bonded in mat form (450g/m\textsuperscript{2}) (Scandinavian Glass Fiber AB). The polyester resins with 3% BDK and 15% TMPTA by weight were prepared as laminates with 35 wt% glass fiber mats.
Preparation of Cured Laminate Samples

Given amounts of multifunctional acrylate monomer TMPTA and photoinitiator BDK were mixed with the methacrylate-modified hyperbranched polyester. For fabrication of the polyester laminates, a mold made of stainless steel with a thin Mylar polyester film at the bottom was used. To obtain a 2 mm thick sheet, four or five layers of the E-glass fiber mats are placed one by one, pouring a preweighed amount of resin on top of each layer, and allowing it to penetrate thoroughly. Finally, another Mylar film was applied as a cover for smooth surface of the laminates and preventing from diffusion of oxygen from the air. A roller was employed to remove air bubbles and enhance the impregnation of the fiber mats with resin.

Both sides of the laminate were UV-irradiated separately in air on a conveyor belt with variable speed under a 300 W/in (120 W/cm) Model F300 D bulb in the exposure chamber (Fusion UV Curing Systems). After curing the Mylar films are stripped off and laminate sheets with smooth surfaces are obtained.

The cured laminates are shaped into test samples of 88 mm length and 12 mm width using a diamond-tooled circular cutting saw blade. For the tensile testing aluminium end tabs were attached to the laminate samples before cutting.

Measurements of Mechanical Properties

For tensile testing the specimen is clamped into a 100 KN INSTRON universal tester with a jaw separation of 50 mm. The specimen is extended at a rate of 0.5 mm /min to failure. For bending testing the specimen is loaded in a three-point holder with a 50 mm span and strained at a rate of crosshead motion of 0.2 mm/min. The Charpy impact strength is measured with a 1.67 Kg pendulum of 100 kg/cm capacity to break unnotched specimens.

RESULTS AND DISCUSSION

Photocrosslinking Kinetics

The physicochemical properties of fiber glass-reinforced polyester laminates largely depend on characteristics of the resin matrix, the fiber, and the fiber/matrix interface. The measurements of tensile
and flexural properties are of particular importance for the monitoring of the cure process of resin from a liquid of varying viscosity to a crosslinked solid. The data in Figure 3 show the tensile strength of the UV cured hyperbranched polyester laminates with D-1, D-2 and D-3 polyesters. After increasing irradiation time there are no big differences in tensile properties. This implies that the laminates containing hyperbranched polyesters are UV cured at a very high speed, and reaching optimal properties in short irradiation time. Further irradiation has little influence on the tensile properties.

![Tensile strength of the laminates versus irradiation time.](image)

Acrylated epoxy resins prepared by reacting an ethylenically unsaturated monomer containing epoxy groups with a carboxylic acid have been reported to have high cure rate due to suppressing the influence of oxygen in the resin on curing. The cured epoxy acrylate resin films have excellent adhesion to a variety of substrates including glass, stainless steel and aluminium, excellent mechanical properties and high chemical and weathering resistance. The hyperbranched polyester composition in the resin matrix is a thermosetting methacrylated polyester which undergo fast photopolymerization by a radical mechanism with a photofragmenting initiator. More than 95% of gel content for all three hyperbranched polyester systems in irradiation times longer than 0.03 seconds are obtained. Therefore, the high tensile

![Flexural modulus of the laminates versus irradiation time.](image)

![Impact strength of the laminates versus irradiation time.](image)
strength can be obtained in early irradiation stage even if a large amount of unsaturation groups are retained in the resin matrix. The tensile strength of the laminate material increases with increasing functionality of the hyperbranched polyester, probably due to increased crosslink density. The flexural modulus of the laminates increase slightly with prolonging irradiation time, as shown in Figure 4. There is not much difference between D-2 and D-3, but between D-1 and D-2/D-3. The impact strength of the laminates with D-1, D-2 and D-3 polyesters increases gradually at increased irradiation time apparently related to the functionality of the hyperbranched polyesters, as shown in Figure 5. In the previous paper we have reported that at increasing functionality of the hyperbranched polyester, the maximum degree of curing decreases. In the resin with D-2 or D-3 polyester there are about 40% methacrylic double bonds trapped in the crosslinking networks. In this case it may be interpreted as due to the intramolecular plasticization from unreacted double bonds in the matrix with D-2 and D-3 polyesters, thus the high impact strength of the laminates with those polyesters are obtained.

Effect of Comonomer on Physical Properties

A well known feature in the photopolymerization process of radiation-curable systems is that the chain propagation stops before the reaction is complete. This is mainly due to gelation of the medium and the related restrictions in mobility of the reactive sites in the cured material. The viscosity of the formulation is a very important factor responsible for the incomplete curing. Therefore, a comonomer of low viscosity is added to the viscous oligomer to improve the processibility of the material and increase the degree of polymerization of oligomer. In the thermally cured laminate systems, 30 to 40% styrene as reactive diluent is added to the unsaturated polyester prepolymer. About 30% multifunctional acrylate monomer is added to the epoxy acrylate-endcapped unsaturated polyester to improve processibility and obtain good mechanical properties of the UV cured laminates.

The tensile strength of the laminates with the three hyperbranched polyesters decreases rapidly with increased amounts of comonomer added (Figure 6). The decrease of the tensile strength of the laminate due to addition of comonomer to the resin matrix implies that the added comonomers are largely cured as a separate aliphatic phase of low strength surrounding the aromatic hyperbranched molecules.

The flexural strength of the UV cured laminates from D-1 and D-3 is increased by the addition of 10 to 30 wt% TMPTA, but 20 wt% TMPTA added to laminate from D-2 (Figure 7). There is a decrease at high additions, which means that flexural strength in this case is largely related to the aromatic
CONCLUSIONS

The hyperbranched aromatic polyester resins have been cured by addition of benzildimethylketal (Irgacure 651) as photoinitiator and trimethylolpropane triacrylate (TMPTA) as comonomer, and irradiated with UV light as laminates with 35 wt% glass fiber mats. After short irradiation times (0.02–0.10 sec.) at room temperature the laminates with excellent mechanical properties were obtained. The addition of 10 to 40 wt% TMPTA had only small effects on the mechanical properties except the tensile strength which decreased about 15%.

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RADIATION CURE TECHNOLOGY
USED IN INKS & COATINGS

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INTRODUCTION:

Curing by the mean of a radiation source, also called radiopolymerisation is used in Europe since 1972 in the graphic arts industry and found a consistent progress in this field since that period.

What is a radiopolymerisation?

This is the curing or polymerisation of an ink or varnish which is initiated by a radiation source such as Ultra Violet light or by an electron beam of accelerated electrons (called electron beam curing).

The curing needs to be instantaneous (less than 1 second exposure time) while the ink and coating do not contain any volatile components like solvents. Even the provided energy from the radiation source is only used to initiate the polymerisation and not to heat the substrate or the ink in order to evaporate the water or the solvents.

Advantages:

The radiation cure technology is the only technology who meets the 3-E rules which are: ECONOMY, ENERGY, and ECOLOGY.

ECONOMY:

- Nowadays high production speed is a need for the printer to remain competitive while producing a high quality end-product, radiation cure inks can cure at very high speed (0.05-0.1 second) in comparison with "fast" heat drying inks which dry within seconds while oxidatively cross-linking inks cure within hours.
- Mean while the tendency exist to increase the web speed for offset printing till 700 meters/minute.
- As the inks and coatings are generally solvent or water free, this means that significant lower ink weights are printed.

ENERGY:

The energy which is needed to cure radiation curable inks is only to initiate the radicallary polymerisation. There is no further need for any energy to drive off solvents or heating the substrate.

The high energy consumption with a low efficiency is necessary to dry conventional inks or to evaporate the solvents, water or mineral oils. Beside that there is consistent increase of energy consumption to incinerate the evaporated oils or solvents as the air pollution regulations become more and more severe.
ECOLOGY:

The relatively high levels of solvents in the conventional drying system provides a high degree of air pollution in case the solvents are not recycled. Radiation cure systems which are considered as being 100% solids are the exact answer to the pollution problem. More and more countries are implementing severe regulations on air pollution by banning the CO₂-emission which is formed by burning gas or oil, or by banning solvent emission into the air.

1. RADIATION CURABLE PRINTING INKS.

Over the past two decades, enormous progress has been made by the resin, ink and equipment manufacturers in order to respond to the continuous pressure from the printer to increase the output, increase the quality of the printing stock while maintaining price competitive.

- UV-curable or electron beam curable inks and coatings developed during the recent years.
  - Letterpress printing inks
  - Screen printing inks
  - Web offset inks
  - Flexographic printing inks
  - Clear overprint varnishes

Each of these inks require special resins and diluents. It has been proven for more than 25 years, that the chemicals used in the radiation curable printing ink need acrylic unsaturations in their backbone in order to provide a fast cure respond when lightened by a UV-source. Recent developments show that other chemistry or other cure systems like cyclo aliphatic epoxy resins provide decent printing results.

However, the ethereal dream of the printers is to obtain an ink which remain stable on the printing press, with no viscosity increase on the rollers due to solvent evaporation and which dries immediately after being printed in order to maintain its high resolution. So far this is almost possible with radiation curable inks. The fact radiation cure inks do not contain solvents remain as such stable on the press. Further all the resins present in the ink have a vapour tension of less than 1 mm of Mercury at 60°.

Curing and drying time of the inks is almost immediately after printing once and the ink is initiated by UV-light. Curing completes further at room temperature.

An advantage of this technology is that a wide range of substrates can be printed such as paper, card board, metal and even heat sensitive plastics.
1.1 DIFFERENT APPLICATION

Following list is a summary of substrates which are printed and coated by the mean of radiation curable inks:

- cosmetic packaging (primary and secondary packaging)
- food packaging
- tooth paste tubes (primary and secondary packaging)
- plastic labels
- book and magazine covers
- compact disk
- video disk
- record sleeves
- bank notes, cheques, credit cards
- postal cards, publications, brochures etc.
- business forms
- beer cans and aseptic packaging
- plastic bottles
- printed circuit boards
- skies
- wind shields and dashboards in cars
- ceramic inks and printed glass
- outdoor resistant advertising panels
- computer parts
- plastic or paper shopping bags
- aluminised labels are printed with UV or EB curable inks

Of course this is an incomplete list because it becomes impossible to keep track of all innovations the market requires. It is a fact that the number substrates an articles printed do not decrease.

2. CHEMISTRY

2.1 ACRYLATED BINDERS:

As a printing ink is produced of a high viscous resin part, non volatile reactive diluents, photoinitiators, pigments, fillers and additives, we can classify the resin materials into different chemical families:

- Polyester acrylates
- Urethane acrylates
- Epoxy acrylates
- Acrylic acrylates
The non volatile diluents called reactive diluents are acrylated monomers or diluting oligomers and are used to adjust the final viscosity of the ink and to increase the cross linking density. Photoinitiators and photo accelerators are necessary only to initiate the cure or polymerization of the ink.

The type of photoinitiators used in the liquid ink determines the cure speed of the ink, while the photo accelerator is responsible to over win oxygen inhibition on the ink surface while exposed to the UV-light and provides as such a faster cure, higher gloss and better rub resistance.

Electron beam curable inks and varnishes have no need for a photoinitiator system.

2.2 CATIONIC CURE RESINS

Apart from paste inks and silk screen inks, low viscosity UV-curable inks gain more and more interest in the printing industry. Because of the need of low viscous oligomers and diluents, the family of cyclo aliphatic epoxy resins can find their use in the liquid printing inks. Even if this chemistry is existing for more than 10 years, it is only in recent years that they found their industrial application in the printing industry. Because of the sensitivity to humidity during curing and to alkaline compositions in the inks, the use of these chemicals can be limited in printing inks.

3. TYPES OF INKS

3.1 LITHOGRAPHIC INKS

While radiation curable litho inks are being used exclusively in Europe, Japan and the USA for many years, acceptance have now been shown in the Asian countries.

Lithographic inks are used in a process which is based on a chemical difference between image and non-image area (in contrast to printing systems with a physical relief difference).

The obtain an image, the lithographic ink needs to be in "competition" with a water solution the so called fount solution. The ink will go preferentially on to the image area and will be repelled from the non-image area by the fount solution. This hydrophilic-lipophilic balance (HLB) is critically but important for the ink to function and to remain stable for extended run times.

If the ink is too fount solution loving, it forms a water emulsion causing dilution and changes in rheology. Even the evaporation of the excessive amount of absorbed water from the ink can cause a lower gloss and even pin holes on the printed ink surface.
On the printing press, the image on the lithographic plate is transferred to a rubber roll which is in contact with the substrate. This indirect printing is also called "offset". The lithographic behaviour of an ink can be measured on a tack-a-scope where tack of the ink is measured after the inks have been in contact and repulsed by the fountain solution.

3.1.1 As the final ink contains 5 to 10 different ingredients attention should be paid to the following points:
- HLB balance
- pigment wetting properties
- low misting properties
- fast cure speed
- good colour hiding
- good print resolution
- exact viscosity
- not being toxic

Resins for lithographic inks must as such fulfill a number of requirements:
(1) The right HLB-balance:
   The hydrophobic character must be high enough to avoid mixing of the fountain solution with the ink. The binders must however be able to emulsify small droplets of fountain solution on the ink surface.

(2) Good pigment wetting properties:
   The choice of the pigment is very important on the lithographic behaviour of the ink. The type of pigment has not only an influence on the viscosity of the ink but also on its lithographic behaviour. Organic pigment are mostly recommend to be used in litho inks.

(3) Low misting:
   The misting effect of an ink are microscopic ink particles in the atmosphere surrounding the rotating rollers. Good resins as well as the formulating know how can over come this problem.

(4) Good reactivity:
   Because printing presses are running at very high speed, one of the basic requirements of an ink is the cure speed or reactivity. This is the speed (expressed in metres/minute or a number of printed sheets/hour output) required to have the ink completely dried and tack free.
3.1.2 Typical characteristics of a litho ink:

- Viscosity: 5000 - 10000 mPa.s
- Thickness of the print: 2 - 4 g/m²
- Cure speed: 3000 - 5000 sheets/hr
- Not toxic
- Low skin irritation
- Solvent free

3.1.3 The cured ink should:

- adhere to the substrate: paper, board, plastic, metal
- have a good chemical resistance
- have the required gloss
- be over printable by a clear varnish if necessary

3.1.4 Typical starting formulation

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binder system, reactive diluents</td>
<td>60 - 80 %</td>
</tr>
<tr>
<td>Pigments</td>
<td>10 - 20 %</td>
</tr>
<tr>
<td>Photoinitiators</td>
<td>5 - 15 %</td>
</tr>
<tr>
<td>Stabilizers</td>
<td>0.01 - 0.1 %</td>
</tr>
<tr>
<td>Additives: fillers</td>
<td>5 - 10 %</td>
</tr>
<tr>
<td>waxes</td>
<td></td>
</tr>
<tr>
<td>pigment wetting additives</td>
<td></td>
</tr>
</tbody>
</table>

Because the binders and diluents are responsible for most of the required properties, special acrylated resins have been developed over the last 2 decades.

3.1.5 Recommended binder systems:

3.1.5.1 Reactive diluents:

- OTA 480: oligo triacrylate
- Ebecryl 150: bisphenol A. derivative acrylate
- Ebecryl 160 - TMPEOTA: ethoxylated trimethylolpropane triacrylate
- TMPTA: trimethylol propane triacrylate
- PETA: pentaerythritol tri/tetraacrylate

P.S. Because of the water sensitivity and the slower cure speed, it is recommended not to use the common monomers like Tripropylene glycol diacrylate (TPGDA) and 1.6 Hexane diol diacrylate (HDDA).
3.1.5.2 Resin systems:

In function of the substrates to print on, different families of resins can be recommended.

a) **Paper and Carton**
   * A combination of:
     + Ebacryl 1608 and Eb 657 1/1 or 2/1 (epoxy acrylate) (polyester acrylate)
     * Ebacryl 3608 > |
     > | modified epoxy acrylates
     * Ebacryl 3702 > |
     * Ebacryl 870 (polyester acrylate)
     * Ebacryl 450 (polyester acrylate)

b) **Metallic and plastic substrates**
   * Ebacryl 438 eventually combined with Ebacryl 657 (polyester)

3.1.5.3 Photoinitiator systems

As the resins and diluents influences the total behaviour of a litho ink, the photoinitiator part has an important role on the overall ink behaviour.

The photoinitiator which is responsible to initiate the radicalary polymerization has as the need to be physically compatible with the resin part, able to absorb the UV-light (energy) and to start a photo chemical reaction. In many cases a photoinitiator is combined with other products the so called photo synergist, initiators or sensitizers in order to increase the cure speed, the cure in depth and the surface cure.

The Photoinitiator system used in the ink can influence the physical properties of the cured ink such as:
- surface hardness and cure rate in depth
- chemical resistance of the ink
- yellowness of the printed ink
- abrasion resistance

Typical photoinitiator families used in litho ink are:
- $\alpha$-Hydroxy alkyd phenones
- Amino alkyd phenones (to over win oxygen inhibition on the ink surface)
- Amino benzoates
- (Acrylated) Benzophenone
- Thioxanthones
- Benzyl dimethyl ketal
- Morpholines
3.1.5.4 Stabilizers:

Once an ink is formulated and photosensitized, stability or shelf life of the ink can be critical if the ink is not stored under proper conditions, or is abused during manufacturing, or if additives and pigments present in the ink contain impurities.

To overcome these problems, inks can be stabilized by adding small amounts of stabilizers like hydroquinone, methyl ethers of hydroquinone etc....

3.2 FLEXO GRAPHIC INKS:

Flexographic inks and gravure inks can be categorized between the fluid or liquid inks because of their extreme low viscosity of approx. 100 mPa.s. These inks have been traditionally solvent based at about 20-30% solids content. However, regulatory pressure on the use of solvents are making it necessary for the printing industry to evaluate the more environmental friendly technologies.

Waterborne flexo inks have made inroads but still suffer from printing quality problems and the recyclability of printed paper. In additions the VOC-problem is not completely eliminated due to the presence of co-solvents in the ink. About 4 years ago, the 100% solids UV-curable flexo inks started to replace the conventional water based and solvent based flexo and gravure inks.

Since there is no solvent/water evaporation that can lead to drying on the printing plates, higher print quality and easier press operations are expected. In addition, there is less waste. Despite these advantages, development of UV-flexo inks has been slow to evolve primarily due to viscosity limitations. UV curable oligomers are generally high viscosity. Thus, making a flexo ink with good hiding (high pigment concentration) and printability (rheology) has been difficult. These limitations have been largely overcome in recent years. Modifications of flexo presses such as new doctor blade. Systems and modified anilox rolls have allowed utilization of higher viscosity inks. Significant advances in the chemistry of UV curable raw materials have also helped make UV-flexo a reality.

Nevertheless, if the modifications on the flexo press are not yet acceptable to the ink viscosity, the use of water as a diluent for an acrylated resin system can be recommended. In many cases, where water is used in an emulsified form the viscosity reduction within the market existing acrylated resins is not sufficient to overcome the printing problems.

New generation of acrylated binders have been developed recently where water is used as a real diluent without the need of any organic co-solvents. This ink system allows already the production of a low viscosity ink with good opacity, high cure response and long term stability. Further the printed ink requires no water flash off prior to curing.
3.2.1 Requirements of the liquid flexo ink

- Low viscosity
- Good pigment wetting properties
- Fast cure speed.
- Good printing properties with good resolution.

3.2.2 Properties of the cured ink such as:

- Good adhesion to a wide variety of substrates
  paper
  polyester foil
  polyethylene / polypropylene
  PVC, etc...
- Good flexibility when printed on flexible substrates.
- High gloss and print resolution.
- Good surface hardness

3.2.3 Typical starting formulation:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pigment paste</td>
<td>40 - 50 %</td>
</tr>
<tr>
<td>Let down vehicle</td>
<td>40 - 50 %</td>
</tr>
<tr>
<td>Photoinitiator system</td>
<td>5 - 10 %</td>
</tr>
<tr>
<td>Additives</td>
<td>1 - 10 %</td>
</tr>
</tbody>
</table>

3.2.4 Recommended oligomer systems:

a) Pigment paste:
   EBECRIL 657
   EBECRIL 450
   IRR 182
   OTA 480
   grinded with 25% pigment in presence of pigment wetting additives.

b) Let Down Vehicle:
   EBECRIL 81  polyester acrylate
   EBECRIL 82  polyester acrylate
   EBECRIL 8402 aliphatic urethane acrylate
   OTA 480    oligo triacrylate
   TMPTA      trimethylolpropane triacrylate
   EBECRIL 160 (TMPEOTA) alkoxylated trimethylolpropane triacrylate
   DPGDA      dipropylene glycol diacrylate

A third family of resins which can be recommended for the use in liquid inks are the cationic curable systems. These cyclo aliphatic epoxy resins have as main property that the cure is not inhibited by oxygen on the printed ink surface, which means that low levels of photoinitiators can be used with as result that they give a low residual odour after cure.
Typical characteristics of the cationic cure systems is the low shrinkage they provide during the curing which improves the adhesion to the so called difficult substrates in comparison to the fast cure and high shrinking UV-curable acrylated systems.

Anyhow these advantages do not always compensate other drawbacks such as the sensitiveness to certain organic bases present in pigments or additives and the sensitivity to the humidity present in the air which inhibits the polymerization or cure of the ink. It is a fact that the cationic curable systems find their use in certain application like metal and plastic printing if the proper environmental conditions or the humidity levels in the air are respected (humidity levels of above 60% can strongly inhibit the polymerization).

A main break through in the flexo printing occurred about 5 years ago. In cooperation with the equipment manufactures who were able to modify the printing presses, ink manufactures in Europe and the USA were able to produce 100% solids UV-curable flexo inks used for printing paper board, plastic labels, bags etc. These inks are based for 100% on acrylated diluents and oligomers, combined with the photoinitiating systems, pigments and additives, they provide excellent print quality, high gloss and high resolution.

The main interest for the 100% solid flexo or gravure inks are a number of unexpected advantages which appeared during the daily experience such as:

1. Improvement of the printing quality
2. In contradiction to the water and solvent based inks, the UV-inks are not sensitive to humidity changes, temperature changes, pH and speed of solvent or water evaporation.
3. Adhesion to plastics.
4. Potential for long and short range print jobs because of the short time necessary to adjust and cleaning the printing press. As a consequence, less waste will be produced.
5. UV-cured flexo inks show better chemical and abrasion resistancy as well as a better light resistancy.

### 3.3 SCREEN PRINT INKS

It is not clear where to categorize the screen inks. Generally the viscosity is too high for being a liquid ink and too low for being a paste ink. Where the film weights for offset or flexo printing generally do not exceed 5 g/m², UV-screen inks are printed at layer thicknesses between 6 and 30g/m².

UV technology has made a major contribution in the area of overprint varnishing and polythene bottle printing. Its growth into general display screen printing has been more modest but it is now being accepted by the industry as offering many advantages over solvent based inks and with the increase in 4 colour process printing, UV has really found a niche.
Environmental considerations have also altered the industry's attitude to UV. Pressures to reduce solvent emissions and concern about health and safety have both been instrumental in advancing the use of UV in screen printing. Developments, such as conventional water based inks, have been found to have serious technical limitations which has made UV the only realistic alternative to achieving a cleaner environment.

UV curing has been found to offer many benefits to the screen printer and its advantages in screen printing are probably greater than those found in any of the other printing processes. A great advantage of UV curable inks in screen printing is undoubtedly that of screen stability. UV inks contain no volatile components. Therefore, they will not dry in the mesh. The closure of mesh apertures leads to a loss of print quality and necessitates frequent stoppages for wash-up.

The excellent screen stability obtained by using UV inks also allows much finer detail to be reported and this has been of particular benefit in 4 colour process printing. The speed of cure achievable with UV systems is an important advantage over solvent based inks and higher production speeds can be obtained. This has been of considerable advantage in such area as overprint varnishing, where line speeds of 70 metres per minute are not uncommon at 3,500 impressions/hour. Label printers have also benefitted from increased production speeds, due to the rapid curing of UV inks.

To many screen printers a major advantage of UV inks and varnishes is probably the greater film weight obtained, which enhances the three dimensional quality of the print. Corresponding levels of gloss are also higher than those conventional screen inks and this has been particularly beneficial in the decoration of polythene bottles, where the improved visual impact is very noticeable.

Savings in energy have been reported in the use of UV inks over conventional hot air drying systems. Such savings are difficult to quantify, but they have been claimed to be up to 50% of a jet air dryer running continuously at print speeds in excess of 3000 impressions per hour.

Space savings are obvious, as a UV lamp system is a fraction of the size of a thermal oven. Polythene bottle printers have found considerable advantages in the much smaller size of the UV dryer compared with the huge elevator basket dryers which operates at 80°C and take up to 10 minutes for the ink to be fully cured.

A major disadvantage of UV curable screen inks is that there are limitations to the opacity of the inks, but developments in photoinitiators and special developed oligomers and monomers mean that much higher density inks are now available. Screen inks are applied in much thicker films than those from the other printing processes. For good hiding power, high pigment levels are desirable. Pigments tend to compete with photoinitiators for the incident UV radiation and use of certain types of pigment is, therefore restricted.

The fast curing of free radical UV materials does involve shrinkage of the ink or varnish film and this sometimes results in the adhesion to non-porous substrates being inferior to that of a slower drying conventional ink. Great improvements have, however, been made in the design of oligomers so that this is not such a great problem as it was.
3.4 Electron Beam Curable Inks

Printing inks cured by the mean of accelerated electrons instead of Ultra Violet light found its first industrial application approximately 10 years ago.

Since than, printing (wet offset) and coating of aseptic packaging for food containers is successfully done in Europe, the USA and in some parts of Asia. Because these inks and coatings are used in application such as indirect food, it means that special attention need to be paid while formulating the ink.

The main characteristics for such products are the extreme low levels of residual extractables and residual odour after curing which need to be guaranteed by the supplier of the ink.

Line speed of EB-curable inks are similar as the UV-curable inks. The main difference of EB-curable inks versus the UV-inks is the presence of a photoinitiator system. These are not necessary for EB-inks and coatings. Photoinitiators do generally not participate in the curing and are responsible for high levels of extractables and residual odour after curing. These extractables and odours are transferred into dry or liquid food and change the taste.

Now a days electron beam curable inks and coatings are clean because a precise selection of pigments, additives and radiation curable resins have been specially developed for this applications. Resins suppliers have to guarantee levels of < 10 ppm of residual solvents in the resins and diluents. Such resins became commercial available over recent years in order to allow the ink manufacturer to produce an ink which complies with the regulations set up by the packaging manufacturer.

4. HEALTH AND SAFETY

For many years, the radiation cure technology has been criticized for its health and safety aspect. Some of the most important critics about the acrylated resins used in printing inks are the so called toxicity and irritation effects on people’s skin. In deed, in the early years there were some acrylate monomers which were formed to be potential skin irritant or toxic, but their use has been discontinued.

4.1 TOXICITY

The toxicity is defined by lethal doses (LD50) oral or dermal. In many cases it has been proven that the majority of radiation cure resins are not considered for being toxic. The table in annex shows the LD50 oral and dermal values for the most for coming oligomers and monomers supplied by our company. On a comparison, the lethal dose of the drug acetyl salicylic acid and kitchen salt (NaCl) are more toxic than any of the acrylated resins.
Even the very contested monomers like 1,6 Hexanediol diacrylate (HDDA) and Trimethylol-propane triacrylate (TMPTA) are considered as not being toxic. It is further worth to mention that these products have a vapour tension of less than 1mm Mercury at 60°C, and such the danger for inhalation by evaporation is practically neglectable.

4.2 SKIN IRRITATION

It is well known that acrylated resins have a potential skin irritating effect. Oligomers are generally less irritant than the monomers. First generation monomers like HDDA and TMPTA have shown for being more skin irritant than the second generation monomers which are alkoxylated monomers.

Generally ink manufacturers avoid the use of skin irritating products if it is possible, but some of these products provide exceptional good properties such that their use is mandatory to produce a high quality ink.

The primary skin irritation index is measured following 2 methods:

The primary skin irritation index (PII) expressed in a Draize value, and there is the skin irritation according to the OECD method.

4.2.1 DRAIZE VALUE

To determine the primary skin irritation index, the liquid product sample is brought in contact to the fur free skin of a rabbit, intact and abraded during 24 hours. According to the aggressiveness of the product, the skin becomes red, swollen or shows blisters.

4.2.2 OECD-Method

To determine the skin irritation value according OECD method, the liquid product sample is also brought in contact with fur free skin of a rabbit but only to the intact skin and not the abraded part, for only 4 hours. Because this test seems to be more realistic for extrapolations to the human skin, the industry now a days pays more attention to the skin irritation value according to the OECD method than the primary Draize skin irritation index.

The irritation index is as such classified into 4 categories:

Index : 
0 = non irritant 
0-2 = slightly irritant 
2-5 = moderately irritant 
5-8 = sever irritant
As an indication, the majority of oligomers and reactive diluents used in the radiation cure applications have a Draize index of less than 3 or OECD-value of below 2, while the famous solvent "white spirit" shows a Draize value of 6 which means severe irritant.

It is evident that these resins, even if they are non-irritant or hazardous, need to be handled with care. All contact with eyes and skin need to be avoided and proper training for the workers needs to be arranged prior to using the products. It is important to notify that all toxicity and irritancy information is obtained on the liquid resins, before curing or before they become in a solid state. After cure the coating or ink becomes even less toxic and not irritant.

Radiation cure inks are now applied for more than 22 years so far nobody has been intoxicated by manipulating or handling objects printed by radiation cure systems.

CONCLUSIONS

The photopolymerisation is in a continuous evolution. One technology never replaces completely another technology, but the tendencies such as:

- the solvent emission in the air has to be reduced
- regulations about the handling of chemicals become more and severe
- we have to save on energy
- the use of dangerous chemicals needs to be reduced
- there is a need for quality improvement

are practically irreversible

This does not mean that all solvent based inks and coatings will be replaced by radiation curable inks, but they will be replaced where it is possible.

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(Tables are omitted)
SYNTHESIS OF PHOTOSENSITIVE POLYIMIDES HAVING CYCLOBUTANE GROUPS AND THEIR PROPERTIES

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ABSTRACT

The thermally stable polyimides with cyclobutane groups can be developed in organic solvents after photolysis using 254 nm UV light. Introduction of fluorine groups to the polyimides results in solubility increase unlike known polyimides. Photodecomposition of imide bonds as well as photosplitting of cyclobutane groups are considered to be the major photodegradation process for these polyimides. The poly(urethane-imide)s (PUIs) with cyclobutane groups, soluble in polar aprotic solvents, can be developed in alkaline solution after photolysis with 254 nm UV light. Photodecomposition of imide and urethane bonds as well as photosplitting of cyclobutane groups are considered to be major photodegradation process for these PUIs.

INTRODUCTION

Polyimides are well known not only for their chemical and thermal stabilities but also for their excellent electrical and mechanical properties. They are used as encapsulants, insulators and flexible substrates for printed circuits in the electronic industry. Recently, the use of photosensitive polyimides as polymer materials for electronic applications has become increasingly important because the number of steps required to pattern polyimide films is greatly reduced by directly photopatterning photosensitive polyimides.1-3 The reduction in the number of process steps and the associated process equipment offers a significant cost savings and yield advantage over wet or dry etching of polyimide.

Most of the reported photosensitive polyimides are negative type. They are cross-linked by exposure to UV light, and unexposed areas can be selectively dissolved by a suitable developer solution. The negative photosensitive polyimides have several drawbacks such as poor shelf life, shrinkage during curing, long exposure time, swelling, and inconsistent photospeed. In general, the resolution for positive features is better than for negative features. The resolution of negative features in photosensitive polyimide is limited by swelling during development, which is a common problem for negative acting or cross-linking photoresists.

On the other hand, there has been reported only a few case of positive photosensitive polyimides, which can be made soluble by UV irradiation. Khanna et
al.\textsuperscript{4} developed hydroxypolyimide precursors containing hexafluoroisopropylidene linking group. The polymers formulated with o-naphthoquinonediazide (NQD) showed the properties similar to cresol-novolak resin and NQD. Omoto et al.\textsuperscript{5,6} developed fluorinated photoreactive polyimides that linked NQD in the side chain and another polyimide using the chemical amplification process.

Irradiation of maleimide derivatives with 300 nm UV light produces cyclobutane dimers, and photolysis of this photodimers with 254 nm UV light results in original maleimide derivatives by cycloreversion process.\textsuperscript{7} I have been interested in the application of photochemical reactions to polymer systems. This present paper reviews the recent results of my work on the application of this photochemical reaction to the preparation of positive photosensitive polyimides having cyclobutane groups.\textsuperscript{8,9} It is expected that the polyimides and the modified polyimides having cyclobutane groups would photodegrade to form low molecular weight polymers by the photosplitting reaction of cyclobutane groups upon exposure to UV light. This would result in solubility increase of the polyimides and enable the polymer to act as positive photoresists.

EXPERIMENTAL

Materials. Maleic anhydride cyclobutane dimer was obtained by irradiation of maleic anhydride with 300 nm UV light in CHCl\(_3\). N-methylol maleimide cyclobutane dimer (MCD) was obtained by irradiation of N-methylol maleimide with 350 nm UV light in CH\(_2\)Cl\(_2\).

Preparation of polyimides. Polyamic acids were synthesized by the reaction of maleic anhydride cyclodimer with diamines in dimethylacetamide (DMAc) at room temperature. The polyamic acids were purified by precipitation of the reaction mixture in MeOH. The polyimides were obtained by heating the polyamic acids stepvisely.

Preparation of poly(urethane-imide)s. Poly(urethane-imide)s (PUIs) were prepared by reacting MCD with an equimolar amount of disiocyanates in N-methyl-2-pyrrolidone (NMP) at 60-110 °C for 2 hours. The polymers were purified after precipitation in methanol.

Measurement of dissolved fraction. The polymer films were casted on the quartz plate. Dissolved fraction of the films after the irradiation were determined from the difference between absorbance at the isosbestic point of UV spectra before and after dipping the quartz plate in the developing solvent.

RESULTS and DISCUSSION

1. Polyimides Having Cyclobutane Groups

The synthetic scheme for the preparation of polyimides containing cyclobutane groups is shown in Scheme I. The precursor of the polyimide, polyamic acid was soluble in polar aprotic solvents and inherent viscosity measured in DMAc solution.
ranged between 0.5–0.9 dl/g indicating relatively high molecular weights. DSC analysis shows that the decomposition of polyimide takes place in the range 390–460 °C and TGA indicated the temperature of 50% weight loss to be around 540–750 °C which shows relatively high thermal stability.

These polyimides were not soluble in any organic solvents even in very polar solvents such as DMAc or NMP but become soluble in THF or DMAc upon irradiation with 254 nm UV light except polyimide [I]. Polyimide [I] could not be photosplit because it has no absorption at 254 nm. This result suggests that the polyimide [II]–[IV] was photodegraded to low molecular weight compounds by photosplitting of cyclobutane ring.

Dissolution properties of polyimide films with time of irradiation at 254 nm were observed. Fig. 1 shows dissolved fraction of polyimide film with time of irradiation in air. About 98% of polyimide film was dissolved after 7 min of irradiation and the relative dissolution rate of polyimide film increased in the order [III] > [II] > [I]. When the experiment was carried out under N₂, the order of increase in dissolution rate was same but the rate was slower. The results suggest that a photodegradation mechanism other than photosplitting of cyclobutane ring is operating in the photolysis of polyimide under aerobic conditions.

To understand the difference of photodegradation mechanism in air and N₂, IR spectral changes of polyimide [III] film before and after the photolysis with 254 nm UV light were studied. All the absorption bands decreased in intensity with increasing irradiation time and the IR spectra of polyimide photolyzed in N₂ show much less change than in air. Plot of the ratio of absorbance $A(t)/A(0)$ with

![Scheme 1](image-url)
irradiation time showed that both of the bands at 839 and 1375 cm\(^{-1}\) decreased faster than 1777 and 1720 cm\(^{-1}\) bands in air, while the band at 839 cm\(^{-1}\) decreased faster than all the imide bands in N\(_2\). This implies that not only photosplitting of cyclobutane ring but also photooxidation of C-N bond take place when the reaction is run in aerobic conditions as reported by Hoyle et al.\(^{10,11}\)

The present results show that the polyimides containing cyclobutane ring is thermally stable and can be developed in organic solvents after photolysis with 254 nm UV light. Photooxidation of imide bond as well as photosplitting of cyclobutane ring are considered to be the major photodegradation processes for these polyimides.

2. Polyimides Having Fluorine and Cyclobutane Groups

Polyimides usually suffer from processing problems due to their insolubility and infusibility. In order to overcome these drawbacks, solvent soluble or modified polyimides have been developed. Although many soluble polyimides are known, the fluorinated polyimides are particular interest since they generally have excellent electrical properties, greatly decreased water sorption, and better solubility in organic solvents than nonfluorinated counterparts.

The synthetic scheme for the preparation of polyimides having fluorine and cyclobutane groups are shown in Scheme II. The polyamic acids were prepared by the reaction of maleic anhydride cyclobutane dimer with aromatic diamines having hexafluoroisopropylidene group. The polymers were purified by double precipitation in chloroform and water. Polyimides were prepared by thermal or chemical imidation. The polyimides are not soluble in water, methanol or acetone but fairly soluble in polar aprotic solvents such as dimethylacetamide or NMP. Intrinsic viscosities measured in NMP in the range of 0.4–0.6 dl/g. DSC analysis shows that the polyimides begin to decompose at the temperatures between 400–435 °C.

The polyimides were not soluble in acetone or THF before the irradiation. However, they became soluble after the irradiation. This result suggests that the fluorinated polyimide [I] and [II] photodegraded to low molecular weight compounds as a result of photosplitting of cyclobutane rings. Dissolved fraction of polyimide films in THF as a function of irradiation time at 254 nm is shown in Fig. 2. Most of the polyimide films were dissolved in THF after 10 min irradiation.
The results show that the polyimides containing fluorine and cyclobutane groups are thermally stable and soluble in aprotic organic solvents unlike known polyimides. It can be developed in THF after photolysis with 254 nm light. Photo-decomposition of imide bonds as well as photosplitting of cyclobutane rings are considered to be the major photodegradation process for these polyimides.

3. Poly(urethane-imide)s Having Cyclobutane Groups

The synthetic route for the preparation of poly(urethane-imide)s (PUIs) having cyclobutane ring is shown in Scheme III. The PUIs are not soluble in water, alkali, or non-polar organic solvents but fairly soluble in polar aprotic solvents such as dimethylacetamide or NMP. Intrinsic viscosities measured in NMP in the range of 0.21-0.46 dL/g. DSC analysis shows that the PUIs begin to decompose at the temperatures between 260-300 °C.

The PUIs are not soluble in acetone or THF before the irradiation. However, polymer [III] and [IV] become soluble after the irradiation. This result suggests that the PUI [III] and [IV] photodegraded to low molecular weight compounds as a result of photosplitting of cyclobutane rings. Also, the aromatic PUI [III] and [IV] becomes soluble in alkali medium after the irradiation, while they are not soluble in alkali before the irradiation. This is likely due to the photooxidation of a C-N bond in the imide group to produce carboxylic acid. Polymer [I] and [II] are not affected by the irradiation because they do not absorb the light at 254 nm.

Dissolution properties of PUI films in alkali as a function of irradiation time at 254 nm were investigated. Fig. 3 shows the changes in the dissolved fraction of PUI film as a function of irradiation time in air. Most of the PUI [IV] films were dissolved.
after 25 min irradiation. The relative dissolution rate of PUI [IV] film was faster than that of PUI [III] film.

To understand the photochemical reaction of PUI upon irradiation, IR spectral changes of PUI [III] films casted on KBr pellet before and after the photolysis with 254 nm UV light were studied. The difference of IR spectra obtained before and after the irradiation showed the increase in the absorption band around 3300-2500 cm\(^{-1}\) and 1699 cm\(^{-1}\), indicating the formation of carboxylic acid. The decrease of the absorption band at 1780 cm\(^{-1}\) indicates the photodecomposition of a C-N bond in the imide group. The increase of absorption band at 1577 cm\(^{-1}\) indicates the formation of primary aromatic amine by photodecomposition of the urethane bond. The increase of the absorption band at 670 cm\(^{-1}\) is due to the photosplitting of cyclobutane ring to form maleimide derivatives.

The results show that the PUIs containing cyclobutane rings in the main chain are somewhat thermally stable and soluble in aprotic organic solvents unlike known polyimides. It can be developed in an alkali after photolysis with 254 nm light. Photodecomposition of imide and urethane bonds as well as photosplitting of cyclobutane rings are considered to be the major photodegradation process for these PUIs.

CONCLUSION

The polyimides and PUIs having cyclobutane groups are thermally stable. Introduction of fluorine groups or urethane bonds to the polyimides results in solubility increase in organic solvents unlike known polyimides. Photodecomposition of imide and urethane bonds as well as photosplitting of cyclobutane groups are considered to be major photodegradation process for these polyimides and PUIs. The polyimides and PUIs may be used as a promising positive deep UV photoresist that can be developable in organic solvents or alkaline solution after photolysis with 254 nm UV light.
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REATIONS OF RADIATION-INDUCED DEGRADATION OF POLY(METHYL METHACRYLATE) AND POLYSILANES

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ABSTRACT

In order to elucidate chemical reactions of radiation-induced degradation of poly(methyl methacrylate) and poly(cyclohexylmethylsilane) as typical examples of radiation-degrading polymers, the yield of main-chain scission, G(S), was studied as a function of irradiation temperature in the range 77-300 K. It was found to be independent of the temperature at 77-300 K for purified poly(methyl methacrylate) and to decrease with lowering temperature below 175 K to zero-value at 77 K for poly(cyclohexylmethylsilane). Based on these results together with the behavior of free radicals observed by the ESR method, the reactions responsible for the radiation-degradation are discussed for these polymers.

INTRODUCTION

Irradiation with ionizing radiations is an efficient and convenient way of modifying properties of polymer materials. Modification of the polymer properties is necessarily resulted from the radiation-induced chemical reactions such as cross-linking and degradation of polymers. However, the mechanism of these reactions has not yet been elucidated in detail.

The present paper aims at elucidating the detailed mechanism of reactions induced in poly(methyl methacrylate) and poly(cyclohexylmethylsilane) by low LET radiations such as γ-rays. These polymers are chosen as typical models of radiation-degrading polymers. The reaction mechanism was investigated mainly based on the dependence of the yield of radiation-induced scission of polymer main-chain, G(S), upon temperature of irradiation in the temperature range below room temperature and the behavior of radical species generated at low temperature and observed during warming. Our results shown here have mostly been reported in previous reports [1-7]; the present paper is a brief summary of these results.

Poly(methyl methacrylate), abbreviated as PMMA thereafter, has been known to be a polymer of purely radiation-degrading nature. It is a promising resist material for electron-beam microlithography and other uses. Recently, Yates and Shinozaki summarized a number of G(S) values of PMMA reported previously and estimated as G(S)=1.47 for γ-rays at room temperature [8]. Reports on the temperature dependence of G(S) have been rather scanty [9], but they seem to show general trend that G(S) increases with rising temperature. However, we show in the present paper that this is not the case for carefully-purified PMMA below room temperature.

Polysilanes with Si-Si skeleton recently attract much attention because of their potential utility for photo- and radiation-resist, one-dimensional conductors, nonlinear optical materials, and optical data storage materials [10]. Poly(cyclohexylmethylsilane), abbreviated as PCHMS thereafter, is a typical polysilane and is suited for radiation-chemical studies due to its solubility
in organic solvents. Although radiation-degrading nature of polysilanes has previously been reported [10], the mechanism of degradation has been still unknown.

EXPERIMENTAL

Commercial PMMA samples were purified to remove residual monomer before use. Occasionally, pure PMMA synthesized by radiation-induced polymerization was used for comparison. Polysilanes including PCHMS were synthesized from corresponding dichlorodialkylsilanes by Wurtz-type reaction. Molecular weight of these polymers were measured by GPC method using polystyrene standards with appropriate correction.

Deaerated polymer samples were sealed in quartz ESR tubes and irradiated with Co-60 γ-rays at the dose rate of 20 kGy/h at various temperature in the dark and stored in liquid nitrogen at 77 K. GPC measurements were made at room temperature. ESR measurements were carried out at 77 K with an X-band ESR spectrometer after annealing the irradiated sample at various temperature generally for 30 min.

RESULTS AND DISCUSSION

POLYMETHYL METHACRYLATE

Radiation-induced degradation of PMMA at various temperatures of irradiation is shown in Fig. 1. G(S) for purified PMMA is calculated from the radiation-induced change of number-averaged molecular weight. It is 1.5 and remains unchanged by lowering temperature from 300

![Graph showing G(S) vs. T/K for purified and monomer-doped PMMA.](image)

Fig. 1. The dependence of the G(S) value on temperature for (○) purified PMMA, and (●) monomer-doped PMMA.
K down to 77 K. This results disagree with those reported previously that \( G(S) \) is dependent on temperature and is 0.5 or smaller at 77 K [11,12].

The big difference in \( G(S) \) at 77 K between the present and previous studies is attributed to the influence of residual monomer in PMMA samples. As shown in Table 1, the PMMA samples presumably containing monomer give considerably smaller \( G(S) \) values compared with that for pure PMMA sample. Even the purified PMMA sample shows significant decrease in \( G(S) \) after being stored for 2 months, probably because of monomer generated by auto-decomposition. The PMMA sample with intentionally-added monomer in it shows no degradation. These results indicate that a trace of monomer inhibits efficiently the radiation-degradation at low temperature.

Table 1. \( G(S) \) values of PMMA for \( \gamma \)-irradiation at 77 K under various sample conditions.

<table>
<thead>
<tr>
<th>PMMA Sample</th>
<th>( G(S) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Immediately after purification</td>
<td>1.50</td>
</tr>
<tr>
<td>Stored for 2 months after purification</td>
<td>0.26</td>
</tr>
<tr>
<td>Purified sample after pre-irradiation to 1 MGy</td>
<td>0.1</td>
</tr>
<tr>
<td>Commercial PMMA as received</td>
<td>0.36</td>
</tr>
<tr>
<td>Doped with monomer to about 5 vol.%</td>
<td>( \sim 0 )</td>
</tr>
</tbody>
</table>

Figure 1 also shows the variation of \( G(S) \) with irradiation temperature for the monomer-doped PMMA sample. \( G(S) \) increases with temperature from zero-value at 77 K to 1.5 at 200 K and is identical with that for the pure sample at above 200 K. The residual monomer inhibits degradation only at low temperature and it does not affect at high temperature. The difference of two curves in Fig. 1, for purified and monomer-doped PMMA samples, gives a support for that the effect of irradiation temperature on \( G(S) \) is adequately determined even though the irradiated samples were warmed to room temperature before GPC measurements.

\( G(S) \) for pure PMMA as a chemical substance is 1.5 and independent of temperature in the range 77-300 K, while \( G(S) \) for PMMA as a material for practical use is different and dependent on temperature because PMMA materials necessarily contain residual monomer in them. Kudoh et al. studied the radiation-induced change of mechanical properties of several polymer materials at various irradiation temperatures [13]. They showed that flexural strength of PMMA decreases much more quickly (about 6 times) at room temperature than at 77 K. This means that \( G(S) \) at room temperature is 6 times as large as \( G(S) \) at 77 K and seems to be understood based on the data in Table 1.

We made ESR studies on the behavior of free radicals in PMMA irradiated with \( \gamma \)-rays [1-3]. It was found that radicals (I), (II), and (III) are generated at 77 K with \( G \) value of 2, 1, and 1, respectively. Among them, radical (I) transforms to radical (IV) without loss of total radical.
concentration when warmed to about 200 K. This ESR observation strongly suggests that the side-chain radical (I) is the precursor for the main-chain scission and that the scission occurs when the polymer becomes mobile at high temperature to change its conformation, as follows:

\[-\text{CH}_2-\text{C}(\text{CH}_3)\rightarrow \text{CH}_3-\text{C}(\text{CH}_3) + \text{CO} + \text{CH}_2\text{O}\quad (1)\]

\[-\text{CH}_2-\text{C}(\text{CH}_3)-\text{CH}_2-\text{C}(\text{CH}_3)\rightarrow \text{CH}_2-\text{C}(\text{CH}_3) + \text{CH}_3=\text{C}\text{-} + \text{CH}_2\text{O}\quad (2)\]

The stability of the precursor radical at <200 K leads to the expectation that G(S) is independent of irradiation temperature.

The influence of residual monomer is understood as scavenging of the precursor radical:

\[-\text{CH}_2-\text{C}(\text{CH}_3)- + \text{CH}_2=\text{C}(\text{CH}_3)\rightarrow \text{CH}_2-\text{C}(\text{CH}_3)\quad (3)\]

Addition of the monomer to radical (I) is the similar reaction as propagation in radical polymerization and occurs even at low temperature. On the other hand, the main-chain scission through reactions (1) and (2) requires large conformation change of polymer, so that it is frozen at low temperature. Therefore, the scavenging of the precursor through reaction (3) predominates over the scission process.

**POLY(CYCLOHEXYLMETHYLSILANE)**

Molecular weight of bulk PCHMS is decreased with γ-irradiation at 300 K. Relationship between the reciprocal of number-averaged molecular weight and radiation dose is expressed as the superposition of two straight lines, from which G(S) is determined to be 17 in the dose range 0-15 kGy and 1.8 in the range 20-400 kGy. PCHMS, a model of polysilanes, is of typically radiation-degrading nature.

It is remarkable that G(S) of PCHMS is extremely large in the very early period of irradiation. During this period, the molecular weight decreases to the half of the initial value. This means that, on average, one Si-Si bond is broken for every polymer chain. Although the reason for this extremely large G(S) is not known at the moment, a possible explanation is the existence of some especially scissile Si-Si bond which is easily broken by radiation. The scissile bond may be generated chemically during synthetic process of the polymer, or physically by the tensile stress due to entanglement of chains.

G(S) is dependent on irradiation temperature as shown in Fig. 2, where the average G(S) value for the dose range 0-19 kGy is plotted as a function of temperature. Obviously radiation-induced degradation does not occur at 77 K, but it occurs at higher temperature. G(S) increases with raising temperature and remains constant in the temperature range 175-300 K. This temperature effect is different from that observed for pure PMMA and suggests that the precursor of the main-chain scission is readily deactivated at low temperature.

ESR of PCHMS irradiated at 77 K shows the formation of cyclohexyl-type free radicals, mainly radical (3) and (4), on the side-chain cyclohexyl group. Although PCHMS molecule is able to capture electron and positive hole to form radical anion and radical cation as evidenced
Fig. 2. The dependence of the G(S) value for PCHMS on irradiation temperature. G(S) values were determined from the decrease in molecular weight caused by 19 kGy radiation dose.

by ESR examination of irradiated frozen solutions of PCHMS [5,6], no radical ions are detected from bulk PCHMS.

Upon warming irradiated PCHMS, all the cyclohexyl-type radicals isomerize at 175 K into the cyclohexyl-type radical (1). The latter radical is stable and survives with 25% concentration of the initial value even after warming at 300 K. No silyl radical is observed during warming. These results indicate that neither observed radical species are responsible for the main-chain scission nor the scission does form anyl radical species.

Based on the above ESR results, a mechanism of radiation-degradation of PCHMS is conjectured as illustrated in the following page. The electronic excitation energy given by radiations moves along the polymer chain due to Si-Si sigma conjugation to fined a scissile bond. Direct scission of the chain without involvement of radical species needs quick rearrangement of the original bonds. The arrangement is slow at low temperature, so that the H-atom shift (or CH₃ shift) leading to the scission of Si-Si bond is difficult to occur.
CONCLUSION

The dependence of G(S) on irradiation temperature is not only interesting from practical point of view but also important for fundamental study to elucidate the reactions of radiation-induced degradation of polymers. Comparison of the temperature dependence of G(S) and the behavior of free radicals observed by ESR during thermal annealing is proved to be especially useful to study the radiation effects on PMMA and PCHMS, typical radiation-degrading polymers.

REFERENCES

THE EFFECTS OF NORMAL PARAFFINS MOBILIZERS ON IRRADIATED POLYPROPYLENE

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ABSTRACT

The n-paraffins blended with polypropylene (PP) as mobilizer had been investigated. The effectiveness of mobilizer (n-paraffins) on irradiated polypropylene is dependent on the molecular weight of mobilizer and its content on polypropylene. The n-docosane (n-C\textsubscript{22}) possesses the best effectiveness of radiation tolerance on PP among the mobilizer paraffins: n-decane (n-C\textsubscript{10}), n-hexadecane (n-C\textsubscript{16}), n-docosane (n-C\textsubscript{22}) and n-hexatriacontane (n-C\textsubscript{36}). The 2\% (w/w) content of a given mobilizer is the most effective at reducing the embrittlement of irradiated PP as evidenced by the elongation at break. The physical properties of polypropylene with mobilizers such as density, Young’s modulus, the Fraction of free volume and the weight swelling ratio in p-xylene at room temperature were measured. Above phenomena are related with the constructive of blended PP and demonstrated by its physical properties.

Key Words: Polypropylene, mobilizer, n-paraffins and radiation

INTRODUCTION

Radiation-induced oxidation of PP causes on the remarkable decrease of its mechanical properties e.g. elongation at break. Various additive were blended into polypropylene to improve its radiation tolerance. Antioxidants hindered phenols or hindered amines have been reported to prevent polypropylene oxidation degradation\textsuperscript{[1,2]}. Mobilizer was blended into PP as a radical scavenger\textsuperscript{[3,4]}. The mobilizer hexadecane and hexadecene-1 were investigated to decrease the rate of post-irradiation oxidation of polypropylene\textsuperscript{[5]}.

The effectiveness of mobilizer n-paraffins with various molecular weight as well as its various contents in the blends of polypropylene were studied. The physical-structural changes were occurring, and the effectiveness of mobilizer n-paraffins for radiation tolerance on polypropylene were different while the molecular weight or the content of mobilizers in PP blends were various.

EXPERIMENTAL

Materials

Two batches of isotactic polypropylene powder (PPA and PPB) with melt flow index (MFI) 5.1g/10min
and 5.5g/10min respectively were produced in the Second Chemical Factory, China. Controlling the MFI range of PP within 5–6g/10min, the different properties of PP for irradiation in various batches can be negligible. Antioxidant and light stabilizer obtained from Ciba-Geigy Co.; Hydrocarbon n-C_{10} made in Germany; n-C_{16} made in Beijing Chemical Factory, China; n-C_{22} made in Fluka, Swiss; As well as n-C_{36} made in Aldrich Chem. Co., USA.

**Instrument**

- Thermal analysis TA 3000 System DSC 30 cell, Mettler Instrument AG, Swiss;
- Spectrophotometer MPVII Leitz DRG;
- Density Meter MD-01, Deqing instrument Factory, Zhejiang, China;
- High Speed Mixer GH-10, Beijing Plastic Machinery Factory;
- Plastic Plate Thermal Press, 25t Model SS, Shanghai First Rubber Factory

**Sample Preparation**

The high speed mixer was used to mix stabilizer and various additives with PP powder. The mixed sample was extruded and cooled down by water. For making a sheet sample the extruded pellets were heated for 6 min at about 200 °C, then kept under a pressure of 150 kg/cm^{2} for 4 min using a spacer of 1 mm then the sheet was quenched at water bath.

**Radiation Source**

$^{60}$Co γ-ray, dose rate 15kGy/h calibrated by cericeros sulfate dosimetry, $G(\text{Ce}^{3+}) = 2.4$

**RESULTS AND DISCUSSION**

I. The effect of mobilizer n-paraffins with various molecular weight on polypropylene

Serious damages in polymeric are undergone during irradiation in air. The radiation induced damages, for instance the damage of mechanical properties of polymer is the most serious problem for practical use. The values of elongation at break (Eb%) of PPA (MFI=5.1) blended without and with mobilizers n-paraffins n-C_{10}, n-C_{16}, n-C_{22} and n-C_{36} versus various doses were shown in Figure 1. Each sample blended with a given mobilizer. The molecular weight of those mobilizers list in regular sequence as follows: 142(n-C_{10}), 226(n-C_{16}), 310(n-C_{22}) and 507(n-C_{36}). The results of Fig.1 show that the addition of mobilizers could enhance the mechanical properties of PP after irradiation. The radiation tolerance of PP with mobilizer by various molecular weight was in sequence as: n-C_{22}>n-C_{16}>n-C_{36}>n-C_{10} shown on the upper right curve in Fig.1. Which indicated that the mobilizer n-C_{22} possessed the best effectiveness of radiation tolerance on PP. In comparison with the other mobilizers, neither the higher molecular weight mobilizer (n-C_{36}) nor the lower mobilizers (n-C_{10} and n-C_{16}) have the less effectiveness than n-C_{22}.
II. The effect of mobilizer with various content in the blends of polypropylene

A given mobilizer (n-C16) blended with PPB was used to observe the effectiveness of the various content in the blends of polypropylene by their radiation tolerance. The contents of mobilizer in each sample were 0%, 1.0%, 2.0%, 2.5%, and 3.5%. The elongation at break in these samples versus various doses were shown in Figure 2. These data indicated that Eb% of the content 2% with mobilizer (n-C16) had the most effectiveness to improve the radiation tolerance on PP as shown upper right curve 1. The Eb% with the mixed mobilizer as shown in upper right curve 2 had similar regulation.

III. The physical-structure of polypropylene blending with n-paraffins mobilizer

Above test results of mechanical properties of PP versus various irradiation dose indicated that the radiation tolerance of PP blends depending mainly on the molecular weight of mobilizer n-paraffins and on its content of a given mobilizer. The physical structural changes of PP blends occurred in the density measurement. Young’s modulus, the fraction of free volume as well as weight swelling ratio at room temperature.

Density measurement
The density of PPA sample containing various molecular weight mobilizer (n-C_{10}, n-C_{16}, n-C_{22} and n-C_{36}) were shown in Figure 3. Figure 4 illustrated the density of PPB sample with various content of mobilizer (n-C_{16}). The results of densities (Fig.3 and Fig.4) had the similar tendency as the results of Fig.1 and Fig.2 respectively, i.e. the lowest density of mobilizer (n-C_{22}) among mobilizers (n-C_{10}, n-C_{16}, n-C_{36}) in PPA blends (Fig.3) and the lowest density of 2% content with mobilizer (n-C_{16}) among the other content in PPB blends (Fig.4).

![Fig.3 The relation of density versus various molecular weight mobilizer in the blends of PPA](image1)

![Fig.4 The relation of density versus the content of mobilizer (n-C_{16}) in PPB blends](image2)

Young's Modulus

The Young's modulus is one of the mechanical behavior of polymer. Figure 5 illustrated the Young's modulus values in the blends of PPA and its values in various blends were as the following orders: PPA(n-C_{22}) < PPA(n-C_{16}) < PPA(n-C_{36}) < PPA(n-C_{10}) < PPA (without mobilizer). i.e. the blends of PPA. The n-C_{22} had the lowest Young's modulus among them. The Young's modulus values in PPB of mobilizer (n-C_{16}) were plotted in Figure 6, its values decrease with the increasing of content of mobilizer until 2%. The Young's modulus values less decrease with the content when the values were higher than 2%.

The changes of densities (Fig.3) and Young's modulus values (Fig.5) versus various molecular weight of mobilizer in the blends of PPA had the similar regulation. The decrease of density implies that the distance between polymer molecular was increased by the addition of mobilizer. The chain of n-C_{22} is larger than that of the n-C_{10} or n-C_{16}, so that the longer chain of mobilizer is, the bigger distance of polymer by addition mobilizer is, the smaller density of the blend is and the more active of polymer chain is. i.e. Young's modulus value in the blend of PPA with n-C_{22} mobilizer is the lowest.

When the mobilizer n-C_{22} is instead of n-C_{36} in blended PPA, the density or Young's modulus was not decrease, but increase. It can illustrated by two possible reasons; the first reason, the expansion of the distance of polymer will be limited until reached a maximum distance; the second reason, the more molecular weight mobilizer (n-C_{36}) is, the more Van der Waals force between polymer and mobilizer is. i.e. the Van der Waals force limited the active of polymer molecular so that the density increase and Young's modulus increased.
The Fraction of Free Volume

The free volume in amorphous phase of the polymer can be increased by the addition of mobilizer, while radicals recombination be accelerated and the embrittlement of polymer be prevented, which have been proposed\cite{23,45}. But no quantitative experimental result of the free volume related with radiation tolerance has been published yet.

The free volume was calculated by:

\[
f = f_g + a_f (T - T_g)
\]  

(1)

\(f\): fraction of free volume in polymer at \(T\) temperature
\(f_g\): fraction of free volume in polymer at glass temperature
\(a_f\): the difference of coefficient of expansion in polymer around glass temperature

Here, \(f\) and \(a_f\) were calculated by WLF equation\cite{9}

\[f_g = 0.025 \text{ (2.5\%)}\]

(2)

\[a_f = 4.8 \times 10^{-5}/\text{C}\]

(3)

The glass temperature of PP blended with mobilizer were measured by DSC, and the fraction of free volume of polymer were calculated by equation (1), (2) and (3). The results of PP blended with 0\%, 1.0\%, 1.5\%, 2.0\%, 2.5\% and 3.5\% content of mobilizer were plotted in figure 7, which indicated that the free volume value of PP blended with 2\% content of mobilizer was the highest. These results coincide with the results of density (Fig.4), i.e. the density became lower due to the enhance of the free volume. It means when the content of mobilizer is 2\%, the distance of polymer chain is reached a maximum, so that the polymer chain flexibility for radiation tolerance also have the most intense.

Weight Swelling Ratio at Room Temperature

The weight swelling ratio (Sw) were measured by immersion PP blends into p-xylene at 20°C for 48h.
It is a quantitative indication of the morphology in amorphous of polymer.

Figure 8 shows the weight swelling ratio (Sw) in the blends of PPA versus various molecular weight n-paraffins. The sequence of Sw values in the blends PPA coincide with the density values (Fig. 3). The Sw values in the blends of PPB versus various content of mobilizer were plotted in Figure 9, which shows Sw decrease with the increasing of content of mobilizer until the content is 2%, then the Sw have less change when the content is higher than 2% of mobilizer. It coincide with the results of Young's modulus (Fig 6). The increasing of the distance of polymer molecular in the blends had a maximum value, which was deduced by above physical properties. Those are relevant to the physical structural and the blends radiation tolerance.
CONCLUSION

Mobilizer played an important role in protection of polypropylene under irradiation. The n-paraffins mobilizer blended into polypropylene had significant effectiveness of radiation tolerance. The effectiveness depending on molecular weight of mobilizer and on the content of mobilizer in blends had been evidenced experimentally. Mobilizer n-C_{22} possessed the most effective of radiation tolerance. The 2% content of a given mobilizer had the most effective among various contents. The proper physical structure of polypropylene was relevant to its physical properties. The changes of physical properties in various blends related with its compositions. The physical structure also was an important factor in its property improvements. The most advantage and the limited conditions for its properties improvement had been concluded.

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RADIATION-INDUCED GRAFTING OF TMPM ONTO POLYPROPYLENE

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ABSTRACT

The gamma radiation-induced graft copolymerization of 2, 2, 6, 6-tetramethyl -4-piperidinyl-methacrylate (TMPM), a very effective hindered amine light stabilizer (HALS), onto polypropylene was investigated by simultaneous-irradiation technique. The various synthesis conditions on the graft content was studied. It was found that benzene, CCl₄ and petroleum ether are more effective than other solvents, the percent grafting reached 7.1% for benzene. The percent grafting is higher when graft copolymerization is carried out in argon atmosphere than those in air. For all the grafting copolymerization carried out in benzene and CCl₄, percent grafting increase linearly from 1 to 5 Mrad and beyond 5 Mrad a tendency to level off appeared. At a constant dose, the percent grafting was found to be higher at high dose rate until 228 rad/s. Percent grafting also increased continuously with increasing monomer concentration up to 2.85 mol/L, but significant increase in grafting was observed only up to 1.14 mol/L.

INTRODUCTION

Polypropylene has become the largest and fastest growing plastics because of its versatility, wide applicability and low cost, but some disadvantages in its properties has impeded its growth in commercial use. One of those is its poor stability to γ-irradiation. The use of γ-irradiation to sterilize plastic devices is increasing in popularity, but all plastics undergo some degradation as the result of γ-irradiation. Polypropylene is particularly sensitive to radiolysis and it need to be stabilized for use.

 Hindered amines based on 2,2,6,6- tetramethylpiperidines are very effective light stabilizers, they are always used as stabilizers as others. They are also very effective in prevention polypropylene from damage of γ-irradiation. Add low molecular weight stabilizers to polymer can improve its irradiation tolerance effectively, but these stabilizers can easily be evaporated and be lost from polymer surface. Polymeric hindered amines are found to be excellent light stabilizers, but the stabilizing effectiveness of a macromolecular stabilizer is restricted by its poor compatibility with the polymer to be protested. An alternative approach to use a polymeric additive is to graft copolymerize a polymerizable stabilizer to the polymer substrate. This method can improve the compatibility and overcome the volatility problems.

A great number of vinyl monomers including styrene, butadiene, ethyl vinyl ether, methyl methacrylate, and methacrylic acid, have been grafted onto polypropylene by gamma radiation. Hindered amine light stabilizer TMPM has been grafted onto polypropylene film by UV initiation.
In present investigation involves the graft copolymerization of TMPM onto polypropylene powder by simultaneous-irradiation techniques using $^{60}$Co as the source of gamma rays.

**EXPERIMENTAL**

**Materials**

Polypropylene powder supplied by Anqing Petrochemistry Factory was soxhlet-extracted with methanol for 48 hours before use in order to remove all the additives. TMPM was synthesized by the authors according to literature, it was twice recrystallized from hexane before use. All the reagents used were of grade AR.

**Radiation Source**

The irradiation of samples was carried out in a $^{60}$Co ($3.7 \times 10^{14}$Bq) gamma chamber. The dose-rates were determined by the use of Fricke dosimeter.

**Grafting Procedure**

Graft copolymerization was carried out in a test tube in air or in Argon. A weighed amount of polypropylene powder and TMPM were put into test tube, then solvent was added, and left for 24 hours in order to attain the equilibrium swelling of the powder. The tube was placed into the radiation chamber at a suitable distance and height for a desired period. Then the polymerization was stopped by the addition of a large volume of acetone to the reaction mixture. The whole mass was filtered and washed with acetone. The residual monomer and homopolymer were removed by soxhlet extraction with methanol for 48 hours. The graft copolymer was dried to constant weight under vacuum at 50°C.

Percent grafting was calculated as follows:

$$\text{Percent grafting (\%)} = 100\left(\frac{W_g - W_0}{W_0}\right)$$

where $W_g$ and $W_0$ represent the weights of grafted and initial polypropylene powder, respectively.

**RESULTS AND DISCUSSION**

1. Effect of solvent and atmosphere on grafting

Variation in the percent grafting in different solvents and atmosphere was presented in Figure 1. All the experiments were carried out at the dose of 2.5Mrad and dose-rate of 376rad/s. About 1 gram polypropylene, 0.2 gram TMPM and 1 ml solvent were used in each experiment.
Figure 1 shows that the grafting is highly dependent on the nature of solvent. The percent grafting is much higher in benzene, dimethylbenzene, petroleum ether (b.p. 60-90°C), chloroform and carbon tetrachloride than that in methanol, ethanol, n-butyl alcohol and acetone. The percent grafting is the highest when reactions are carried out in benzene, whereas the percent grafting is very low when alcohols are used as solvents.

Polypropylene is nonporous material and it swells to some extent in organical solvents. Many solvents are used in grafting experiments to enhance the accessibility of monomer to grafting sites within the polymer. The swell behavior of polypropylene in several solvents has been studied. It was found that 10-12h is required to attain equilibrium swelling. In our experiments a period of 24 hours was used to ensure enough swelling. It was observed that white polypropylene powder turned to be semi-transparent when swelled in benzene, dimethylbenzene, petroleum ether, chloroform or carbon tetrachloride separately. But this phenomenon was not observed in methanol, ethanol, n-butyl alcohol and acetone. This shows that the degrees of swelling for polypropylene are much higher in the former solvents than those in the latters.

A conclusion can be drawn experimentally that solvent is a very important factor in the radiation grafting of TMPM onto polypropylene. The effect of solvent on grafting may be attributed to another factor, the stability of solvent under gamma irradiation. Benzene is a very stable reagent because of its $\pi$ bond structure which can disperse radiation energy. So the free radical yield of benzene is very low and it leads to the degree of homopolymerization of TMPM is low in benzene. Dimethylbenzene is not so stable in comparision with benzene, the two methyl groups in it can easily be attacked by radiation, then more free radicals are formed and more homopolymerization are initiated.

The grafting copolymerization in argon atmosphere was also studied. The reaction system was deareated by bubbling argon gas for 8 minutes, after that the test tube was sealed. The percent graftings were found to be higher in argon than those in air. This may be account of that the oxygen in air participates in the homopolymerization of TMPM and leads to the degree of grafting become lower.
2. Effect of total dose on grafting.

The effect of total dose on grafting is shown in Figure 2. All the reactions were carried out at the dose rate of 376 rad/s. A total dose up to 10 Mrad was used. About 1 gram polypropylene, 0.2 gram TMPM and 2 ml solvent were used in each experiment.

It can be seen from the Figure 2, for all the grafting copolymerization carried out in two different solvents, benzene and CCl₄, percent grafting increases linearly from 1 to 5 Mrad and beyond 5 Mrad a tendency to level off appeared.

In the initial stage of polymerization, the monomer can diffuse easily to the active sites on polypropylene powder and the grafting copolymerization can take place smoothly. At the same time, homopolymerization is also not much affected. At the higher doses more homopolymers are formed and the viscosity of the reaction solution become higher. The homopolymer act as a barrier against the monomer reach the grafting sites on polypropylene. This results in the decrease of the grafting and the increase of the homopolymerization.

3. Effect of monomer concentration on grafting.

The effect of monomer concentration on percent grafting of TMPM onto polypropylene using about 1g polypropylene, 0-1g TMPM and 2ml benzene at dose-rate of 376 rad/s and at a constant total dose of 1 Mrad is described in Figure 3.
Fig. 3. Effect of monomer concentration on the percent grafting of Polypropylene powder: total dose, 1 Mrad; dose-rate, 376 rad/s.

The results show that the percent grafting increases with monomer concentration. However, percent grafting increases significantly only up to 1.14 mol/L of monomer, beyond which the percent grafting increases very slowly. At much higher monomer concentration, for instance 5.7 mol/L, percent grafting seems to decrease.

In grafting, the rate of grafting is dependent on the polypropylene macroradical yield and the monomer concentration in their vicinity. At a given dose-rate, the polypropylene macroradical yield is a fixed value. So the monomer molecules available in their vicinity is the decisive factor. Grafting yield increases with monomer concentration in a limited range justify this behavior. But when the monomer concentration increased, the homopolymerization of TMPM also increased, beyond a value of monomer concentration the rate of homopolymerization overpasses that of grafting, percent grafting increases no longer and even decreases.

4. Effect of dose-rate.

The effect of dose-rates on grafting was studied at a total dose of 0.5 Mrad under dose-rates of 73, 110, 160, 228 rad/s respectively. The results have been shown in Figure 4.

Percent grafting increased almost linearly with dose-rate in the range of 0-228 rad/s. The number of monomeric and polymeric radicals formed during irradiation is directly proportional to the dose-rate. Monomeric radical can react either with polymer backbone (grafting) or with other monomer molecules (homopolymerization). Because the rate of homopolymerization usually obey the classical square-root relationship, while the dose-rate exponent in grafting copolymerization often exceeds 0.5. As a consequence, an increase in the dose-rate may favour the grafting process with respect to homopolymerization and thus increase the grafting yield.
CONCLUSIONS

The gamma radiation induced grafting copolymerization of TMPM on polypropylene in various solvents, at different total doses and dose-rates as well as in a range of monomer concentration was studied. Solvent plays an important role in the grafting reaction. It is found that the percent grafting increase with total dose and monomer concentration, beyond a value the grafting shows a tendency to level off. The percent grafting increases linearly with dose-rate in a large range.

The grafting need to be studied in detail in further work. The percent grafting is still very low and it can not satisfy the practical requirements. The stability of grafted Polypropylene also need to be studied.

REFERENCES

HAMC'S FILM AND HOT-POINT ANALYSIS OF PHOTOGRAPHIC PATENT STUDY IN RECENT 10 YEARS IN CHINA

Wang XingHui
(HARBIN AIRCRAFT MANUFACTURING CORPORATION)

ABSTRACT: This paper introduces technical performance and need of the HAMC’S film and presents HAMC’S product. The paper analyzes mainly 2,293 photographic patent applications Composition in the fields of silver image, non-silver image and electronic image.

And their characteristics and trends in order to provide economic-legal information and service for market competition, scientific study, product development and protection of intellectual property rights.

Keywords: HAMC’s film, silver-salt image, non-silver image, electronic image, application for patent and quantitative analysis.

COMPOSITION OF APPLICATIONS FOR PHOTOGRAPHIC PATENT IN RECENT 10 YEARS IN CHINA.

Electron publications---CD-ROM, CD-I and CD-PHOTO. It is known that there are 2,261 patent applications searched through result of G 03 by the disc data bank prepared by the Patent Office of China (ie Part G 03 classification in international Patent is a sensitive Patent) From date of April, 1985 of the patent law of the people’s republic of China came into effect to the date of Dec.31, 1994.

There are 2,293 applications for photographic patent (given from paper disc prepared by the Patent office of China. The paper applications for photographic patent are more than applications of disc patent, the reason for this is that some patent applications are withdrawn.

The composition of applications for photographic patent in recent 10 years in China can be summarized with the method of three more and three less and about the same quantity:

• Much of the product patent and less of the method patent-The method patent is less than the product patent, that indicates the method patent should be studied for long period with extremely difficulty and the applicant is full of worries for that.

• Much of the silver-salt patent and less of the non-silver patent. The silver-salt patent applications which are called in “The stone Age” are not less so that this proves the useful value of solver-salt image.

• Domestic Applications are more and foreign applications are less, but these displays ideals of the foreign enterprises to Occupy the Chinese market.

• Utility model and invention patent are about the same quantity-this shows that the applicant want to obtain the patent rights and economic benefits.

• Individual patent and professional patent are about the same quantity. This shows that the individual patent invention and creation are participating the
economic competition and these productive force sources are not ignored.
The mathematical statistic is shown in the following figure and tables:

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Fig.1 State of applications for photographic patent (Three classification image) in recent 10 years in China.

Fig.2 State of first ten places of foreign patent applications
First ten places of foreign enterprises applications for Chinese professional inventions in China (Arrange in Chinese alphabetical order). First three places of non-professional inventions in China (Arrange in Chinese alphabetical order)

<table>
<thead>
<tr>
<th>Classification</th>
<th>Total Qty.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inventions by Chinese enterprises and professions</td>
<td>509</td>
</tr>
<tr>
<td>Inventions by foreign enterprises and professions</td>
<td>720</td>
</tr>
<tr>
<td>Chinese individual inventions</td>
<td>1,045</td>
</tr>
<tr>
<td>Foreign individual inventions</td>
<td>19</td>
</tr>
<tr>
<td>Total</td>
<td>2,293</td>
</tr>
</tbody>
</table>

The patent applications by foreign enterprises in China are more than patent applications by Chinese enterprises.

There are 211 patent applications made by foreign enterprises in China, which is more than patent applications made by Chinese enterprises in China. This indicates that the patent law of the People's Republic of China is a good law which respects intellectual property rights and attracts foreign merchants. The development of Chinese economy provides a fairly business chance for foreign countries. In the photographic field, the individual invention in China is over one time than professional invention. This shows that the invention sources of Chinese photographic are not only in the enterprises but also in the "private achievements in China" held in Beijing in March 3, 1995 and declared that forty-five thousand patent applications are received, twenty thousand applications are filed, and 14% of files are made up. This developing is a seldom situation in the world patent history.

Making a comprehensive survey of 2,293 patent applications in recent 10 years in China. Their contents are rich and varied and it is well worth to read them. Whether read the patent digest or read patent instruction, it is surprising that: "why didn't I think it is?" "what is claim?" and "why the patent enclosure figure is without dimensions?". All these give one much food for thought.

The photographic patent applications in recent 10 years in China are epitome of forty-five thousand patent applications in recent 10 years. It allows image, characters and sound to be in a integral with varied images at this age. Patent belongs to technical invention. Technical invention and scientific discovery are in competition. The photographic patent applications in China reflect a strong attraction for foreign merchants in the market of China and the competition condition between Chinese scientific study institute, enterprise personnel and...
foreign merchants. It is specified in Article 9 of patent law: "here two or more applicants file applications for patent for the identical invention-creation, the patent right shall be granted to the applicant whose application was filed first." This principle establishes the set up of the invention-creation in "patent competition" of commodity economy in socialist initial period in China, and exhibits strong aspirations of domestic and foreign applicant in protection of intellectual property rights.

APPLICATIONS FOR PHOTOGRAPHIC PATENT OF SILVER SALT IMAGE

There are 1,249 applications for patent of silver salt image system in recent 10 years of patent applications in China. It made up 55% of application quantity and reflects that the silver-salt imaging system has great vitality.

Applications with method classification are as follows:
---Silver halide emulsions, 85100887 85100891 85104127 85104288 85106372 85108217 85108256 85109626 86104070 88103542 88106075 89100569 89101103 89102651 89102651 89104667 89104705 89106402 89107537 89108698 90109276 90110428 91101983 91102341 91102359 91102470 91102359 91103961 92223915 93116634 93117090 94101433

85100887 is a first application for patent of improving characteristics of silver-salt film. The applicant is from chemistry institute of the Chinese Academy of sciences and it mainly protect monodisper-sity methyl acrylic acid emulsions with diameter of grain in 0.40 in its 10 article claim.

85104127 is a first foreign patent application of silver halide. Its applicant is from FUJI with 36 sheets of instructions in details. In this application, there is one right requirement and the protective limit is that there should be a compound at least on silver halide grain. See fig 3:

fig.3: A compound which is protected by first foreign patent application on silver halide grain.

Applications with product classification are as follows:
---Film, 85106901 85107228 85109330 85204253 86103522 86108446 86202452 86204093 86205340 86207530 87100804 87107348 87107841 87206717 87207599 88101406 88106980 88208190 88210784 88211585 88215165 889107929 88217327 88217629 88219926 89101510 89101582 89101761 89103038 89103270 89103307 89103508 89107425 89107544 89109093 89208289 90101082 90101281 90102624 90102895 90104746 90104893 90106087 90107485 90107860 90110175 90201771 90202321 90205242 90214769 90216014 90218457 90218804 90220643 90224940 90226876 90228856 91101185 91101340 91105279 91108992 91200899 91205646 91206336 91209189 91212835 91224357 91221537 92102825 92105371
there are 746 applications for photographic patent of non silver-salt image. these make up 32% of 2,293 photographic patent applications in China in recent 10 years.

non silver-salt photographic materials are called non silver salt record materials these materials takes place chemical reaction to from images under the direct action of light. electricity. heat . and magnetism some of them have substituted silver halide record materials with respect to duplicating printing. reduction. holographic recording. transistor technology , large screen display. atomic energy technology. health electrical beam record etc. the non silver salt materials are considered as life force new type recording materials.

• Electronical photography creates of a static latent image making use of difference of light guide of optical transistor in the exposure and after
development and fixation, the permanent image can be obtained.

- Optical imaging system. It means that the light with sensitive layer is acted by the activity and to form an image with nitrogen photosensitive materials, photosensitive resin, and discolor materials.

- Thermosensitive recording materials. These materials are reacted to image making use of resistor heating, strong lighting source, laser scanning. These methods include thermal melt, volatilization transferring, chemical colour display lighting-heating image and electrical heating image system.

• Hot transfer 89104243.

• Plate making of print 92106447 92107507 92108340.

- Plate making machine 91229853 91230202 92102077

- Stamp technique 93110147 93110148.

- Transistor technique, 87104516 89109481 89109483 90109497.

- Silicon corrosion 92020633.

- Large screen display 85204070 86204819 88104255 90224829 93212326 93215168.

- Election beam recording 86105432.

• Plate making machine 91229853 91230202 92102077

- Guard against theft recorder 892202025 90208711.

- Radiation solidify magnetic record body. 92111427.

- Magnetic control tube 87106755.

- Magnetic paint 89108186 85105147.

- Recording materials 89108332 90108331 90106842 90109389 90109259 92114265 92115102.

- silicon corroson 92020633.

- Large screen display 85204070 86204819 88104255 90224829 93212326 93215168.

- Election beam recording 86105432.

- Guard against theft recorder 892202025 90208711.

92111427 is an application for magnetic recording patent. This application for magnetic recording patent. This applicant is from a Miningco of America. The invention name is magnetic recording body with methyl phenylethylene non-saturation radiation solidify adhesive magnetic recording body. There are 39 pages for this patent instruction. The article 13 in the right requirement protect radiation solid part of methyl phenylethylene.

Table 5

<table>
<thead>
<tr>
<th>classification</th>
<th>photosensitive</th>
<th>copy</th>
<th>holographic</th>
<th>blueprint machine</th>
<th>plate making</th>
<th>printing</th>
<th>Heavy nitrogen salt</th>
<th>Electrical photography</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quantity</td>
<td>105</td>
<td>93</td>
<td>70</td>
<td>47</td>
<td>28</td>
<td>24</td>
<td>15</td>
<td>13</td>
</tr>
<tr>
<td>Number</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8</td>
</tr>
</tbody>
</table>

**APPLICATIONS FOR PHOTOGRAPHIC PATENT OF ELECTRONIC IMAGE**

It is said that today has entered the age of chemical image and electronic image. That is to mark the times of multi-media is coming with respect to establishment of information expressway.

At that time the people does not require to purchase television, sound set, computer and telephone set and just only to buy an multi-media computer. There are 298 applications for patent of electronic image in recent 10 years in China, and these make up 13% in photosensitive applications in recent 10 years. Electronic image in the photosensitive field is a new type specialization. Because electronic image has made considerable headway in the areas of image capture, enlargement, treatment, store and display. The characteristics of electronic image has approached silver halide image with respect to resolving power.
adjustment scope and colour reveal. and numerals are used in a series of
electronic imagings.

The applications for patent of electronic image are as follows:
- Electronic photography 85105022 88108175 90109099 90109863 92110452
  92114626 93102536 93106207 93106367 93116843
- Colour mixer detecting device 86108832 86108833 86210535
- Image false colour 85100001 85100002 85100003 85103614 85103690 85108044
  87103046 87106523 88105422 88105947
- Colour correction device, cassette, plate 88211932 91220419 89205337
- Track information 89107799 89107800 89107795
- Magnetic film 89107802 89107803 89107804 89107805
- Magnetic numbering card 92202097
- Television prosection 91204106
- Photo-drawing machine 89215561 90214407 91225021 92104030 92110007 93207282
- Picture tube, screen 88100287 90100417 91105537 91107126 91108799 911111882
- Three-dimensional photograph without using film 94100215

94100215 is a latest application for patent in China by picture technical
international corp. of America in 5.oct. 1994. The date of priority for this patent
in America is 1.June.1993. There are 8 claim enclosed 8 pages of figures. It mainly
protects directe photographing, enlargement method and device without using film.
This can be used to blueprint the picture produced by computer, and real image.

(HAMC’S FILM)

I type of HAMC’s film was developed in 1976. In October in the same year,
original third industrial ministry held a technical appraisal meeting in HAMC.
The I type film has been developed jointly by HAMC, SAMC, XAMC and 301 institute.
X type of HAMC’s film was developed in 1986 and sold in the market. At the
same time patent application is granted. Its patent number is 86207979.9.
Economical benefit for it reached the users for this product are in 29 provinces.
W type of HAMC’s film was developed in 1990, and granted the patent of number
of 91108830.X.

HAMC’s positive blueprinting film is used widespread to aircraft, missile,
shippings automobile, coal mine, city plan, and capital construction filing. Main
characteristics for this film are as follows:
- Exposure: ultraviolet photosensitive and daylight operation
- Develop: Humidity/method
- Average density: D >2.0
- Store period: more than 7 years
- Store period of second original negative indefinite duration inside room
  and no fade outside room.
- No film layer at non line area.
- Blueprint can be made with second original negative
Harbin Aircraft Manufacturing Corporation is an aviation enterprise with a history of 43 years. Now HAMC is manufacturing Y12 aircraft, Z9 helicopter, and EC120 helicopter as well as minicar etc. We need the following items:

- Polyester base film with large size for high precision drafting and blueprinting:
  - 1.2m wide, 0.127 mm (0.005 in) thick with single side applied layers or double sides applied layers;
  - To ISO 9958-1 first part of Engineering drafting medium-polyester base film Requirements and mark;
  - To ISO 9958-2 second part of Engineering drafting medium-polyester base film Performance measuring;
  - Length of roll: 30m, 100m or 200m
- 2,1,6. photosensitive agent.
- Positive type heavy nitrogen salt.
- Negative type photosensitive resin.
- Scanner (1.2m -- 1.5m wide).
- Organic ink for Plotomat.
- Drawing paper for drawing machine (1.2m, 1.5m, 1.8m wide).
- Transmission optical density meter.

I would like to take this opportunity to get in touch with domestic or foreign manufacturer so as to promote sales of these products. Our telephone number is (0451) -8602122-3353. FAX (0451) -8602273, or 8601070. Post code 150066. Cable 2288. Tax register number 230108100110232. Bank: Xinjiang office, Harbin, industrial-commercial bank. Account: 801035001-80.

**CONCLUSION**

Today, the development of science and technicals in photographic field changes day after day and competition is sharp. On the one hand the manufacturer wants to occupy the market and to obtain a profit on the other hand the manufacturer wants to monopolize the market and get a legal protection so as to be not violated the rights. Because everyone is clear that the product is of the money and the technicals also of the money and it is a profit source.

In other words, if someone wants to occupy a larger market, he would applied for patent and get a patent certificate and possess a patent right. Meanwhile trademark application and bar code register should be carried out to complete protection of intellectual property rights. The purpose for issuing paper, and extending well-known condition is different from it.

Therefore, I put forward to carry out quantitative analysis for photosensitive patent application in recent 10 years in China. This involves photosensitive patent application and is an investigation and probing for the subsect.

The paper classifies photographic application for patent depending on three system and it is not exact systems. These systems are different as well as cross.
infiltration each other and are difficult to differentiate. Article 2,293 photographic application for patent in China is different from advertisement information. Patent literatures are information which is integrated with economical, legal information, and they are a material which has a potential market and also a study information for developing a new product.

I would like to discuss this subject with experts and personnels who are interested in it to follow the applications and analyze other technical and legal conditions in order to provide service for product development, science study and protection of intellectual property rights.

REFERENCES

ABSTRACT

The extraction of thematic information from TM images and the selection of optimal composition scheme have been a subject requiring a deep research in the fields of remote sensing application. However, so far there have been no complete sets of norms or standards to be followed, especially, in the quantitative calculation and prediction of image colorimetry as well as the related determination of optimal composition schemes.

Using TM images and applying separation exposure method, this paper discusses the standardization issue of extracting image thematic information, puts forward the method of quantitative calculation of colour difference and the theory of selecting the optimal composition scheme, and provides corresponding mathematical model.

Key words: TM image, Thematic information extraction, Standardization, Optical composition, Optimal composition scheme

1. INTRODUCTION

With the progress in space science and technology, remote sensing technology has been widely applied in the field of geoscience. In the field of atlas cartography, the extraction and processing of thematic information by using the data tapes and image materials received from satellites is a quick and efficient means to make thematic image maps and chart thematic map series. Obviously, the standardization of the original data and that of thematic information extraction serve as the basis for remote sensing cartography and quantitative calculation. Research on nonstandardized cartography and quantitative calculation will undoubtedly lead to confused conclusion and make it hard to compare with one another. Research shows that after several nonstandardized copyings, the image densities of some satellite negatives are, in fact, hardly transferable proportionally, and as a result, they have caused serious damage and loss of authenticity in image information and composite tones and also caused grey scale to lose the meaning of determining standard colour. Therefore, the issues concerning standardization of this nature have currently drawn the attention of some domestic scholars and they have conducted some corresponding research.

In May 1987, we had a field inspection in Shuangyang County, Jilin Province, and we chose as experimental zones the Yangjiandingzishan in the south mountain area and the Dasanjianzi region in the southwest of the County. Taking some typical vegetation types as experimental targets, we carried out a series of exploring research on the issue of standardization of optical image information extraction.

II. THE QUANTITATIVE PREDICTION OF THE COLORS OF GROUND OBJECTIVES IN TM IMAGES

Colours are the most essential elements and characteristic quantities of all colour composite images. The description and measurement of the spatial distribution and characteristics of colours are the basis for chromaticity measurement and its relevant analysis.

Given \( D_i \), as random variables in the two-normal distribution in TM images, then the
density function of this distribution equals to
\[
f(D_n, D_p) = \frac{1}{2\pi\sigma_n\sigma_p\sqrt{1-r^2}} \exp\left\{-\frac{1}{2(1-r^2)} \left[\frac{(D_n - m_n)^2}{\sigma_n^2} + \frac{(D_p - m_p)^2}{\sigma_p^2} - 2r(D_n - m_n)(D_p - m_p)\right]\right\}
\]
(1)

In the formula, \( m_n, m_p \) are respectively the mathematical expectations of random variables \( D_n \) and \( D_p \); \( \sigma_n, \sigma_p \) are their standard deviations and \( r \) the correlation coefficient.

Obviously, if we pick up a subsample \((D_{n1}, D_{n2}, \ldots, D_{nN}; D_{p1}, D_{p2}, \ldots, D_{p*})\) with a capacity of \( n \) from the population available for two-normal distribution, then in the straight line section of the characteristic curves in sensitometric materials, the following regression statistic equation is established
\[
D_p(\lambda) = a + bD_n(\lambda)
\]
(2)

As far as the separation exposure composite is concerned, the formula (2) can be revised as
\[
\begin{align*}
D_{p_{kij}}(\lambda) &= a_k + b_kD_{n_{kij}}(\lambda) \\
D_{p_{gij}}(\lambda) &= a_g + b_gD_{n_{gij}}(\lambda) \\
D_{p_{bij}}(\lambda) &= a_b + b_bD_{n_{bij}}(\lambda) \quad (i = 1, 2, \ldots, \pi; j = 1, 2, \ldots, 7)
\end{align*}
\]
(3)

Here, \( D_{p_{kij}}(\lambda), D_{p_{gij}}(\lambda), D_{p_{bij}}(\lambda) \) are the spectrum densities of the separation images of TM colour composites and the lower marker stands for positive photographic material, \( R, G, B \) respectively represent sensing red separation (or black), sensing green separation (or magenta) and sensing blue separation (or yellow) on the colour photographic paper. \( \lambda \) stands for wave length; \( D_{n_{kij}}(\lambda) \) the negative film density of its corresponding TM image band; lower marker \( N \) the negative photographic material; \( n \) the carrier distance; \( \beta \) the gradient; \( j \) for any ground objective image; \( \pi \) the number of TM band.

According to the standard equation established by the Commission Internationale de l'Eclairage (CIE) to calculate the colour tristimulus values, we can work out the expression formula to reproduce colour tristimulus values of TM colour composite images by using colour photographic paper.

\[
\begin{align*}
X &= 10^{-D_{p_{kij}(\lambda)}} \int_{\lambda_1} s(\lambda)\bar{x}(\lambda)d\lambda + 10^{-D_{p_{gij}(\lambda)}} \int_{\lambda_1} s(\lambda)\bar{y}(\lambda)d\lambda \\
&+ 10^{-D_{p_{bij}(\lambda)}} \int_{\lambda_1} s(\lambda)\bar{z}(\lambda)d\lambda \\
Y &= 10^{-D_{p_{kij}(\lambda)}} \int_{\lambda_1} s(\lambda)\bar{y}(\lambda)d\lambda + 10^{-D_{p_{gij}(\lambda)}} \int_{\lambda_1} s(\lambda)\bar{y}(\lambda)d\lambda \\
&+ 10^{-D_{p_{bij}(\lambda)}} \int_{\lambda_1} s(\lambda)\bar{y}(\lambda)d\lambda \\
Z &= 10^{-D_{p_{kij}(\lambda)}} \int_{\lambda_1} s(\lambda)\bar{z}(\lambda)d\lambda + 10^{-D_{p_{gij}(\lambda)}} \int_{\lambda_1} s(\lambda)\bar{z}(\lambda)d\lambda \\
&+ 10^{-D_{p_{bij}(\lambda)}} \int_{\lambda_1} s(\lambda)\bar{z}(\lambda)d\lambda
\end{align*}
\]
(4)
Here $s(\lambda)$ stands for spectral power distribution of illuminant; $x, y, z$ CIE 1931 Standard colorimetric observer spectrum tristinulus values.

Suppose $a_{11} = \int_{\lambda_1}^{\lambda_2} s(\lambda)d\lambda\,;\, a_{12} = \int_{\lambda_1}^{\lambda_2} \lambda s(\lambda)d\lambda\,;\, a_{13} = \int_{\lambda_1}^{\lambda_2} \lambda^2 s(\lambda)d\lambda\,(\lambda_1 = 380 \text{ nm};\, \lambda_2 = 500 - 600\text{ nm};\, \lambda_3 = 600 - 780\text{ nm})$

Following this example, suppose $a_{11}, a_{12}, a_{13}$, $a_{21}, a_{22}, a_{23}$, $a_{31}, a_{32}, a_{33}$, respectively, then we reach the matrix expression formula of (4)

\[
\begin{bmatrix}
X_i \\
Y_i \\
Z_i
\end{bmatrix} =
\begin{bmatrix}
a_{11} & a_{12} & a_{13} \\
a_{21} & a_{22} & a_{23} \\
a_{31} & a_{32} & a_{33}
\end{bmatrix}
\begin{bmatrix}
10^{-D_{Pr}_{i(4)}} \\
10^{-D_{Pc}_{i(4)}} \\
10^{-D_{Pr}_{i(4)}}
\end{bmatrix}
\]

Or simplified as

\[
\begin{bmatrix}
X_i \\
Y_i \\
Z_i
\end{bmatrix} = \begin{bmatrix}
10^{-D_{Pr}_{i(4)}} \\
10^{-D_{Pc}_{i(4)}} \\
10^{-D_{Pr}_{i(4)}}
\end{bmatrix}
\]

The coefficient matrix $A$ can be calculated according to the relative spectral power distribution of the adopted standard illuminant and with CI 1931 standard colorimetric observer tristimulus values, and when the wave length $\lambda = 380 - 780\text{ nm}$ and with $\Delta \lambda = 10\text{ nm}$ as spectral sampling interval. Apply coefficient matrix $A$ to formula (6), thus obtaining

\[
\begin{bmatrix}
X_i \\
Y_i \\
Z_i
\end{bmatrix} = 
\begin{bmatrix}
14.978 & 39.594 & 41.071 \\
5.392 & 75.173 & 19.435 \\
86.425 & 5.648 & 0.012
\end{bmatrix}
\]

Suppose the colour chromaticity amount to be

\[
C = X + Y + Z,
\]

Then the chromaticity coordinates of any ground objective colours in the colour composite image are

\[
x = X_i / C, \quad y = Y_i / C.
\]

Therefore, according to Munsell's renotation system, we can specify corresponding colour markings. It is not difficult to understand that after we have established the functional relationship between TM band image negative film density and the separation image spectral density of colour composite images, if we can predict the density value of the ground objective image in TM band negative film participating colour composition, then by applying formula (3), we can get the estimated values of spectral reflection density of the corresponding separation images; and then apply it to formula (7) and also according to formulas (8) and (9), we will be able to calculate the coordinate value of the image ground objective colour of any composite scheme. Thus we are able to determine its corresponding position in the chromaticity diagram and obtain through calculation the colour parameters, such as dominant wave length, colorimetric purity, and illuminance factor (or tone, saturation and brightness).

III. THE COLOUR STANDARDIZATION CONTROL ON TM COLOUR COMPOSITE IMAGE
The conditions of the colour balance and saturation of colour composite images chosen for qualitative and quantitative analysis directly affect the results of calculation and analysis. Consequently, it is of great importance to have standardization control on the colours of composite image.

As to separation exposure composition, a composite image meeting the requirements of colour balance and saturation should be applicable to the following formula

\[ D_{p1}, \ldots, D_{pn}, \ldots, D_{n}, \ldots, D_{np} = D_{p}, \ldots, D_{n}, \ldots, D_{np} \] (10)

In the formula \( D_{p1}, \ldots, D_{pn}, \ldots, D_{n}, \ldots, D_{np} \) stands for the separation images' standard density of the colour photographic paper's sensing red separation, sensing green separation and sensing blue separation (namely yellow, magenta, and cyan) required by Munsell standard colour samples.

Formula (10) shows that the mere control on colour balance does not necessarily guarantee an ideal colour saturation at the same time. That is to say, the identical densities of yellow, magenta, and cyan colour standards do not necessarily guarantee an ideal saturation. This is because the quality of saturation is closely related to density values. Therefore, only under the conditions that the 3 colours have equal densities and simultaneously reach the required standard density, can we eventually guarantee the correct reproduction of the original colours.

In theory, in order to convey the colours of images correctly, the relative sensitivities of the 3 separation emulsions on colour photographic paper must be identical. However, in manufacturing the paper, the relative sensitivities of the 3 separation emulsions are not the same. Therefore, when using TM image black and white negative films of TM images to compose, in order to get the same results of colour balance, we must see that the separation exposure times are impossibly equal, usually we use the following formula to calculate

\[
\begin{align*}
\tau_p &= \left( \frac{K_2}{F_2} \left( \beta + 1 \right)^2 \right) / \left( E_{pR} S_{pR} \right) \\
\tau_g &= \left( \frac{K_2}{F_2} \left( \beta + 1 \right)^2 \right) / \left( E_{pG} S_{pG} \right) \\
\tau_b &= \left( \frac{K_2}{F_2} \left( \beta + 1 \right)^2 \right) / \left( E_{pB} S_{pB} \right)
\end{align*}
\] (11)

Here, \( \beta = I_p / u_n \); \( E_p = \frac{1}{4} E_n T_n T_o T_{10} \). In the formula \( F \) stands for the diaphragm number; \( \beta \) for the lateral magnification (i.e., magnification factor); \( E_{pR}, E_{pG}, E_{pB} \) are colour triad illuminations cast by illuminant on the colour photographic paper; \( E_n \) is the illumination on the negative film; \( T_n, T_o, T_i \) are respectively negative film, lens and the transmissivity of the filter; \( S_{pR}, S_{pG}, S_{pB} \) stand for the separation sensitivities of colour photographic paper; \( K_2 \) for a specified constant used to measure the separation sensitivities of colour photographic paper; \( u_n \) the side length of negative film; and \( I_p \) the side length of magnified image.

Clearly, it is a rather time-consuming matter to get the separation exposure times through calculating method. Therefore, in actual composing process we may draw a curve of D-t to determine the separation exposure times. This method is both simple and accurate.

The theoretical basis for drawing a D-t curve is the sensitometric characteristic curve of D-lgT. Because the exposure amount \( H = E / T \), on the straight line section of the curve, when illuminance \( E \) remains the same, density \( D \) is the function of exposure time \( t \), namely \( D = f(t) \). So it is feasible to determine the separation exposure times which produce the predicted density (i.e., standard density) by using \( D - t \) curve. Moreover,
because the curve is drawn in accordance with real conditions, it is more pragmatically significant than sensitometric measurement.

It should be pointed out that after the correct separation exposure time is determined, under the same processing conditions, this time should be the same to any composition schemes since the determination of separation exposure time is set appropriately to any kind of colour photographic paper, which has nothing to do with the density of TM negative film images. Otherwise, it would cause change in TM image band density distribution and loss of balance in the fixed proportional relationship among band densities; it would also bring random change of image tones to the same composite scheme. And as a result, it would lead to the uncertainty of interpretation signs and to errors in aspect of quantitative analysis. Obviously, this is not allowed in the standardized composition of images.

In image processing, the correct implementation of operating regulations is the essential prerequisite to guarantee the optimal quality of images and to realize the standardized control.

The standardized control on TM colour composite images not only affects the correct reproduction of colours but also concerns the accurate conveyance of information capacity. As a matter of fact, the quality of some TM images is very bad indeed and the primary reason is that, in the process of replaying and afterwards copying the data tapes, the standardized operations were not implemented. This case, in which man makes the loading capacity of composite image information decrease, has affected the results of qualitative and quantitative interpretation to various degrees for a long time, and also it is very often overlooked. This should be given sufficient attention.

IV. THE SELECTION OF OPTIMAL COMPOSITE SCHEME FOR TM IMAGES

TM image has 7 bands altogether and there are various schemes for its composition. According to the theory of permutation and combination, for instance, if we choose any 3 bands (positive print and negative film) and use blue, green and red filters respectively for each band, the total number of the composite schemes $M$ will be

$$M = C_3^7 P_{K^w}$$ (12)

In the formula $n$ is the total number of the participating combination bands (for TM image, $n = 7$); $m$ is the randomly selected number of bands; $K$ is the number of the kinds of participating images. When we only use TM negative film images to combine, then

$$M = C_3^7 P_{K^w} = \frac{7!}{3!(7-3)!} = 35$$

Similarly, if the kinds of participating images increases, TM negative film, positive prints and their corresponding ratio images (i.e., $K^w = 4$), then the total number of the combining schemes will rapidly increase to 13440. This is really a startling figure. Obviously, we are unable to conduct experimental inspections of all this. Naturally, we have to find out a simple way to calculate, so as to select an optimal combination scheme quickly.

Research shows that different ground objectives vary in their spectral reflection
capacities. So in the same or different image combinations, colours vary from one another (except for metamerism). Namely, different ground objectives have chromaticity parameter differences from one another. Generally speaking, the bigger colour differences among ground objectives, the more convenient it is to have visual interpretations. Clearly, this composition scheme is, what we call, the optimal scheme. Biggest colour difference of different ground objectives.

According to the theory of colorimetry, we select CIE1976(L*, a*, b*) uniform colorspace and color difference formula to calculate the colour difference values of different ground objectives. Namely:

\[
\begin{align*}
L^* &= 116\left(\frac{Y_i}{Y_o}\right)^{1/3} - 16 \quad Y_i/Y_o > 0.01 \\
a'^* &= 500\left(\frac{X_i}{X_o}\right)^{1/3} - \left(\frac{Y_i}{Y_o}\right)^{1/3} \\
b'^* &= 200\left(\frac{Y_i}{Y_o}\right)^{1/3} - \left(\frac{Z_i}{Z_o}\right)^{1/3}
\end{align*}
\] (14)

In this formula, \(X_o, Y_o, Z_o\) are the tristimulus values of white object colour stimulus that CIE standard light source (D65) illuminates on the perfect reflecting diffuser and then reflects back in the observer's eyes; \(L^*\) is metric lightness; \(a'^*, b'^*\) are metric chromaticities.

The total colour differences between the above-marked 2 ground objectives can be worked out in the following formula

\[
\Delta E_{\text{CIE1976}} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}
\] (15)

Suppose among the \(n\) kinds of composition schemes, there are \(m\) kinds of colour difference values between every two ground objectives of \(i\) kinds in every composition scheme; then among all the available composition schemes, forms an \(n\) dimension colour difference value matrix \(\Delta E\), that is:

\[
\Delta E = \begin{bmatrix}
\Delta e_{11} & \Delta e_{12} & \cdots & \Delta e_{1i} \\
\Delta e_{21} & \Delta e_{22} & \cdots & \Delta e_{2i} \\
\vdots & \vdots & \ddots & \vdots \\
\Delta e_{n1} & \Delta e_{n2} & \cdots & \Delta e_{ni}
\end{bmatrix}
\] (16)

Obviously, \(\Delta e_{ki}\) (stands for the \(k\) number colour in \(i\) kind of scheme) stands for a multi-dimension random variable, namely, among \(n\) kinds of composition schemes there are \(m \times n\) number of colour difference values altogether. Hence we have worked out a computer programme instructing the computer to compare and put in order the \(m\) number of colour difference values of each scheme among the \(n\) kind of composition schemes. And then rearrange the order of the \(m\) number of the smallest color difference values in all the available composition schemes (from big to small).

Colorimetry study shows that 2 colours with big colour difference values are unnecessarily different in tones. This is closely related to the positions of chromaticity coordinates in the chromaticity diagram. If chromaticity coordinates are located incidentally near the border of 2 different colour gamuts, even though the colour difference value is very small, the 2 colours are likely to appear in different tones. Therefore, when we want to determine the optimal composition scheme, we must take hue into our considerations.

In order to make the computer provide corresponding colour marking number in accordance with the chromaticity coordinates, a data band should be established to offer Munsell
standard colour sampling chromaticity parameter. Thus we can refer to the corresponding hues and select as the optimal schemes kind of composite schemes with relatively bigger colour difference values.

V. RESULTS AND ANALYSIS

1. The quantitative analysis on colour balance of TM colour composite images

In order to make a quantitative judgement about colour balance situation of composite images, colour standards; yellow, magenta, cyan, blue, green and red should be marked on the margins of each image. Yellow, magenta and cyan are used to measure reflection densities, and to check the situation of colour balance; blue, green and red are used to check the colours of colour standards to see if they fit the standards of corresponding Munsell colour samplings. If conditions permitting, photoelectric colourmeter can be directly used in the measurement. Using American Machbath RD 519 reflection densitometer, we measured the density of the colour standards; the results of sampling measurement are shown in Table 1.

<table>
<thead>
<tr>
<th>Composite scheme</th>
<th>Density reading</th>
<th>Density to be deleted</th>
<th>Chromatic balance situation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B G R</td>
<td>Y M C</td>
<td></td>
</tr>
<tr>
<td>2 3 4</td>
<td>1.91 1.95 1.92</td>
<td>1.91</td>
<td>0.00 0.04 0.01 good tone</td>
</tr>
<tr>
<td>3 7 1</td>
<td>1.95 1.94 1.98</td>
<td>1.94</td>
<td>0.01 0.00 0.04 good tone</td>
</tr>
<tr>
<td>2 5 1</td>
<td>1.99 1.97 1.96</td>
<td>1.96</td>
<td>0.03 0.01 0.00 good tone</td>
</tr>
<tr>
<td>3 5 4</td>
<td>1.96 2.20 1.09</td>
<td>1.09</td>
<td>0.07 0.31 0.00 somewhat yellow &amp; red</td>
</tr>
</tbody>
</table>

It is easy to see in the above table that, except that chromatic balance effect of composition schemes 3(B) 5(G) 4(R) have shown some slight deviations because of the unstable voltage, the chromatic balance and chroma of other composition images have all achieved optimal effect.

2. Analysis on regression accuracy and prediction results

The TM images we use are standardized products by the country’s will determine the received satellite images strictly according to the standards set by American Look-up table (Please see Table 2) and finally output them in the form of grey scale together with image information. Therefore, grey scale of images can be used not only to identify image grey degrees (of illuminance), but also as checking standards for some quantitative calculation.

<table>
<thead>
<tr>
<th>Scale value</th>
<th>0</th>
<th>16</th>
<th>34</th>
<th>50</th>
<th>68</th>
<th>84</th>
<th>102</th>
<th>118</th>
<th>136</th>
<th>152</th>
<th>170</th>
<th>186</th>
<th>204</th>
<th>220</th>
<th>238</th>
<th>255</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear grey scale density</td>
<td>2.20</td>
<td>2.07</td>
<td>1.93</td>
<td>1.80</td>
<td>1.67</td>
<td>1.53</td>
<td>1.40</td>
<td>1.27</td>
<td>1.13</td>
<td>1.00</td>
<td>0.87</td>
<td>0.73</td>
<td>0.60</td>
<td>0.47</td>
<td>0.23</td>
<td>0.20</td>
</tr>
<tr>
<td>Band density</td>
<td>2.30</td>
<td>1.67</td>
<td>1.43</td>
<td>1.26</td>
<td>1.10</td>
<td>0.97</td>
<td>0.85</td>
<td>0.75</td>
<td>0.65</td>
<td>0.57</td>
<td>0.49</td>
<td>0.43</td>
<td>0.37</td>
<td>0.33</td>
<td>0.28</td>
<td>0.24</td>
</tr>
<tr>
<td>Beyond &amp; density</td>
<td>2.20</td>
<td>2.20</td>
<td>2.16</td>
<td>2.01</td>
<td>1.76</td>
<td>1.50</td>
<td>1.20</td>
<td>0.95</td>
<td>0.70</td>
<td>0.49</td>
<td>0.32</td>
<td>0.24</td>
<td>0.22</td>
<td>0.20</td>
<td>0.20</td>
<td>0.20</td>
</tr>
</tbody>
</table>
In accordance with this standard, we checked the grey scale in the negative film of TM bands 1-7 respectively. The result indicates that the range of grey scale densitise is about $0.12 \leq d_N \leq 2.31$, which basically accords with the standard set in the Look-up table. And then, we also checked the monochromatic wedges of yellow, magenta and cyan in the colour photographic paper printed with the negative film grey scales and conducted some statistical analysis on received data. Figures 2 and 3 and Table 2 are partial results of statistical analysis.

From the curves we can see that the 3 relation curves on Japan's Sakura color PC paper appear a reversed S type, only the central parts of the curves approach straight lines. Hence, in order to guarantee the predicting accuracy of the model, we only select the sample points on the linear section to form the regression equation.

Statistical analysis proves that $D_p$ and $D_N$ show a high negative correlation and their standard deviations are very small, which shows that the model's predicting accuracy is very high, too. (See Table 3). The coincidence between the result of actual prediction See table(4) and the curves also proves this conclusion. Although some predicted values of some ground objectives are somewhat bigger, which were mainly caused by random errors, apart from this, the degrees of predicted accuracy of other ground objectives points fluctuate within ±0.09. This accuracy can meet the requirements for chromaticity calculation.

Table 3 Regressive accuracy analysis of grey scale level on monochromatic image of TM image

<table>
<thead>
<tr>
<th>regression equation</th>
<th>standard deviation $S$</th>
<th>confidence probability $P(D_p)$</th>
<th>confidence interval</th>
<th>correlation coefficient *</th>
<th>degree of freedom $n - 2$</th>
<th>threshold of level of significance $\alpha_{1,\alpha}$</th>
<th>significance testing</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{p(y)}(\lambda) = \frac{2.042}{1.324D_{n(y)}(\lambda)}$</td>
<td>0.028</td>
<td>99.796</td>
<td>1.958</td>
<td>2.126</td>
<td>-1.324D_{n(y)}(\lambda) - 1.324D_{n(y)}(\lambda)</td>
<td>-0.999</td>
<td>13</td>
</tr>
<tr>
<td>$D_{p(m)}(\lambda) = \frac{2.465}{1.755D_{n(m)}(\lambda)}$</td>
<td>0.007</td>
<td>99.796</td>
<td>2.204</td>
<td>2.726</td>
<td>-1.755D_{n(m)}(\lambda) - 1.755D_{n(m)}(\lambda)</td>
<td>-0.991</td>
<td>13</td>
</tr>
<tr>
<td>$D_{p(c)}(\lambda) = \frac{1.972}{1.618D_{n(c)}(\lambda)}$</td>
<td>0.149</td>
<td>99.796</td>
<td>1.525</td>
<td>2.419</td>
<td>-1.618D_{n(c)}(\lambda) - 1.618D_{n(c)}(\lambda)</td>
<td>-0.973</td>
<td>13</td>
</tr>
</tbody>
</table>

Note: *** stand for high level of significance
Table 4 Predicting values compared with real measurement values of typical ground objective points on monochromatic image of TM image

<table>
<thead>
<tr>
<th>typical objective ground value</th>
<th>Snuavanz reservoir</th>
<th>Shitoukounen reservoir</th>
<th>Xinlicheng reservoir</th>
<th>larch</th>
<th>oak</th>
<th>cultivated land</th>
<th>colour standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>real measured value</td>
<td>( D_{N}(\lambda) )</td>
<td>0.94</td>
<td>1.03</td>
<td>1.22</td>
<td>0.66</td>
<td>0.69</td>
<td>0.69</td>
</tr>
<tr>
<td>predicting value</td>
<td>( D_{PR}(\lambda) )</td>
<td>0.79</td>
<td>0.67</td>
<td>0.48</td>
<td>1.15</td>
<td>1.10</td>
<td>0.91</td>
</tr>
<tr>
<td>error</td>
<td>( \delta )</td>
<td>0.01</td>
<td>0.01</td>
<td>-0.05</td>
<td>0.02</td>
<td>0.03</td>
<td>-0.09</td>
</tr>
</tbody>
</table>

| real measured value           | \( D_{N}(\lambda) \) | 0.25                  | 0.25                | 0.23  | 0.06                             | 1.13                             | 1.07                             | 0.10 |
| predicting value              | \( D_{PR}(\lambda) \) | 2.10                  | 2.12                | 2.10  | 0.84                             | 0.55                             | 0.51                             | 2.20 |
| error                         | \( \delta \)       | 0.07                  | 0.09                | -0.04 | 0.12                             | -0.07                            | 0.00                             | 0.09 |

| real measured value           | \( D_{N}(\lambda) \) | 0.41                  | 0.35                | 0.40  | 0.88                             | 1.14                             | 0.94                             | 0.10 |
| predicting value              | \( D_{PR}(\lambda) \) | 1.31                  | 1.49                | 1.13  | 0.39                             | 0.24                             | 0.27                             | 1.89 |
| error                         | \( \delta \)       | 0.00                  | 0.00                | 0.07  | 0.16                             | 0.11                             | 0.10                             | -0.08 |


3. Analysis on the results of the preferred composition schemes

In remote sensing interpretations, it is very hard to distinguish oak from larch and arbor from bush in 2(B), 3(G), 4(R) standard false colour composite images. For this end, we selected as typical experimental sample areas a man made larch wood and an oak wood in the Yangjuandingishan, southern mountain area in Shuanguang County, and near Dasanjiazi, we selected a comparatively larger area of bush and arbor. We used the method given in the paper to extract information. The results are shown in Tables 5a and 5b.

Table 5. Arrangement of colour difference order of typical ground objective classification by using scheme of the TM image composition

<table>
<thead>
<tr>
<th>time</th>
<th>May 31, 1986</th>
<th>September 23, 1987</th>
</tr>
</thead>
<tbody>
<tr>
<td>item</td>
<td>B</td>
<td>G</td>
</tr>
<tr>
<td>No.</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>7</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>12</td>
<td>2</td>
<td>3</td>
</tr>
</tbody>
</table>

Note: After Shuangyang figures 118-30, data Sept. 23, 1987
Table 5b Arrangement of color difference order of typical ground objective classification by using scheme of the TM image composition

<table>
<thead>
<tr>
<th>Time</th>
<th>May 31, 1986</th>
<th>September 23, 1987</th>
</tr>
</thead>
<tbody>
<tr>
<td>Item</td>
<td>B</td>
<td>G</td>
</tr>
<tr>
<td>No.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>41</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>60</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

Note: Colour marking number N VJC = tone brightness value /chroma, B—blue, P—purple, N—neutral, PB—purple blue, and infer others in the same way.

In order to reduce the calculating work load, we deleted TM 6 thermal infrared band, which is irrelevant to vegetation. Then the would-be schemes were 120 kinds (See Table 5). Because the TM negative film lacked band 7 in May, we deleted the TM band 7 in September for the convenience of comparing with different times. So the available schemes for selection in Table 5 are only 60 kinds.

All the calculating work of parameters has been completed by IBM - PC computer.

The calculating results show that the optimal composition schemes to distinguish oak forest from that of larch are not schemes 3(B) 7(G) and 1(R), which gave the biggest color difference values, but are schemes 2(B) 7(G) 1(R) which have smaller colour difference values, but better tone, chroma and brightness. This accords with the above-mentioned theoretical proofs. However, the effect of this scheme appears to be the worst in distinguishing settlements from cultivated lands. This shows that the scheme does give prominence to vegetation information.

From Table 5b we can see that the TM images of different times greatly affect the effects of composition. For example, if we select the TM image composition in May and use the composition schemes 4(B) 5(G) 3(R) to distinguish arbor from bush, the effect is relatively much better. However, if we use TM images composed in September, the effect of the scheme is far from being ideal. From the data in composition schemes 2(B) 3(G) 4(R), we can see that several types of the above-mentioned vegetations are truly hard to distinguish.

It should be pointed out that when the research theory and methods in this paper are applied to extract thematic information, the results are closely associated with the quality of satellite images, the times and many other factors. If the image data used for composition are very bad themselves, then the results of information extraction and of scheme selection can not be very satisfactory. Therefore, the so-called "optimum" is only a term relative to the basic image data.

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THE FUNDAMENTALS OF THE RADIATION THERMAL TECHNOLOGY FOR CEMENT PRODUCTION

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ABSTRACT

The fundamentals of principally new radiation thermal way of cement production are presented. The peculiarities of qualities and structure of clinker obtained by this way are given. The technical economic advantages of the new technology are shown.

INTRODUCTION

Radiation thermal (RT) way of obtaining cement clinker, based on the usage of the powerful beams of accelerated electrons as the source of energy have been suggested in the 70th (1). Despite the far-off perspectives of industrial realization (mainly due to the insufficient power of the recent accelerators and relatively high prime cost of generated energy) the development of cement technology on the base of RT way was stimulated by energetic and ecological situation and by the need in the intensification of cement production. At present the fundamentals of RT way technology is possible to consider as already developed. Among the number of electrotechnological methods RT is one of the most effective as it provides practically unlimited concentration of energy, introduction it into the bulk of material (on the depth of the electron range) and as a consequence the heating of the raw material to the temperatures of clinker formation in a seconds in the conditions closed to the adiabatic.

EXPERIMENTAL PART

At the initial laboratory stage of work on the accelerators up to 20 kw the kinetic properties of RT clinker formation and the main interrelations between chemicominaleralogical composition and the structure of the clinker, energetic parameters of the clinker formation process and the quality of the cement obtained have been studied(2,3).

For the further improvement of RT technology of cement and other energy capacity products an experimental device on the base of industrial accelerator ELB-6 with a power of electron beam up to 100kWt (4) and the energy of electrons up to 1.5 MeV has been put into operation in Novosibirsk. Accelerator alongside with the emission of electron beam through the foil has a system of concentrated emission through the aperture of a small diameter.
very perspective for the high temperature processes.

A number of constructions of radiation thermal apparatus (RTA) of clinker obtaining in a beam of electrons have been tested on this device. Conveyor schemes with the translocation of material perpendicular to the linear transverse beam do not provide the uniformity of the clinker and demand surplus (on 50% and more) energy expenses. The shaft-conveyor and particular shaft types of RTA proved to be significantly more effective. They provide the translocation of material particles from the surface into the depth of the radiation zone and in result obtaining a product more uniform in properties with minimal energy costs. Applied to shaft apparatus the questions of uniform distribution of raw flow and electrons along the surface of radiation zone, the interaction of chemically active clinker obtained with elements of RTA is excluded. The generation of ozone is practically eliminated. The systems of formation of radiation fields of rectangular type, providing the coefficient of beam power use about 80% in space were established.

RESULTS AND DISCUSSION

To the number of main results of the laboratory stage of work should be refereed the discovery of the effect of radiation (superthermal) activation of solid phase interaction in the process of clinker formation which alongside with the realization of known advantages of rapid burning sharply intensifies the process in a whole.

Experimental data obtained in the investigations of chemico-technological interrelations of RT clinker formation on the apparatus of shaft type coincide in the main with the conclusions made earlier (1-3) on the laboratory stage (see fig. ). It was confirmed that from the viewpoints of even changes of size the safe limit of free lime content in RT clinkers comprise 3.0-3.5%. At the same time in burning in the kiln the clinker with the free CaO content = 1.7% have not stand the test on the even changes of size. Clinkers with the free CaO content up to 2.5 -3.0% have as a rule high strength parameters (45-59 MPa after 28-day hardening). Comparative study of strength parameters of clinkers obtained from one and the same raw mixture in the rotary kiln and RT way and containing close values of free CaO have shown significantly higher activity of the latter on all timings of hardening (on 5-15 MPa) than the activity of clinkers from the rotary kiln.

The phenomenon of overradiation which was found out in the laboratory experiments and is characterized by the decrease of RT clinkers activity with the occurrence on the microsections fused zones with large acicular alite crystals 200 µm and more takes place in clinkers obtained in the shaft type. However the decrease of activity is observed when significant part of the microsection space has the structure of fused clinker and maximum size of alite crystals attain 700 µm and above. Sometimes the indication of alite decomposition and its solution in the intermediate substance and secondary belite is fixed.

The dependence of clinker activity from the free lime
Interrelation between clinker activity $A$ and alite $C_3S$ (a) content in it, deviation $\Delta A = A - A$ and clinker microstructure parameter $L_{\text{max}}$ (b) as well as $\Delta A$ and the dose absorbed $D$ (c) when hardening during 3, 7, 14 and 28 days.
content has an extreme character and the maximum of activity is observed in dependence from the power of the dose absorbed in the different content of free CaO. The observed decrease of activity with the free CaO = 1.8% (for the dose P= 60 kGy/s) correlates properly with the petrography data according to which these samples have all signs of clinker overradiation.

The relationship of RT clinkers activity obtained on the experimental device and their alite content is linear and rather strong for clinkers without signs of overradiation. With the increase of alite content the activity of these clinkers on all timings of hardening increase on 10-20 MPa. With overradiation which has a negative effect as on energetic and strength parameters the influence of chemico-mineralogical composition on the clinker activity sharply decreases.

Investigations on the sequence and way of mineral formation in radiation of raw mixtures do not revealed any significant anomalies in the mineralogical composition of clinkers and intermediate products in comparison with traditional thermal burning. The difference can be seen only in the kinetic of these processes which is stipulated by the different heating rates. With high intensities of radiation and corresponding rates of heating the RT clinker formation processes shift to the more high temperatures. Particular distinctly the temperature shift is observed with the rates of heating over 50 K/sec, though this shift in the conditions of radiation-thermal processing is smaller than in the analogous change of heating rate in the case of rapid thermal burning. Exposure of material under maximal temperature after completion of radiation practically always promote more complete proceeding of clinker formation processes. From the other hand rapid cooling of clinker after indicated exposure totally remove such unpleasant phenomenon as alite decomposition.

Conditions of rapid heating of raw mixture by the electrons beam with following (during several minutes) exposure of material under high temperature and then fast cooling of clinker after its grinding most effectively are realized in the RT apparatus of shaft type.

The results of investigations of chemico-technological interrelations and process and succession of mineral formation in RT synthesis of cement clinker allowed to choose the most rational scheme of sintering process which gives the possibility of more full proceeding of all clinker formation reactions and obtaining of optimal crystalline structure and hydraulic activity. From the viewpoint of productivity increase of RT apparatus it is better to use more high power values of absorbed doses. This, however, can lead to the not uniform sintering processes. The way out is in the definite exposure of material at the final temperature of the processes which could compensate unfavorable aftermaths of the too fast heating. For the optimization of technological process it is necessary to find rational correlation between the rate of material heating and time of isothermal exposure which would allow with the maximal productivity to get good quality clinkers. The temps of heating in the shaft RTA are determined by the density of beam current.
(and with the given full current by the square of shaft section). The time of exposure at the maximal temperature is determined by the height of clinker block forming in the shaft (to be more precise - by the distance from the surface of the radiation zone to the rolls of mill). The rate of clinker cooling in the block is not high, this is provided by the cementation of the material at the high temperatures and only after grinding in the mill the rate of cooling increase in many times. This prevent decomposition of the main mineral of the clinker - alite which takes place at the slow cooling.

CONCLUSIONS

The basic advantages of the radiation technology are as follows:
- no need for natural organic fuel for production purposes;
- improvement of strength quality and special properties of cement;
- significant reduction in dust and harmful matter emission to the atmosphere;
- essential reduction of the dimensions and metal content of the production units due to the hundredfold rise in the clinkering rate;
- the possibility of getting the valuable by-product-high concentration CO₂.

Despite all indicated advantages in the economic relation radiation technology of common cement forms would become competitive to the modern dry method of production there and then where and when the share of conventional electric power plants appear to be less than 50% of the general electric energy balance of the country. That is why it is expedient the first experimental-industrial technological lines to orient on the production of expensive special kinds of cement by radiation method.

From the ecological point of view the radiation technology and today if it was worked out in the industrial conditions would be out of competition. It should be kept in mind that every year demands of environment protection to the industrial production would increase and correspondingly would increase expenses spend on the environmental protection means and therefore prime cost of the product increase. One of the global problems - the struggle with the hotbed effect, caused by the increasing production of carbonic gas. In result the objective tendencies towards curb of introduction new conventional electric power plants and propellant capacious productions.

These factors can call for the radiation technology as inevitable alternative to the classical one in the coming XXI century.

The existence of unique electrophysical equipment and universal qualities of accelerator as a source of energy allowed to conduct on the experimental device a wide spectrum of works on the obtaining nonorganic materials and thermal processing of metals. The perspective of usage of electron beams for the fulfillment of high temperature synthesis of ceramic compounds,
abrasive, special glasses, catalysts and so on have been shown in experiments. Economically effective production of complex oxide materials which are the base for the obtaining ceramic with unique characteristics was organized on the experimental device.

One of the perspective directions is the usage of radiation thermal processes for the obtaining particular fireproof, electrotechnical and a number of other kinds of cement for the synthesis of which it is necessary more high temperatures than in obtaining the common portland cement and higher demands are placed to the purity of the product.

The development of radiation thermal method of cement clinker obtaining gave start to the outgrowth of a new effective area of high temperature nonorganic technology, allowing to obtain diverse materials which is difficult to synthesize by the other methods.

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RADIATION PROCESSING of POLYMER INSULATORS, as a METHOD of IMPROVING THEIR PROPERTIES and PERFORMANCE

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ABSTRACT

Polymer insulators for electric apparatus and high-voltage overhead lines are promising for replacing porcelain and glass insulators. It was showed the possibility of application of radiation-chemical technology by manufacture of rod-shaped polymer insulators. It this work was used an ethylene and vinyl acetate copolymer as the polymer basis of the composition for insulators. By forming a three-dimensional network in polymer bulk radiation processing improves service properties of polymer insulators: shape and heat stability > 200 °C and stability to tracking erosion > 200 h.

INTRODUCTION

Rod-shaped polymer high-voltage insulators are increasingly used in power engineering for electric apparatus and overhead power transmission lines (35-110 kV) (1). Their advantages are due to the properties of the polymer material: it is dielectric, exhibits low density, the absence of brittleness, and higher discharge characteristics in the wet and soiled condition. Their mass is smaller because metal details are absent and plastic fiber glass rods with a high tensile strength are used. Moreover, the use of polymer insulators simplifies transport, mounting, and other operations and reduces their cost. It is particularly advisable to introduce these insulators in the electrical engineering for constructions in regions difficult of access. In order to prepare polymer insulators, their coatings are made from polymer composites based on silicone rubbers, fluorine-containing copolymers, and other thermoplastics (1). However, all these polymers are relatively expensive.

We used an ethylene-vinyl acetate copolymer (EVA) as the polymer basis of the compositions for high-voltage insulators. It is relatively cheap and can be processed by molding. However, products made from these polymer compositions exhibit low shape stability at high ambient temperatures because their Vicat thermal stability is ∼85 °C. Moreover, these compositions are insufficiently stable to tracking erosion when insulators operate under the conditions of wet and dirty surface.

In order to eliminate these defects it is desirable to carry out radiation processing which induces the formation of a three-dimensional network throughout the polymer bulk (2). In order to optimize the process of radiation crosslinking of EVA functional additives were proposed by us. The stable to tracking erosion was ensured by introducing aluminium hydroxide as filler.
Polymer compositions. The composition contained EVA with a vinyl acetate unit content of 12 mole % and a filler, aluminium hydroxide, in approximately equal molar ratios. This composition is known in the CIS countries under the trademark SEVA-II3-I2. This composition also contains a light stabilizer and a thermostabilizer. As additive of sensitizer of radiation-induced crosslinking was used N,N' -m-phenylene dimaleimide (PDMI).

Radiation processing. The radiation processing of the EVA composition was carried out with use of 60Co on K-30000G radioisotope unit (2,3). The content of the gel fraction was determined by extracting the polymer portion soluble in hot xylene.

Properties of radiation-processed polymer compositions and insulators. DSC thermograms were recorded in air in the temperature range from 20 to 350 °C with a DSC-D instrument. Thermomechanical curves (TMC) were obtained with a Hexpler consistometer. Stability to tracking erosion; this test was carried out in according with procedure described in (4).

RESULTS AND DISCUSSION

I. Radiation processing.

Gamma radiation not only ensures the permissible uniform formation of a three-dimensional network throughout the polymer bulk but also makes it possible to control easily the network density by varying the absorbed dose. In order to determine the effect of the filler and the sensitizer on the rate of radiation-induced EVA crosslinking, pure EVA not containing these components was used in control experiments (Table 1).

Table I. Radiation processing of EVA and its compositions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Medium</th>
<th>% of gel fraction and (M x 10^-3) at an absorbed dose, (kGy)</th>
<th>D_g</th>
<th>G_g/G_x</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>100</td>
<td>200</td>
</tr>
<tr>
<td>EVA</td>
<td>Argon</td>
<td>63.0</td>
<td>75.4</td>
<td>94.0</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>47.9</td>
<td>50.2</td>
<td>53.0</td>
</tr>
<tr>
<td>SEVA-II3-I2</td>
<td>Argon</td>
<td>49.5</td>
<td>63.9</td>
<td>75.6</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>38.5</td>
<td>15.0</td>
<td>75.5</td>
</tr>
<tr>
<td>SEVA-II3-I2+</td>
<td>Argon</td>
<td>57.5</td>
<td>61.6</td>
<td>75.3</td>
</tr>
<tr>
<td>+ 2 % PDMI</td>
<td>Air</td>
<td>31.2</td>
<td>49.2</td>
<td>56.0</td>
</tr>
</tbody>
</table>

These data indicate that in the investigated range of absorbed dose EVA and its compositions are mainly crosslinked and the values of G_g/G_x are in agreement with the published data (5). Thermostabilizer and probably aluminium hydroxide and PDMI slightly decrease the yield of the gel fraction and the effect of degradation, but the presence of PDMI profoundly affects the network density. In all cases air oxygen leads to greater degradation. Consequently, these experiments have shown that by increasing the network density PDMI plays the role of the sensitizer of the radiation-induced crosslinking of the poly-
aer composition based on EVA. PDMI was also effective for other polymers undergoing radiation processing: polyisoprene, polyethylene, polyvinylidene fluoride, etc (2,5,7).


Shape stability. Since the main aim of radiation-processing of composition based on EVA was to increase shape stability at raised temperatures, in investigating the composition properties the main attention was devoted to this parameter. For this purpose TMC were obtained. The analysis of TMC showed that the dose rate and the absorbed dose do not change essentially the softening temperature \( T_s \) as compared to that of non-irradiated samples \( T_s = 90-100 \, ^\circ\text{C} \). However, a sample that obtained the absorbed dose of 200 kGy at 0.4 kGy/h is more readily deformed and decreases \( T_s \) to 35 \( ^\circ\text{C} \) than those irradiated with the same dose but at 2 and 10 kGy/h \( T_s = 95 \, ^\circ\text{C} \). This phenomenon is probably due to partial polymer degradation caused by the action of ozonized air which is accumulated in the irradiation chamber cell upon prolonged exposure. For filled EVA composition with 2 mass \% PDMI irradiated with different doses at different dose rates, TMC show (5) a region of equilibrium deformation, which probably combines with the formation of network of different chemical nature. This we obtained early at crosslinking of polyvinylidene fluoride (5).

The evaluation of the yield point determined by the stress at which the sample begins to flow, i.e. to lose its primary shape at 100 \( ^\circ\text{C} \) showed that SEVA-II3-12 and its composition with PDMI can flow at low loads before radiation processing (Fig. 1). Radiation processing increases the flow limit to 0.9-1.2 MPa depending on the dose rate, and the addition of 2 \% of PDMI increases it to 5 MPa. This performance of the composition can guarantee high shape stability of products in service. These data also are agreement with DSC results.

![Fig. 1. Flow rate of SEVA-II3-12 and its compositions with 2 \% PDMI vs. load at 100 \( ^\circ\text{C} \).](image)

DSC curves (Fig. 2) showed the melting temperatures of the crystalline phase of EVA, the beginning \( T_n \), the maximum rate and the end of the first stage of the exothermic process which probably corresponds to sample oxidation not accompanied by mass loss. DSC thermograms were used to calculate
the total heat evolution \( (\Delta H) \) in J/g. Beginning from 190 °C DSC thermograms show the development of oxidizing processes in the non-irradiated EVA. The components of SEVA-I13-I2 increase polymer resistance to oxidation, and \( T_b \) rises 253 °C. The addition of PDMI to the non-irradiated composition increases \( \Delta H \) from 10 to 35 J/g as compared to EVA, which results from the thermal crosslinking of the polymer. This process occurs simultaneously with oxidation and \( \Delta H \) characterizes the overall exotherm. Radiation processing decreases the resistance of the composition to oxidation, and \( T_b \) is displaced to lower temperatures. Moreover, a distinct negative effect of low dose rate is observed. Thus, for SEVA-I13-I2 irradiated with a dose rate of 0.4 kGy/h the \( T_b \) of oxidation is 190 °C whereas for the non-irradiated sample it is 263 °C. Irradiated samples of SEVA-I13-I2 with the addition of PDMI it are characterized by a decrease in \( T_b \), in particular at a dose rate of 0.4 kGy/h. However, in the presence of PDMI \( \Delta H \) is lower for ~3 times than that of the radiation-processed composition without the additive. Hence, PDMI prevents the occurrence of thermo-oxidative degradation of the polymer. This fact agrees with the data obtained for the EVA without a filler but containing 2-5 mass % PDMI.

Consequently, this investigation made it possible to establish the following optimum conditions of radiation processing of insulators based on EVA in the presence of PDMI from the standpoint of the formation of a three-dimensional network: the absorbed dose up to 200 kGy at a dose rate of 10 kGy/h in air.

The parameters of shape stability and stability to tracking erosion were also studied for finished insulators. For this purpose a SEVA-I13-I2 coating consisting of several sheds was applied to fiber glass plastic rod by compression molding and the insulator obtained was subjected to radiation-processing of optimum dose rate and absorbed dose.
Table 2. High-voltage rod insulators based on a copolymer of EVA manufactured by radiation-chemical procedure at St. Petersburg State Technical University

<table>
<thead>
<tr>
<th>Insulators type</th>
<th>Purpose</th>
<th>Nominal voltage, operating voltage, kV</th>
<th>Highest stress, kN</th>
<th>Minimum failure stress, kN</th>
<th>Path length of leakage, cm</th>
<th>Height, mm</th>
<th>Shed diameter, mm</th>
<th>Mass, kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPS-0.8/10-II UKhL I</td>
<td>Line post insulator for 10 kV</td>
<td>10</td>
<td>12</td>
<td>0.8</td>
<td>30</td>
<td>215</td>
<td>100</td>
<td>1.3</td>
</tr>
<tr>
<td>IPS-0.8/10-IV UKhL I</td>
<td>Used as line-post rotational insulator elements for 10 kV voltage, frequency up to 100 Hz</td>
<td>10</td>
<td>12</td>
<td>0.8</td>
<td>42</td>
<td>305</td>
<td>90</td>
<td>1.6</td>
</tr>
<tr>
<td>IPP 70/35</td>
<td>Suspension insulator for substations and overhead power lines, 35 kV voltage, frequency up to 100 Hz</td>
<td>35</td>
<td>42</td>
<td>70</td>
<td>95</td>
<td>650</td>
<td>60</td>
<td>2.0</td>
</tr>
<tr>
<td>IPSP 110/70 UKhL I</td>
<td>Strain insulator for contact systems of railways and for circuits of 110 kV and frequency up to 100 Hz for general industrial use</td>
<td>110</td>
<td>73</td>
<td>70</td>
<td>276</td>
<td>1270</td>
<td>90</td>
<td>3.0</td>
</tr>
</tbody>
</table>

457 a) Intershed distance 30 mm; b) Bending stress; c) Operating conductor-earth voltage.
The evaluation of shape stability consisted of maintaining polymer insulators in boiling water for 4 h. At this case the change in the shed shape which initially had been conical was followed visually. All irradiated insulators (100-200 kGy) passed these tests successfully, whereas non-irradiated insulators lost their shape in the first hour of maintenance in boiling water and subsequently the sheds melted. The tests for shape stability above 100 °C in a heat chamber showed that irradiated insulators retain their shape up to 200 °C, but with the addition of PDMI is higher 200°C. This is probably due to the inclusion into the polymer network of rigid-chain maleimide fragments exhibiting high heat stability (2).

Stability to tracking erosion. This test showed that radiation processing does not decrease the main insulator property: its stability to tracking erosion (200 h), which is due to the presence of the filler aluminium hydroxide. For the composition containing PDMI this parameter is even slightly higher at absorbed doses of 100-200 kGy, which is probably caused by greater network density and the nature of the imide fragments present in it.

At present in St. Petersburg regions (Russia) several types of high-voltage polymer insulators based on EVA are manufactured with the application of radiation-chemical technology (9) and are being successfully used in practice in the central region of Russia (Table 2).

In our opinion, the characteristics of the shape- (heat) stability of radiation-processed polymer insulators make it possible to use them in regions with hot climate as well.

CONCLUSIONS

Hence, the radiation processing of polymer insulators based on the compositions of EVA is very suitable to the manufacture of insulators with high shape stability for high-voltage overhead power transmission lines (35-110 kV) and electric apparatus. The use of PDMI as the sensitizer of radiation-induced crosslinking decreases the required absorbed dose and increases the product shape stability and its resistance to oxidation.

REFERENCES

SAWDUST-CLAY-CEMENT-PLASTIC COMPOSITE PREPARED
BY GAMMA IRRADIATION

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ABSTRACT

A new material of sawdust-clay-cement-plastic composite has been prepared by impregnation of unsaturated polyester resin with different parts of styrene and methyl methacrylate (MMA) monomers into the void spaces of completely dried and molded specimens followed by exposure to Co-60 gamma radiation to induce graft copolymerization of the impregnated monomers onto the sawdust-clay-cement matrix. For each monomer mixture, suitable impregnation time and the radiation dose has been determined. High compression strength and bending modulus of specimens show that this material is comparable with high strength concrete. The hydration of sawdust-clay-cement matrix after molding for 1 up to 28 days shows that hydration products which deposited within the pore-spaces, decrease the porosity of the composite. The effect of the polymer loading content, as affected by the porosity, on mechanical properties is more effective than hardening of cement portion after hydration.

KEYWORDS

composite; impregnation; unsaturated polyester; irradiation.

INTRODUCTION

Polymer-impregnated materials have received increasing interest in recent years due to the improvements in their physico-mechanical properties such as high strength, low permeability and good durability. These composites are also attractive because of their potential for utilization of relatively cheap or even waste as the initial raw material for their production. In this type of composites, polymer simply fills the void spaces of the body so that the strength of the composite begin to approach the idealized strength of space-free materials. Wood plastic- (Sheikh, 1993), clay plastic- (Wang, 1981, Dessouki, 1986), paper plastic- (Wang, 1979), sugar maple plastic- (Schneider, 1990) and concrete plastic-composite (Swamy, 1979) are the most famous polymer-impregnated materials.
Sawdust is a wood waste material which is produced in very large quantities in forests and timber factories. One possible use of sawdust is in the preparation of sawdust-clay-cement-plastic composite (SDCCP) by radiation processing. This material could be used as new industrial or housebuilding material Wang prepared sawdust-clay-polymer composite by impregnation of liquid vinyl monomers (Wang, 1983).

The object of the present work is to study the making of polymer impregnated sawdust-clay-cement composites and optimization of impregnation time and irradiation dose for different monomer systems. Compressive and bending strength of the composites and its relation to the polymer loading content have been studied.

**EXPERIMENTAL**

In this work "Beech" which is one of the Iranian hardwoods has been used. A "Retsch muhle" grinder was used to produce the needed wood particles which passed through a 20 mesh screen and remained on a 40 mesh screen. Woods (especially hardwoods) show inhibiting reaction on the curing mechanism of cement (Moslemi et al., 1984). To improve wood particles compatibility with cement, some type of treatments can be done (Lee et al., 1989). Hot water extraction treatment was used to remove water soluble components in wood such as sucrose and resinous substances.

The cement used in this study was type I Portland cement.

Two types of unsaturated polyester comonomer system were used by mixing of unsaturated polyester from "Iranketone" company (grade No. 121 L) with styrene and methyl methacrylate with the following formulations:

<table>
<thead>
<tr>
<th>Unsaturated polyester</th>
<th>Type A</th>
<th>Type B</th>
</tr>
</thead>
<tbody>
<tr>
<td>styrene</td>
<td>35</td>
<td>30</td>
</tr>
<tr>
<td>methyl methacrylate</td>
<td>0</td>
<td>10</td>
</tr>
</tbody>
</table>

**Methods**

Forty tons hydraulic press was used for measuring compressive strength of 5x5x5 cm samples.

The prepared samples with dimensions of 14.5x5x0.5 cm were tested for bending strength by the Instron 6025 (three point test, velocity: 1 mm/min), using the standard ASTM 1037-72a.
Sample Preparation

A wet mixture of wood sawdust, clay, cement and water with ratios of 1:2:1:3 was molded in suitable specimen mold. The specimens were divided into two parts, one for studies on unhydrated composites, while the other part was for water treatment. After molding the unhydrated samples were dried at a constant temperature of 105 °C for 24 hr. The other part of molded specimens when cured at 100% R.H. for 24 hr and then immersed in water at room temperature until the desired times of hydration, produced the hydrated samples. The specimens were hydrated for 1, 3, 7 and 28 days, then they were immersed in methanol/acetone mixture (1:1 by volume) for two hours and then dried at 105°C for 24 hr.

Latter step comprises the impregnation of two unsaturated polyester-monomer systems (type A and B) into the void spaces of completely dried molded specimens under vacuum, followed by exposure to cobalt-60 source of the Gamma-cell-220 (Dose rate: 9 Gy/sec) to induce graft copolymerization of the impregnated monomers onto the sawdust-clay-cement matrix.

RESULTS

Determination of Suitable Impregnation Time

The dry molded samples allowed to soak in the monomer systems under vacuum for different impregnation times from 1 to 5 hours. After irradiation (at 15 and 30 kGy respectively for comonomer systems type A and B) percentage of polymer formation is increased until three hours of impregnation time. But, after that time percent of polymer formation decreases (Fig. 1 and 2). This might be due to the fact that after irradiation, the formed radicals induce curing of the impregnated monomer system. By increasing monomer concentration, with longer impregnation time, more radicals are formed. These excess radicals which have remained in the sample and do not initiate polymerization reaction, cause scission of some chemical bonds and therefore decreasing of properties. So, the best impregnation time for this composite is selected three hours.

Determination of Suitable Dose

After impregnation of both comonomer systems into the dry molded samples, they were irradiated at different doses. Maximum compressive strength of the irradiated samples was reached for comonomer system type A at a dose of 15 kGy (Fig. 3). For type B a dose of 25-30 kGy was required to obtain the maximum compressive strength (Fig. 4). So, for impregnated samples with monomer system type A, irradiation dose of 15 kGy and for type B dose of 30 kGy was selected.
Determination of Homocopolymer

The extraction of homocopolymer from samples which are impregnated for three hours, was carried out using Aceton-Benzene cosolvent (70:30 Vol.%) for 100 hours with soxhlet extractor and the results are summarized in table 1.

Table 1

<table>
<thead>
<tr>
<th>Sample specification</th>
<th>Monomer type</th>
<th>Dose (kGy)</th>
<th>Wt. before extraction (gr)</th>
<th>Wt. after extraction (gr)</th>
<th>Extracted homocopoly. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>15</td>
<td>2.0025</td>
<td>1.8966</td>
<td>5.29</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>30</td>
<td>2.0008</td>
<td>1.8947</td>
<td>5.30</td>
</tr>
</tbody>
</table>
It is obvious from this table that formed homocopolymer from both monomer types in the impregnated and irradiated samples is low. This is due to nearly complete grafting reaction which has occurred between composite constituents and unsaturated polyester comonomer.

**Compressive and Bending Strength**

a - Unhydrated samples

Compressive and bending strength of the composites which are impregnated at different times indicate that for both comonomer systems impregnation for three hours gives maximum compressive strength (Fig. 5 and 6) and bending strength (Fig. 7 and 8) which are consistent with the polymer formation results. Compressive strength of this composite is 700-900 Kg/cm² while this property for concrete is normally 200-400 Kg/cm².

Enhancement of the mechanical strength of the impregnated composites relate to:
1- The penetration of monomer into the wood cells and pore spaces existed by initial hydration of cement.
2- The amorphous clay constituents increase the number of crosslinks to form a network structure (Ahmed et al., 1986), particularly the amorphous silicate in the clay's chemical structure to be effective to the radiation in situ graft copolymerization (Wang, 1981).

![Compressive strength vs impregnation time](image1)

**Fig. 5** - Compressive strength vs impregn. time for SDCCP impregnated by comonomer system type A and irradiated at 15 kGy.

![Compressive strength vs impregnation time](image2)

**Fig. 6** - Compressive strength vs impregn. time for SDCCP impregnated by comonomer system type B and irradiated at 30 kGy.
b- Hydrated Samples

In SDCCP composite system, sawdust act as the fibrous filler for reinforcing the composite system. Clay and cement are binder ingredient in this composite, and water cause hydration of cement's silicates and aluminates. Volume of formed voids depend on water content in the formulation and cement hydration amount, which is very important in monomer impregnation into the composite (fig. 9). So, hydration effect of cement on mechanical properties of composite has been studied. The results show that with increasing the aging time of hydration from 1 day up to 28 days, the hydration products of cement formed and act as binding centers between the partly

- Polymer formation into the pore spaces of cement.
hydrated cement grains. On the other hand, as hydration proceeds, larger amounts of hydration products were deposited within the pore-spaces and therefore, the total porosity decreases. This decrease in the porosity of the hardened matrix with increasing age of hydration, accounts for the decrease in the polymer load content and therefore causes decrease in the compression strength of the composite (Fig. 10).

Fig. 10 - Effect of hydration age on compressive strength for SDCCP impregnated by comonomer system A and irradiated at 15 kGy.

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γ-RADIONYSIS OF 18C6 COMPLEXES WITH ALKALINE EARTH METAL CHLORIDS.

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ABSTRACT

Paramagnetic and gaseous products of γ-radiolysis of complexes 18C6 with alkaline earth metal chlorides were studied by ESR-spectroscopy and gas-chromatography. Stabilized at 77 K radicals were identified and the paths of products formation were proposed. The main process of γ-radiolysis is C-O bond cleavage and -O-CH-CH₃ radicals formation. The nature of cation captured in crown-ether hole effects on mechanizm of polvether ring rupture significantly.

INTRODUCTION

The danger of liquid radioactive waste is well known. The existing methods of diluted waste utilization aren't effective ones and very intensive investigations are conducted in this field. It have been established earlier that macrocyclic polvethers or crown ethers formed stable complexes with metal ions in wide pH range of aqueous solutions [1]. From this point of view it seems very perspective to use crown ethers (CE) for selective extraction of radioactive metal ions from multicomponent solutions. A number of extraction systems, membranes and sorbents on the base of CE were created. The efficiency of macrocyclic polvethers with oxygen atoms appears to prevail traditional agents (e.g. TBP) one [2]. Reprocessing of radioactive solutions proceeds in conditions of high energy radiation action. It's necessary to know the behaviour of extractant or sorbents in this conditions. Very important factors are radiation stability of CE and their complexes with metal salts and the nature of products forming under irradiation.

The investigation of processes proceeding under γ-irradiation of CE complexes has significant scientific interest. Radiation chemistry of heterocyclic and macrocyclic compounds is studied insufficiently. Earlier it was found that γ-radiolysis of "free" CE included both H-atoms abstraction from polyether ring and C-O bond cleavage [3]. Influence of metal cation captured in macrocycle on mechanizm of radiation-chemical reactions is unknown. The aim of present study was to investigate the behaviour of 18C6 complexes with alkaline earth metal (AEM) chlorides under γ-irradiation at 77 K.
EXPERIMENTAL

The complexes BeCl$_2$18C6, MgCl$_2$18C6, CaCl$_2$18C6, SrCl$_2$18C6 and BaCl$_2$18C6 were chosen for study. The results of elemental analysis. NMR and IR-spectroscopic data demonstrated the absence of impurities. The pumped specimens were γ-irradiated by Co at 77 K and 293 K. ESR spectra were registered on "Bruker ER-420" and "Rubin" radiospectrometers in X-range at 77-293 K. Irradiation of the sample by UV- and visible light was conducted in resonator directly by means of mercury lamp. The gaseous products were analysed chromatographically [4].

RESULTS AND DISCUSSION

ESR spectra of γ-irradiated at 77K 18C6 complexes are shown in Fig.1. γ-irradiated BeCl$_2$18C6 (D=10 kG) gives a triplet with hyperfine splitting of 1.2 mT, $g$=2.0031 and relative intensity of components 1:1:1 (Fig.1.a). When the temperature of the sample is increased to 293 K triplet transforms to quintet with 1.0 mT splitting and intensity of lines 1:2:3:3:1.5. Increasing of UHF power leads to saturation of central line of triplet. Unfreezing and UV-irradiation ($\lambda$=340-380 nm) of the sample result in similar changing of spectrum. Amplitude of the central line begins to increase.

The spectrum of γ-irradiated at 77 K MgCl$_2$18C6 is shown in Fig.1.c. It represents an inequidistant septet with $g$=2.0025 and relative intensity of the lines 1:2:1.5:3:1.5:2:1. Total width of spectrum is about 8.0 mT. Both UV-irradiation and unfreezing of the sample result in irreversible transformation of the signal to triplet.

ESR spectrum of γ-irradiated CaCl$_2$18C6 (77 K) contains a poor resolved quintet with 2.0 mT splitting and $g$=2.003 (Fig.1.e). Under UV-irradiation of the sample quintet transforms to triplet with 2.0 mT splitting and relative intensity of lines 1:1:1. When the sample temperature is increased quintet transforms to inequidistant quartet with equal ratio of components intensity. When CaCl$_2$18C6 is irradiated at room temperature (293 K), the spectrum of stabilized radicals represents a doublet with $g$=2.0038, equal intensity of components and splitting of 1.8 mT.

ESR spectrum of γ-irradiated SrCl$_2$18C6 is shown in Fig.1.g. It contains a inequidistant asymmetrical multiplet. Total width of the signal is about 8.5 mT. Unfreezing of the sample results in increasing of the central line and decreasing of the side lines of the spectrum. UV-irradiation of the sample doesn't cause noticeable changes in the ESR spectrum. Keeping the sample at room temperature leads to transformation of multiplet to doublet with $g$=2.0037 and splitting of 1.7 mT.

γ-irradiated BaCl$_2$18C6 gives a spectrum consisting of triplet with splitting of 2.0 mT and intensity of lines 1:3:1 (Fig.1.h).
The analysis of ESR spectra shows that under γ-irradiation of CE complexes at 77 K several different radicals stabilize simultaneously. It's easy to notice the signal of -O-CH-CH₃. Spectrum of this radical has been interpreted earlier [5]. It represents a quintet with 2.0 mT splitting and g=2.0023. We suppose that the broadening of the spectrum lines may result in unresolving of the side component in case of BeCl₂18C₆ and BaCl₂18C₆. The increasing of spectrum central line under UV-irradiation of BeCl₂18C₆. MgCl₂18C₆ and CaCl₂18C₆ is caused by phototransformation of -O-CH-CH₃ radicals to -C=O ones [6].

![ESR spectra diagram](image)

a.c.e.g.h - experimental spectra of BeCl₂18C₆. MgCl₂18C₆. CaCl₂18C₆. SrCl₂18C₆ and BaCl₂18C₆ at 77 K. b.d.f.i - simulated spectra of BeCl₂18C₆. MgCl₂18C₆. CaCl₂18C₆ and BaCl₂18C₆.

Fig.1. Experimental and simulated ESR spectra of 18C₆ complexes with AEM chlorides.
It should be noticed that quintet is the most intensive signal in spectra of 18C6 complexes. The doublet with splitting of 1.7-1.8 mT and $g=2.0037-2.0038$ seems to belong to $-\text{CH-CH}=\text{O}$. Such parameters of signal are typical ones for aldehyde radicals [7]. As in case of "free" 18C6 doublet is the only signal in $\gamma$-irradiated at 293 K complexes $\text{CaCl}_2\text{18C6}$ and $\text{SrCl}_2\text{18C6}$. The lines of doublet are registered in spectra of $\gamma$-irradiated at 77 K $\text{BeCl}_2\text{18C6}$, $\text{CaCl}_2\text{18C6}$ and $\text{SrCl}_2\text{18C6}$.

Analyzing the spectrum $\text{MgCl}_2\text{18C6}$ quartet with 2.3 mT splitting and $g=2.0023$ was found. The components of quartet dissappear quickly under UV-irradiation and unfreezing of the sample. We attributed this signal to $\text{CH}_3$ radicals formed after C-C bond cleavage. In addition we suggest that intensive central line in spectrum $\text{BaCl}_2\text{18C6}$ with $g<g_e$ represents to acyl radicals $-\text{C}=\text{O}$.

The proposed interpretation of ESR spectra was confirmed by computer simulation. The results of simulation and used radical parameters are given in Tabl.1.2 and Fig 1(b.d.f.i).

Table 1. The weights of radicals in simulated ESR spectra.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Weights of radicals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$-\text{C}=\text{O}$</td>
</tr>
<tr>
<td>$\text{BeCl}_2\text{18C6}$</td>
<td>-</td>
</tr>
<tr>
<td>$\text{MgCl}_2\text{18C6}$</td>
<td>-</td>
</tr>
<tr>
<td>$\text{CaCl}_2\text{18C6}$</td>
<td>-</td>
</tr>
<tr>
<td>$\text{BaCl}_2\text{18C6}$</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Table 2. Radical parameters used in ESR spectra simulation.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Parameters of radicals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$-\text{C}=\text{O}$</td>
</tr>
<tr>
<td>$\text{BeCl}_2\text{18C6}$</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$g=2.0035$</td>
</tr>
<tr>
<td>$\text{MgCl}_2\text{18C6}$</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$g=2.0027$</td>
</tr>
<tr>
<td>$\text{CaCl}_2\text{18C6}$</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$a(H)_1=41.0$</td>
</tr>
<tr>
<td>$\text{SrCl}_2\text{18C6}$</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$g=2.0037$</td>
</tr>
<tr>
<td>$\text{BaCl}_2\text{18C6}$</td>
<td>$g=2.0015$</td>
</tr>
<tr>
<td></td>
<td>$g=2.0029$</td>
</tr>
</tbody>
</table>
Thus the following scheme of radicals formation may be suggested:

![Scheme](https://example.com/scheme.png)

Similar processes are observed under irradiation of unsubstituted CE and 15C5 complexes with AEM chlorids [3, 8]. Main process of 18C6 complexes γ-radiolysis is C-O bond rupture following by rearrangements and formation of final functional groups -CH₃, -OH, -CH=O.

Recently we have studied radiation stability of 18C6 complexes [9]. Radiation-chemical yields of radicals and molecular hydrogen are situated in range $G_r=5.6-10.1$ and $G_H=0.7-1.1$ respectively. Radical products is formed in process 1 mainly because $G_r >> 2G_H$.

It's known that complexing ability of CE is determined by undamaged state of their cyclic structure. For example, the linear molecules with the same number of donor atoms have weak cation binding properties. On the other side complexing ability depends on the structure of final groups. The stabilization of aldehyde and alcohol groups under γ-irradiation of CE and their complexes is favour for keeping of complexing ability. Moreover it may lead to high selectivity of cation binding. Such effect was found when the properties of CE with aldehyde groups have been studied [10].

One of the factors determining the selectivity and efficiency of complex formation is the correspondence the cation diameter $D_{cat}$ to macrocycle hole size $D_{macr}$. Analogous dependence was found for radiation stability of complexes of unsubstituted CE with AEM chlorides [4, 9]. Radiation-chemical yields of
stabilized at 77 K radicals seems to be maximum in case of complexes with Dc~t~Dc~cr. The results of present study show that cation size influences on the mechanism of γ-radioysis (Table 1). This effect may be caused by different coordination number of cation and distinction of cation-donor atoms interaction energy in investigated complexes.

CONCLUSION

The radicals -O-CH-CH₃ formed after C-O bond cleavage of macrocycle are main product of 18C6 complexes with AEM chlorides γ-radioysis. In addition the processes of polyether bond destruction accompanied by H-atom abstraction and rearrangements of final groups are observed. Diameter of cation influenced on the paths of macrocycle destruction significantly. It may be caused by difference of interaction energy between cation and donor atoms, coordination number of cations etc.

The authors are grateful to Dr. E.I.Grigor'ev for helpful discussion of results. The study was carried out with the financial support of the Russian Foundation of Fundamental Research (grant N93-03-4648).

REFERENCES

High speed coating machine for radiation curing

Tony Zimmermann, Polytype Fribourg, Switzerland

During the past 2 years Polytype has built half a dozen coaters with radiation curing and for high production speeds.

This paper deals with some of these installations and their subassemblies.

UV curing silicone coater

The following layout shows a silicone coater with the following technical data:

1 Unwinder
2 Flexo printing unit
3 Corona station
4 Coating unit
5 UV-Processor system
6 Edge trimming unit
7 Rewinder

Width: 2200 mm
Machine speed: 400 m/min
Type of silicone: UV curing (not requiring inerting)
Substrates:
   Paper 45 - 140 gsm
   LDPE 25 - 100 microns
   PET 12 - 50 microns
Main components of the line

- **Unwind with automatic flying splice**

Both heavy and lightweight materials can be handled, thanks to double tension control with D.C. motors. Complete with movable and independent reel-holding shafts on which two reels with different web widths can be loaded.

- **Silicone coating unit**

- This unit is amongst the most sophisticated available on the market.
- The coating cylinders, some of which are of a deflection compensating type, the lever groups and the micrometric controls are assembled on an extractable trolley. The trolley is fitted with an air-cushion system which, in spite of its weight, allows easy extraction and replacement by the operator.
- All cylinders are driven by D.C. motors, which allow precise speed setting over a wide range and most of all excellent settings.
- Besides very accurate face finishing, the cylinders are temperature controlled for thermal stability thus ensuring coating accuracy over time.
- Silicone coating can either be full width or in strips. For quick changing of the coating width rubber-covered speedwell cylinders are used, i.e. a steel mandrel and a rubber covered sleeve, which can be changed directly through the machine frame.
- All control systems are complete with gap pre-setting, stop-settings, silicone level control and feed system.

- **UV polymerisation unit**

Supplied by Fusion who have accumulated a lot of practical experience in the field. This unit is assembled around a driven chill drum which allows perfect control of the web at the outlet and prevents possible temperature increases of the substrate, which is very important with heat sensitive substrates such as PE.

- **Slitting unit**

The slitter is equipped with knives and razor-blades both for web trim and a central cut for rewinding of two reels on the same shaft.

- **Rewinder with automatic flying splice**

- The rewinder is equipped with both surface and centre winding. The reel can be wound both in contact and with gap winding relative to a pulling drum. The gap is kept constant as the reel diameter increases.
- Constant web tension or pre-set taper tension. This flexibility gives the operator the possibility to choose the characteristics of the final reel.
- Hydraulic reel unloading onto various transport systems available at the customer's factory.

**Framework and idle rolls**

Robust construction for high-speed operation, with rolls of high precision and sensitivity.
Between unwind and coating unit a two colour printing unit will be added with UV polymerisation technology.

**Supervision system**

The machine is equipped with modern, high production features and is fitted with a man-to-machine interface system with computer-aided controls for parameter reading and setting. This is integrated with a recipe memory, particularly important for the coating unit.

**Combined UV and EB curing silicone coater**

This layout shows a coater for EB and UV curing silicone systems requiring inertings. This machine can later be extended so that a substrate can be coated on both sides.

The lay-out of the machine permits step-by-step extensions, such as drylaminating equipment.

1. Unwind  
2. Edge guide unit  
3. Corona treater/Pull roll unit  
4. Coating head  
5. EB-Unit with Chill roll  
6. UV-Unit  
7. Edge guide unit  
8. Cooling roll unit  
9. Rewind

31710mm (1248.4)
Technical data

Webs:  
PE       0.5 - 10 mil (0.012 - 0.254 mm)  
PETP     0.25 - 10 mil (0.006 - 0.254 mm)  
PP       0.5 - 4 mil (0.012 - 0.100 mm)  
Paper    12 - 90 lbs per ream (20 - 150 gsm)

Min / max web width  40 inch (1016 mm) / 80 inch (2032 mm)  
Max machine speed     1700 ft/min (~ 518 m/min)  
Web tension in the machine 40 - 1250 N (guide rolls with tendency drive)  
Coating weight       0.25 to 1 lbs per ream (0.4 to 1.6 gsm)  
Precision obtained during acceptance tests: ± 0.03 lbs per ream (± 0.05 gsm)

This high precision can be obtained due to a special arrangement of the coating rolls, the use of a patented deflection compensating roll and especially the dimensions of the coating rolls, which are calculated with appropriate mathematical models.

- Supervisory Computer

The system has been designed specifically to perform data collection of all parameters which are available through the PLC system. The computer displays will be designed to allow the operators convenient access to displaying parameters in a historical format so that the machine operator can use the computer as a tool to perform adjustments. The system is also provided with the capability to be utilized for process and machine analysis. Process variables can be selected for long term storage or for real time trending. This data can be used for generating dedicated to performing alarm logging. Every occurrence of alarm on, off and acknowledge is date and time stamped and printed.

Proserve +

Proserve + is a modern based PLC maintenance service, available to Customers who have a Circonix PLC and supervisory system.
Coater for EB curing coatings

This installation is a coater for technical coatings regarding radiation curing.

The lay-out of the machine permits step-by-step extensions, such as drylaminating equipment.

1. Unwinder
2. Embossing Roll
3. Coating unit
4. Corona station
5. Edge guide unit
6. Electron Beam-Unit
7. Rewinder

Width: 1700 mm
Speed: 200 m/min
Subrates: Film and paper with a wide range of thickness
Highly flexible pilot plant for thermal UV and EB curing coatings

I would like to take this opportunity to present once again the pilot plant in our Tech. Centre in Fribourg, on which all basic and specific R-D work was done for all the solventfree, 100% solids application requiring radiation curing for which we built installations lately.

Layout

1. Unwinder
2. Multipurpose coating unit
3. Infrared ramp (short wave)
4. Infrared ramp (medium wave)
5. Flotation drier
6. Dry laminating station
7. Unwinder
8. Corona treater
9. Edge guiding
10. Remoisturizing station
11. Cooling rolls
12. Cooling rolls
13. Rewinder
14. Electron beam unit "BroadBeam®"
15. Unwinder
16. Corona treater
17. Laminating unit
18. UV system

- Web width 400 - 840 mm
- Mech. machine speed 10 - 1000 m/min
This installation, which is operated by four full-time specialists, is used for testing technologies, and is also available to our customers for trials.

The multipurpose coating unit on the pilot plant is equipped with various types of trolleys, allowing about 40 different applicator systems. The pilot plant also includes EB equipment capable of 1200 MRad meters per minute at 250kV as well as a UV unit with 2 rows of F600 Fusion-lamps and 2 rows of lamps that can be inerted to 20 ppm oxygen, a short-wave and medium-wave infrared drying unit, and a floatation dryer with 3 upper and 3 lower drying zones, each independently temperature controlled. The floatation dryer can be changed quickly and easily to a guide-roll dryer with impact jet nozzles. Two laminating stations are incorporated, one which can operate at temperatures up to 230° C. The pilot plant, furthermore, includes three corona treatment units and a rehumidification unit, as well as various instrumentation systems and auxiliary equipment such as FID monitoring, inline infrared coating-thickness measurement, etc. In view of the high EB performance, the machine is designed to run at speeds between 10 and 1000 m/min (33 - 3300 ft/min). In order to simulate production conditions as closely as possible, the pilot installation is made of standard components of our production machines.

In order to handle the very low coating weights all the installations which were introduced are equipped with 5 roll cooling heads.
Roll coating unit for 100% solids, solvent-free cooling media

Due to a special arrangement of the rolls, using deflection compensating rolls, we can guarantee that the variations in the width of the footprint are negligible.
During tests of 3000 ft/min (900 m/min) we have found that footprints up to 3/4" are required, therefore, line pressure must go up to 20 N/mm.

Special attention has to be paid to misting; not all silicone formulations are suitable for such high speeds. Polytype always provides exhaust equipment with the critical roll configurations.

For speeds above 2000 ft/min. (600 m/min.) edge wipers as width limitations are no longer suitable to prevent splashing, that means that the coating width has to be adjusted between the first two rolls.

At extremely high speeds, special attention must be paid to the winding equipment. Unwinds with lap-splice must have provision to ensure that the length of the tails remains within close tolerances over the full speed range.

Using this coating head, we can guarantee a coating tolerance of ± 0.05 gsm over the whole width and the full speed range.
The paper deals with the electron accelerator pilot station in Bucharest, Romania - the Scientific Research Institute for Electrostatic processes and Electrotechnologies (S.C ICPE ELECTROSTATICA SA).

I. Introduction

The research programme in the fields of radiation chemistry using accelerated electrons and of the electron accelerator construction started in ICPE, ELECTROSTATICA Laboratory, in 1970, taking over the experience acquired by the Institute of Atomic Physics, Bucharest, founded in 1950 and equipped with ion accelerators, a 12 MeV cyclotron purchased from the former Soviet Union, a 15 MeV Tandem purchased from H.V.C.-U.S.A. and a 30 MeV Betatron for electrons, constructed within the Institute of Atomic Physics. The research activities have allowed for the main aspects with direct applications to the economy, namely:

- graft production of textile materials with improved properties (non-crease materials, higher resistance to high temperatures, high adherence to paints, improved mechanical properties);
- production of wires and cables with reticulated polyethylene insulation (with a considerable increase in the operating temperature, in the resistance to the solvent action, etc.);
- production of shrinkable polyethylene tubes for the electric cable insulation, characterized through thermal resistance and a low value of the dielectric losses;
- production of low density expanded polyethylene with a severely controlled cellular structure and with improved thermo-mechanical properties;
- achievement of semiconductor devices by ion implanting;
- sterilization of medicines, animal or human textures or organs meant to the transplants, of certain medical instruments which do not allow the sterilization through boiling;
- preservation of food products with the complete maintenance of their nutritive value;
- seeds disinfection or their treatment with a view to increasing production per hectare, or the quality improvement of certain cultures;
- longer period of warehousing for certain agricultural farm produce.

In order to achieve the research foundation ICPE - ELECTROSTATICA Laboratory has constructed a series of electron accelerators since 1972, (Fig 1) namely:

- an electron accelerator of 2 MeV, 600 W direct electron accelerator, with Van Graaff electrostatic generator, as a high voltage source, which was mounted at the Bucharest University, The Faculty of Chemistry, the Atomic Power Plant of the Radiation Chemistry Department, in 1974 (Fig 1a);
- in cooperation with the professorial staff of this department and the scientific researchers from the Scientific Research Institute for Physical Chemistry, ICPE- ELECTROSTATICA Laboratory has developed the main aspects of the programme:
  - an electron accelerator of 600 KeV, 30 kW, with insulated core transformer, for a pilot designed for the drying of the varnishes deposited on wooden plates (Fig 1b);
  - an electron accelerator of 2000 KeV, 40 kW, with insulated core transformer for the pilot station of the institute (Fig 1c).

2. Pilot station structure

2.1 Electron accelerators

a) ILU - 6 M electron accelerator (Fig 2 a,b) constructed by the Academy of Sciences, The Institute of Atomic Physics - Novosibirsk;

b) ADE - 2000/40 electron accelerator (Fig 3 a,b), constructed by S.C ICPE ELECTROSTATICA SA, with the following features:

<table>
<thead>
<tr>
<th>The main features</th>
<th>ILU-6M</th>
<th>ADE-2000/40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron energy</td>
<td>1.0-2.5 MeV</td>
<td>0.4-2 MeV</td>
</tr>
<tr>
<td>Beam power</td>
<td>* within the range, min 20 kW</td>
<td>40 kW</td>
</tr>
<tr>
<td></td>
<td>* in the middle of the range, max 40 kW</td>
<td>100 kW</td>
</tr>
<tr>
<td>Energy stability</td>
<td>+ 5 %</td>
<td>+ 5 %</td>
</tr>
<tr>
<td>Current instability</td>
<td>+ 5 %</td>
<td>+ 5 %</td>
</tr>
<tr>
<td>Sizes:</td>
<td>* height, max 1880 mm</td>
<td>7000 mm</td>
</tr>
<tr>
<td></td>
<td>* diameter, max 1219 mm</td>
<td>2400 mm</td>
</tr>
<tr>
<td>Weight:</td>
<td>* accelerator 2200 kg</td>
<td>1200 kg</td>
</tr>
<tr>
<td></td>
<td>* additions 6112 kg</td>
<td>6500 kg</td>
</tr>
<tr>
<td>Power supply</td>
<td>* voltage 380/220 V±10 %</td>
<td>380/220 V±10 %</td>
</tr>
<tr>
<td></td>
<td>* number of phases 3 with null</td>
<td>3 with null</td>
</tr>
<tr>
<td></td>
<td>* frequency, consumed power 50 Hz, 120 kW</td>
<td>50 Hz, 100 kW</td>
</tr>
</tbody>
</table>

2.2 Equipment for the transport of materials under electron beam

- devices: drum diameter 500 mm; output 10-600 m/min; speed stability 5 %; the transport diameter of the products that are going to be irradiated (cables and conductors 1.4-1.5 mm; tubes 2.6-20 mm; installed power 10 kW).
Fig. 2  ILU - 6M electron accelerator

Fig. 3  ADE - 2000/40 electron accelerator
2.3 Machines for the thermoshrinkable tube expanding

<table>
<thead>
<tr>
<th>Features</th>
<th>Type RR-C1</th>
<th>Type RR-S2</th>
<th>Type ES-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter range</td>
<td>1.2-7mm</td>
<td>6-19mm</td>
<td>20-60mm</td>
</tr>
<tr>
<td>before expanding</td>
<td>2-3</td>
<td>2-3</td>
<td>2-3</td>
</tr>
<tr>
<td>Contraction in length max</td>
<td>5%</td>
<td>5%</td>
<td>5%</td>
</tr>
<tr>
<td>Number of swelling lines</td>
<td>4</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Rate of absorption</td>
<td>120m/h</td>
<td>120m/h</td>
<td>120m/h</td>
</tr>
<tr>
<td>Supply voltage</td>
<td>3x380V; 50H</td>
<td>3x380V; 50H</td>
<td>3x380B; 50H</td>
</tr>
<tr>
<td>Installed power</td>
<td>6.5kW</td>
<td>9kW</td>
<td></td>
</tr>
<tr>
<td>Air pressure</td>
<td>0.4MPa</td>
<td>0.4MPa</td>
<td>0.4MPa</td>
</tr>
<tr>
<td>Sizes:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>* length</td>
<td>3600mm</td>
<td>7000mm</td>
<td>3000mm</td>
</tr>
<tr>
<td>* width</td>
<td>1150mm</td>
<td>3600mm</td>
<td>3000mm</td>
</tr>
<tr>
<td>* height</td>
<td>1300mm</td>
<td>1350mm</td>
<td>4000mm</td>
</tr>
<tr>
<td>Weight</td>
<td>1000kg</td>
<td>1000kg</td>
<td></td>
</tr>
</tbody>
</table>

2.4 Construction

2.4.1 Building construction

The building designed and executed for the Pilot station belongs to an assembly of modulated constructions. The building body is a construction lying on 6 bays of 8.00 m and 2 openings of 9.00 m and consisting of: basement, being 4.5 m in height; ground floor, being 4.5 m in height; three floors, each being 3 m in height; roof, being 12.50 m in height (Fig. 4). The laboratories, the service, research and design workshops are distributed on the floors according to the necessary technological functions and they are provided with an adequate lighting and natural ventilation.

2.4.2 The building body is a construction lying on 6 bays of 6.00 m and openings of 9.00 m and consisting of: basement, being 4.5 m in height; ground floor, being 4.5 m in height; three floors, each being 3 m in height; roof, being 12.50 m in height (Fig. 4). The access between the floors is ensured through the location of a staircase and elevator for materials weighing 500 kg. The staircase was calculated function the total number of employees.

2.4.3 Facilities - The building is provided with all the facilities: electrical power, thermal energy, inside and outside lighting, hydro-thermal equipment, equipment for compressed air, ventilation.

3. Control of the working area

3.1 Some considerations about electron accelerators

3.1.1. ILU-6M accelerator

The operating principle of the ILU-6 accelerator is the following: it is a linear RF accelerator with only one resonance cavity, in tune with the frequency ranging between 115 and 120 MHz (Fig. 5). The resonance cavity is supplied by a RF pulse-modulated generator with high-power tube (triode GI-50A). The resonance cavity is mounted in a vacuum enclosure, the electrons are injected by means of a thermo-electronic cathode injector and they cover only once the cavity acceleration interval after they are focussed and introduced in the sweep and beam extractor.

There are two types of sweep beam extractors:

a) classical, of linear type (funnel);

b) with double passing of the product (tubes, cables), for irradiation from opposed directions, of the "first" type.

The beam energy and current are continuously measured on the control panel. The control system is provided with the connecting, disconnecting and adjustment controls in the proper order.

3.1.2. ADE-2000/40 accelerator

This is a DC accelerator with voltage generator. The high voltage generator is three-phase transformer with 3 primaries and 40 secondaries. The core is divided in 3 columns and each column, in the area covered with the outside lighting, hydro-thermal equipment, equipment for compressed air, ventilation.

The resonance cavity is mounted in a vacuum enclosure, the electrons are injected by means of a thermo-electronic cathode injector and they cover only once the cavity acceleration interval after they are focussed and introduced in the sweep and beam extractor.

Fig. 4 The ground floor:

1 - the small hall with 16.95 m height and the 64.13 m² useful area; 2 - the great hall with 16.95 m height and the 294 m² useful area; 3 - the hall of gamma radiation sources with 8.95 m height and the 37.20 m² useful area; 4 - the ventilation station; 5 - the mechanical workshop with tool machines for maintenance; 6 - the mechanical workshop with tool machines for maintenance; 7 - the health units; 8 - the biological protection with 8.95 m height; 9 - the lift house; 10 - the house of stairs; 11 - the great hall with equipment with 2.5 m height and the 15 m² useful area.
different conditions of the irradiated products. However, the combination of the parameters for various conditions are stored in the programmable logic controller and a setting of a code number corresponding to a given combination will be sufficient for the control of each apparatus for the desired operation.

3.2. The irradiation process

In the atomic power plant, the following products will be achieved through accelerated electron beam irradiation:
- thermoshrinkable tubes (with memory effect of polyethylene and other compositions);
- cross-linked polyethylene for electric conductors and cables;
- other products of the chemistry under radiations obtained through polymerization, cross-linking, grafting, etc.
- adhesive tapes;
- products of medicopharmaceutical technique sterilized through accelerated electron irradiation.

The technological irradiation process develops in the following way: the products pass through the beam, before the output window of the beam extractor, driven and guided by two starting-driving devices existing in two adjacent chambers; one for the non-irradiated product and the other for the irradiated product. These two passages through the protecting screen are compulsory and will be dealt with later on.

In the case of the thermoshrinkable tubes, it is necessary to have, in addition, a pre-tension equipment which is placed just in the irradiation room. It can be displaced in order to enable the access in case of need.

The control is ensured by the control panel mounted in the control room. The access of the personnel to the irradiation room is possible only through one protecting door.

3.3. Radio protection assurance

3.3.1. Premises and calculation methodology of the shielding (Fig.8)

In the case of the extracted beam accelerators, the shield is calculated for the breaking radiation which is penetrating. Its shielding (bremsstrahlung = BSS) is much covering in comparison with the accelerated electrons.

It is mentioned that, considering the electrons low energy, maximum 2.5 MeV, there do not take place creations of activations or of neutron generation.

The breaking radiation (BSS) arises in all the bodies hit by the accelerated electron beam, in a covering way, as a breaking target, in the absence of any irradiated product. In order to increase the safety coefficient ever more, one will consider the beam breaking on a thick heavy metal target.

BSS includes the following components one will take into account on the shielding calculation:
- direct BSS in the forward direction (at an angle of 0° as against the electron direction).
b) direct: BSS in lateral directions at various angles;
c) BSS, simple and multiply, after covering a difficult route (broken trajectory)

In order to calculate the admissible doses and the necessary attenuation, one makes the following calculation assumptions:

A) The operation factor \( w = 1 \), the accelerator being able to run in continuous regime;

B) The occupation factor \( T = 1 \), respectively a person can stand in the area allowable to the professionally exposed personnel a complete programme of 40 hours/week.

As admissible doses, the facts proposed in the standard specifications of the AIEA-Vienna will be taken into consideration although they are not adopted yet, but it is possible that they should be adopted in the future. For the time being, this calculation assumption raises the safety coefficient ever more. The admissible doses (AD) expressed in the real dose equivalent (RDE) are:

- 20 mSv/year for professionally exposed persons (in comparison with 50 Sv/year in the present standards);

- based on the above-mentioned factors \( w \) and \( T \), there results a RDE output of 10uSv/h (in comparison with 25\( \mu \)Sv/h at present);

- 1 mSv/year for persons out of the population (in comparison with 5mSv/year at present); there results an output of 0.5μSv/h (as against 2.5μSv/h at present).

3.3.2. The screening of the irradiation room walls

The real dose output in all the considered points of the occupied area is below the admissible value even for persons belonging to the population (5 + 10 μSv/h).

3.3.3. The screening of the protection door

The access door to the irradiation hall (Fig. 4) has a concrete thickness equal to that of the wall screen and exceeds the screen opening, on the sides, by 20-25cm. There is one exception to this constructive rule, namely on the inferior side of the door, the thickness is reduced by approximately 20 cm (because of the driving system location) and there is no opening exceeding. For this reason there was necessary to exist an exceeding of the admissible dose in the occupied area, on the inferior side of the access door. This exceeding was experimentally confirmed.

Consequently, it was necessary to perform a local additional screening, built inside the hall, in the area located between the radiation source and the access opening, being at least 1 TDA in thickness. For reasons of space and constructive possibilities, this additional screening was made of load, being 5cm > 4cm (1TDA) in thickness.

3.3.4. The screening of the scattered radiations

The radiation scattering of the Compton effect results, together with the change of the propagation direction, in a reduction of the photon energy and fluency. The energy reduction depends on the incident photon energy and on the scattering angle. It is theoretically proved that for the scattered radiation at relatively high angles, which is important for the screening calculation, the energy of the scattered photon becomes, practically, equal to 0.5 MeV, respectively one can use the attenuation data of a BSS, with the admissible energy of 1 MeV.

By contrast with the direct BSS radiation at high angles, results a negligible contribution of the radiation scattered on the floors.

4. Aspects concerning the research and production in the pilot station

At present, in the pilot station there is organized an industrial production of thermo-shrinkable materials (tubes, caps, etc.).

The scientific research carried out since 1972 has materialized in products, technologies and aspects of fundamental research in the following fields:

- experimental and technological researches concerning the application of the accelerated electrons for water disinfection and, the application of combined methods (ozone electrons, electrons and chlorine, etc) [28];
- researches concerning the SO2 and NOX removal from the flue gases, the application of the accelerated electrons for the polymerization of some acrylic monomers under the influence of the accelerated electrons on polyethylene terephthalate support; studies concerning the UV and NOX removal from the flue gases, the application of the accelerated electrons, as well as some combined methods (electrons and lightning discharges, electrons and ozone) [32];
- researches in the field of the accelerated electron application to the seed disinfection with a view to raising the safety coefficient ever more. The admissible doses (AD) expressed in the real dose equivalent (RDE) are:

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A 600KEV ELECTRON RADIATION ACCELERATOR

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INTRODUCTION

In this paper we describe a 600keV two-body multi-functional electron and positive ion radiation accelerator based on a 400keV Cockcroft-Walton. Which was successfully used to accelerate electron and positive ion. The 400 keV horizontal Cockcroft-Walton multiplier existed in the captioned institute was produced in 60s and when it was put into service the multiplier had been employed in times of nuclear experiments, especially functioned as neutron source in a great many neutron data tests. To follow up the study works of coating solidification by radiation undertaken by the institute, the reconstruction of the old multiplier was started in a circumstance of sever shortage of manpower and fund, it was required then that the rebuilt multiplier would not affect the various indexes the old one had, but be able to conduct a great deal of electron radiation works. It was finalized after selections of several alternatives that means of co-usage and swift switch-on/off should be used as many as possible to satisfy the requirements that both positive ion and electron can be accelerated. A multi-functional electron radiation accelerator co-existing with horizontal 600kV positive ion multiplier was built up. Though test on coating solidification of decoration materials, such as colorful surface plaster plate and relief plate, and researches on metal plate, plastic plate, wood and paper coating decorations and radiation workmanship, as well as experiment of brach-linking by radiation for filling materials of petroleum pipings, it is proved that the device is reliable and stable in operation and reaches the pre-set design indexes and satisfies the requirements called for. The multi-functional accelerator reconstructed is very fast in change over from drawing electron to drawing positive ion and vice versa. Without any change in the indexes of the old multiplier.

The electron radiation accelerator is of the following main specifications:
- Electron energy 100-600 keV, continuously adjustable
- Electron beam current >7 mA
- Electron beam scanning width >1200 mm
- Electron beam scanning frequency 50-250 rpe, adjustable
- Dimension of Scanning frame 4500 x 1400 mm
- Transmitting speed of Scanning frame 0.1-5m/m. continuously adjustable.

DESCRIPTION OF MAJOR COMPONENTS
During the whole process of the reconstruction, the guidance is to make the newly-built accelerator and the old one co-use and meet the needs of generating positive ions and electrons by using simple, swift and reliable switching. Descriptions of the fundamental elements are given as follows:

1. Co-usage and Switching of HV Multiplier Power Supply
   The power supply of the old 400kV Cockcroft-Walton is fed by a two-stage multiplication power resource consisting of a 8 kW step-up transformer, 4 HV capacitors and 4 electron tubes. The filament of the electron tubes are electricity fed by a filament isolated transformer. It used to be difficult to make conversion of the rectified positive and negative polarities. So the HV supply was replaced by 6 HV rectification silicon rods and 6 HV capacitors. To facilitate the switching of the rectified voltage polarities connections of both ends of the silicon rods with the capacitors is fixed by screw rods and nuts. After such an innovation, the efficiency of rectification can be increased, and more convenient and reliable conversion of HV rectification polarities can be achieved.

2. Co-adjustment and swift Switching of the Power Supplies of HF Ion Source and Electron Gun System
   The power supplies of the high-frequency ion source and the electron gun system are placed in two high voltage large receptacles respectively (the two are of equivalent potential level and connected each other by aluminum piping that accommodates the power cables for all power supplies). Gauges for all power supplies are also mounted on the receptacles. The two sets of power resources co-use one set of controlling, regulating, protecting and monitoring system. In oregate co-use the controlling, regulating and protecting devices of the old system, co-usage by regulating the input voltage of the two sets of power resources are adopted, i.e. double-pole and double-throw switches are connected with every output ends of the voltage regulators. When the high frequency ion source is to be put into operation, the switches will be positioned on the outputs of the voltage regulators to energize inputs of the power supply of the HF ion source, and meanwhile, the inputs of the power supply of the electron gun system will be tripped, and vice versa.

   In this way, the trouble for re-regulation of each sub-resources of power, when conversion of beams is needed, can be eliminated, and the installation of a new set of isolated power supply, regulation, control and protection system for the electron accelerator is not required. This system is also convenient, swift and reliable in operation.

3. Irradiation Scanning System and Irradiation Conveying Device
   The electron irradiation scanning system is composed of scanning power supply, scanning magnet, scanning box and drawing window, whose function is to make the accelerated electrons scan horizontally. The scanning angle is 60 degree, scanning width 1200mm and adjustable scanning frequency 50-250
circles/s. Generally the scanning signal is of triangle wave current. However, it is indicated by theoretical analysis and experimental results that under circumstances of a large horizontal scanning angle and scanning width, an ideal current of triangle wave cannot achieve an uniformed current intensity at the drawing window. This is because, the bigger the scanning angle is and the wider the scanning width is, the bigger the linear velocity of electron scanning at a further place from the window center will be, causing decrease of beam intensity. In order to improve the uniformity of scanning, a scanning signal of a compound wave with triangle wave superposed by sine wave is used, and the output voltage, output current wave and frequency of the scanning power supply can be adjusted. So the flexibility for regulation as to achieve a uniformed electron beam at the drawing window is provided. In addition, for preventing the scanning system from fault operation that may run the risk of breaking the titanium film by a concentrated striking of electron beam at the center area of the window, on interlocking protection is furnished between the power supplies of electron gun system and scanning system. It means that the signals of the interlocking protection are taken from the output signals of the scanning power resource. So, when no output is available of the scanning power supply, the power supplies of electron gun system are deenergized, and no electrons can be down out.

The vertical scanning of electron beam is realized by mechanical movement of the irradiation conveying device. The conveying frame is 1400mm wide and 4500mm long. The transmitting speed is continuously adjustable from 0.1m/m to 5m/m. The conveying direction of the frame can be either forward or backward, and conveniently controlled as requested. The gap between the frame and the drawing window can be easily regulated according to the thickness of the irradiated samples, with max. regulation range of 150mm. The regulations of the device are done in the control room with industrial TV monitoring.

ACCELERATION & FOCUS SYSTEM

The accelerating and focusing system is of vertical configuration. The main acceleration tube is 1100mm long, HV resistors and HV capacitors are utilized to reach 40 sections of equivalent voltages, for forming a equal gradient accelerating tube.

The electrons shot form the filament of the electron gun, other being drawn out by the positive pole, will be focused by electrical focusing lens. Then the electrons will be injected into the acceleration tube acted by the guide magnet. In the acceleration tube, a thick lens system is formed by two diaphragm lenses of the inlet and the outlet and the central uniformed field. The electrons, through accelerating and focus in the system will fly through a certain space when moving out of the acceleration tube and form image of the outlet of the scanning magnet. The scanning magnet sweeps the electron beam uniformly with angles of 60 degrees and achieve uniformly intensity-distributed electron
beam at the titanium window. At last, the electrons go through the titanium window and irradiate sample. In order to have an unchanged point position of image formation of the whole system under different energies, i.e. the final image point is kept on the center of the inlet of the scanning magnet, regulation of the electrical focusing lens is available to modify the objective point positions of the electron beam injecting into the acceleration tube, aiming at achieving a focus matching.

By regulation of the potential level of grid pole or that of the positive pole of the electron gus system, the intensity of the electron beam accelerated can be adjusted.

The magnetic fied of the guid magnet is adjustable. It was found that, when the electron beam is out of the acceleration tube during beam regulation process, its deviation from the central point of the inlet of the scanning magnet is about 5 mm. It couised electron loss when a portion of the electrons struck on the scanning box after scanning. The tracks of electron beam were then corrected by adding a guide magnet after the focusing pole. In this way, the problem of image deviation generated from alignment, acceleration and focus was well resolved.

The whole acceleration and focus system is now of good performance after overall adjustment. As energy varies from 100 keV to 600 keV, the electron beam spot is about 2-3 mm in diameter as measured of the inlet of the scanning magnet.

APPLICATIONS

The following experiments have been conducted since being put into service of the 600 kV multi-fuctional electron irradiation accelerator.

Research and tests on irradiation solidification of coatings on decoration materials such as colorful plaster plates, relief plates, metal plates, glass, wood and paper, etc. Experiments of branch-linking by electron irradiation for filling materials of petroleum pipings; Damage-detecting test by electron irradiation on monocrystall silicon. Test on irradiation of heat-shrink film of polyethylene; Electron irradiation tests on HgTeCd. Thousands of hours experiments of neuton data measurements on the old horizontal 400 kV multiplier.

CONCLUSIONS

The successful operation of the two-body and multi-functional 600 kV electron irradiator ion accelerator has opened a new way of electron irradiation applications on the horizontal ion accelerator. Also, it provides a novel and feasible method to extend application field with no affection on the old accelerator and less fund and manpower.
REFERENCES


ABSTRACT

The main field of the TEKRA company (St.-Petersburg, Russia) is the development of small low-energy (up to 300 keV) electron beam processors (EBP) the use of which is related to the technologies of thin-layer materials [1].

An accelerating gap is formed by a cathode surface and an anode grid. Anode plasma, which provides positive ions, is generated between the anode grid and an exit window. Ions passing through the anode grid are accelerated by the electric field and bombard the cathode's surface causing it to emit secondary electrons. A beam of accelerated electrons exits from the gun through thin foil.

In the curing of varnishes, and dyes small-scale low energy electron accelerators successfully compete with the technologies of thermal or IR-drying and UV-curing.

The line for producing facing plates based on inorganic astringents and the technological line for wood processing contain an electron-beam units based on EBP-240-5-34-20. The desired products are protecting decorative coatings. The thickness is 50-200 μ. It is also possible to cure media which are not transparent for UV-radiation because mineral fillers are applied or design elements are sprayed on the surface (fibers, polymer or mineral particles of various diameters).

The use of EBP switched toward each other in the technology of obtaining film materials made it possible to develop a compact low-energy unit equivalent to high-energy units with respect to penetration thickness. This unit is used in the technology of manufacturing of heat-shrinkable polyolefin bands with "shape memory" effect for anticorrosion protection of pipes for water, air, oil, and gases. The productivity of a line containing two EBP 300-15-60-20 for the production of heat-shrinkable double-layer band up to 1.2 mm thick is 1000 t/year.

INTRODUCTION

The development of new generation of low-energy electron-beam processors is stimulated by the needs of manufacture interested in use of highly effective scientific technologies. This is a general direction of TEKRA Company activity. Among the benefits of new generation of low-energy processors are:

• reduced overall dimensions;
• protective shielding;
• automatic control system, which allows them to integrate into different technological lines easily.

Nowadays a broad range of such processors are being produced and working actually. All the advantages, that have been predicted during construction works, are supported by the practical experience.

LOW-ENERGY EBP BY TEKRA COMPANY

The decisive factor in base model creating was the abandonment of traditional heathen cathodes. The generation of electron beam is as follows: switching of the low voltage discharge in the region between the anode and supporting grid makes ions move towards the
cathode surface and bombard it. Secondary-emission electrons are then accelerated as they move from the cathode to the perimeter of the tube.

As a result the electron-beam having a cross-section square area up to 1.0 Sq. m. and ununiformity less than 5% is generated. Necessary to make it clear, that because of electron scattering, the beam expansion occurs and it enhances in the air gap, but it can be rather insignificant.

Fig 1 shows, that the availability of the anode grid leads to the certain losses, determined by absorption of accelerated electrons. But this drawback has been overcome due to high parameters of the generated electron beam and also due to other advantages of the EBP unit in whole. For example the lack of accelerating tube, allows to abandon traditional electron-optical focusing and beam scanning systems. The processes of producing, setting up and service for such systems are rather difficult.

![Figure 1: Structure of EBP](image)

Fig. 1. Structure of EBP: 1 - exit window foil; 2 - supporting grid; 3 - plasma region; 4 - anode grid; 5 - cathode

The parameters of the vacuum system of EBP are determined by work conditions in the helium plasma region, which requires rather low level of vacuum (about $1 \times 10^{-3}$ Tor). Loss of vacuum inside of accelerator due to fault conditions is not critical. Thus, the vacuum system is quite simple in service and maintaining. It consists of low capacity roughing pump, evaporating pump, automatic control system. The design enables the operator to exchange the vacuum pump's cathode and electron-emission window; both parts are subject to wear. Replacing worn parts including vacuum pump and readjusting the accelerator requires, in total, less than one hour.

By this means, electron beam processors developed by TEKRA Company have a number of substantial benefits in radiation-technology processes.

Among these benefits are:
- reduced overall dimensions and weight of machines (including protective shielding);
- simple construction that makes easier technical operating;
- simplicity of maintaining, repairing and exchanging parts subjected to wear;

The technical specifications of electron beam processors manufactured at the present time are given in the Table 1:
Table 1
Specifications

<table>
<thead>
<tr>
<th>Type of processor</th>
<th>EBP 140-0.5-15-5</th>
<th>EBP 240-5-34-20</th>
<th>EBP 240-5-120-30</th>
<th>EBP 300-15-60-20</th>
<th>EBP 300-15-120-20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accelerating voltage, kV</td>
<td>140</td>
<td>240</td>
<td>240</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>Electron beam current, mA</td>
<td>1</td>
<td>5</td>
<td>8</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Beam cross-section area, sm</td>
<td>15 x 5</td>
<td>34 x 20</td>
<td>120 x 30</td>
<td>60 x 20</td>
<td>120 x 20</td>
</tr>
<tr>
<td>Power consumption, kW</td>
<td>1.5</td>
<td>5</td>
<td>7</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Physical dimensions (W-L-H), m</td>
<td>0.7 x 0.7 x 1.8</td>
<td>1 x 1.7 x 1.8</td>
<td>1 x 4 x 1.8</td>
<td>1.2 x 3 x 1.5</td>
<td>1.2 x 3.6 x 1.2</td>
</tr>
</tbody>
</table>

Accelerating voltage is regulated within limits from 120 kV up to the maximum value. The lower value is determined by the capacity of the exit window foil. The electron beam current is regulated in the range from 0 up to value ratings. The distribution of ununiformity of absorbed dose throughout e-beam cross-section area even in the most fault conditions does not exceed ±10%.

The EBP efficiency, that is the ratio between electron beam power and the power consumption exceeds 30-35%. The efficiency of EBP reduces with decreasing electron beam power, as the power consuming auxiliary systems (vacuum, control, cooling systems) are practically independent of beam power. It's necessary to note, electron beam power account for 35-45% of a high-voltage source power.

The utilized radiation factor can modified within 85-98%. Such high values can be reached due to striking a compromise between dimensions and shapes of the exit window, the main beam parameters, in some cases of double-sided curing and other expedients. As far as the base model of EBP has to do with technological process, all the mentioned above expedients are available.

Thus, it's possible to say that the set of low-energy electron beam processors possessing a number of substantial benefits have been created. And the benefits correlate with specific technological process. The main question is: in what measure low-energy electron beam processors comply with processes which have been developed for e-beam processors of higher energies (from 400 keV and higher).

LOW-ENERGY EBP IN RADIATION TECHNOLOGIES

Our experience has verified several important advantages of low-energy processors. Low-energy EBPs by TEKRA Company successfully compete with high-energy processors in a number of radiation technologies.

As the example we can consider the use of EBP-240-5-34-20 in technological line manufacturing decorative tiles of gypsum with EB-cured organic coatings (Fig.2).

The tile dimensions are 300*400 mm. The thickness of cured coating is up to 250µm. The parameters of the exit window 340*200 mm provide the value of utilized radiation factor at the level of 88%. The comparably large curing dozes (about 200 kGy) are justified by high speed, absence of solvents and excellent quality of achieved surfaces.

The technological line includes following equipment: lacquer coating unit, two technological conveyers, electron beam processor and protective shielding. Two conveyers allows to transfer the tiles with lacquer coating into the curing zone with necessary speed. Besides the main protective shielding of EBP, the extra radiation shielding against diffused X-rays is sided on the elements of conveyer.
To realize the project, a new EB-cured lacquer on the base of epoxy acrilated resin has been developed. One of the most important advantages is the absence of solvents, therefore curing can be carried on immediately after the process of applying a coating composition to the surface of the tile.

The same process is used in the technological line for curing of wood with output capacity of 250,000 square meters per a year. The line is equipped with two EBP units on the base of EBP-240-5-120-30 (Fig. 3). Among the production are: high-quality parquet floors, furniture and wall-boards, doors table tops, veneer decorative products. The thickness of cured layers is about 50-200 μm. Electron beam technology allows to cure materials not transparent to UV-rays, besides that, coatings with layers of polymer fibers or other polymer or mineral particles of different shapes and sizes.
The use of two EBP-300-15-60-20 (Fig. 4) for simultaneous double-side curing in the technological line, manufacturing heat-shrinkable band allows to produce 1000 tons band of the thickness up to 1.2 mm. The heat-shrinkable band with "shape memory" effect is used for hermetic sealing of pipelines transporting oil, gas, hot water, air and other gases and liquids. The band provides effective anticorrosion protection for pipes. All the properties of double-sided cured band are identical with properties the band being manufactured by one-side EB-curing (with electrons energy more then 700 keV.)

Fig. 4 EBP unit of the line manufacturing heat-shrinkable anticorrosive band: 1 - EBP; 2 - drawing unit; 3 - cured band.

CONCLUSIONS

Low-energy electron beam processors developed by TEKRA Company used in a number of radiation technological processes for manufacturing thin-layer laminated materials. They successfully compete with high energy accelerators due to their specific technical parameters. Further intentions of TEKRA Company are to extend the range of low-energy EBP applications.

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RESEARCH OF UVA HIGH INTENSITY DISCHARGE LAMP

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ABSTRACT

In the process of photochemical reaction of photo materials, for example, the photo polymerization of photosensitive lacquer and photosensitive ink, solidified speed of the photo layer is an important parameter. The spectra of UV light sources and the absorbed spectra causing photopolymerization of photo sensitive layers must be matched, it's important for solidified speed. The absorbed spectra for most photosensitizers are in the region of about 365.0nm. At present, UV high pressure mercury lamp is a main light source in photochemical reaction, but its UV radiation power is only 17 percent of the whole input power. There is a stronger radiation in visible region.

Based on the discharge mechanism of metal halide, we can select such metal elements which radiate spectra near 365.0 nm as luminescent materials and make them into metal halide additives. These additives can be used to make different kinds of high intensity UVA lamps (UVA spectra range is from 320.0 nm to 400.0 nm). These lamps can greatly increase UVA radiant energy and photoelectric transform efficiency, as a result, they can accelerate the photochemical reaction speed, save energy and raise productive efficiency. That is the main content of this article.

INTRODUCTION

By adopting the method of making halide lamps and letting some elected elements radiate, we can obtain many special spectrum lines needed to strengthen spectral radiation in useful wavelength range and restrain that in other range, so that the photoelectric transforming efficiency and work efficiency can be increased. This method has been used in visible radiation, can we find some chemical elements which radiation spectra concentrate in the wavelength range (350~400nm) absorbed by photoactive materials, and make them into halide additives to radiate and emit light in the discharge tube? How does the element affect spectral distribution? How does the halide affect the photoelectric parameter? How to control additives effectively? These problems are well worth studying. This article will expound some experiments and results.

EXPERIMENT METHOD
1. Experiment Content

By comparing some elements that have stronger radiation in UV range, iron element had been finally elected which has dense line spectrum in UV 350~400nm. We make Fe into FeI₂ pills which have different weight, and add different quantity into lamp, to observe the following phenomena.

①. Radiant spectrum distribution of luminescent element Fe and luminescent condition.

②. The effect of the filling amount of FeI₂ on lamp voltage and spectrum distribution.

2. Experiment Method

This experiment was carried out on a 2kW lamp, this lamp electrode distance is 11cm; external diameter is 2.9cm; wall load 20W/cm²; lamp voltage 250V; lamp current 8.5A; on the basis of the additive for high pressure mercury vapour lamp, add different quantity of FeI₂ to observe the effect on spectrum distribution and lamp voltage. Fig.1 shows the experiment circuit.

Fig.1 Experiment circuit
1. ballast 2. ignitor 3. switch 4. lamp 5. spectrophotometer

RESULTS and DISCUSSION

FeI₂ exert a great influence on the spectral distribution when different quantity of FeI₂ is filled into lamp. That is the spectral distribution curve depends on the quantity of halide, different quantity of halide additives will cause different partial pressure of halide in the lamp, this means halide molecular quantity on vapor in the lamp is different. Experiment show, when FeI₂ is less than 0.05 mg/cm³, radiation spectra still take mercury spectra as the dominant factor, iron spectra exist, but they are weaker than mercury. It is shown in Fig.2, the reason is there isn't enough quantity of Fe which is resolved from FeI₂ in the lamp and take part in exciting radiation, and the metal atoms appear less on excited state, the spectrum radiation intensity in needed range looks weak. Although iron's excitation potential for UVA spectrum region (between 3.3~4.3 ev) is lower than mercury (about 9 ev), but the density of FeI₂ halide is lower and the amount of Fe atoms is less on excited state, the spectrum distribution isn't satisfying.
Fig. 2 is a spectrum photoelectric current response curve when FeI₂ additive is less than 0.05 mg/cm².

Fig. 3 is a spectrum photoelectric current response curve when FeI₂ additive is about 0.15 mg/cm². We can see from Fig. 3 that the spectrum radiation is better than Fig. 2 and the spectrum distribution is much ideal. The covered area by the spectra is 2.5-3 times than single mercury spectra in the range of 350-400 nm. Iron's spectrum line peak rises, it is higher than mercury spectrum line 365.0 nm. On condition that the density of luminescent element is suitable, the spectrum distribution take iron atom as dominant factor, because iron atom has lower excitation potential and ionization potential than mercury atom. This spectrum distribution is that we need.

Fig. 4 is the spectrum photoelectric current response curve when FeI₂ additive is about 0.25 mg/cm². With the increasing of FeI₂, spectrum lines intensity of iron drops, the proportion of iron radiant intensity is lower than that of mercury. It is obvious that self-absorption of iron element is very serious in the lamp. If excessive additive is added and halide density rises in the lamp, radiation loss increase, so we can't obtain ideal result.
The influence of halide additive on lamp voltage:

It is very obvious that FeI₂ filler exert an influence on lamp voltage. FeI₂ isn't like GaI₃ which variation in filling amount can't cause great variation in lamp voltage, therefore we must readjust mercury quantity filled in the lamp when certain quantity of FeI₂ is filled to obtain ideal spectrum output, so the lamp can work under standard tube voltage. If we calculated the mercury quantity according to the mercury lamp, FeI₂ can increase the lamp voltage by about 12.5 V/ag after some FeI₂ is filled, it is shown in Fig. 5. FeI₂ has higher melting point than GaI₃ and Fe atom has higher ionization potential than Ga atom, so at the same high temperature area around the arc, the amount of Fe atoms participating in electric conduction (that is Fe atom is in a state of ionization after FeI₂ was resolved) is much less than Ga atoms, contraction of arc column will happen and discharge section will be narrower. This cause a rise in lamp voltage.

CONCLUSIONS

Thus it can be seen that we can obtain ideal spectrum distribution after proper amount of FeI₂ is filled in lamp. Spectrum lines of Fe (358.1nm, 372.0nm, 373.7nm, 374.5 nm, 382.0nm and so on) strengthen radiant energy in UVA, its radiant power is 2 to 3 times higher than that of high pressure mercury lamp, but the filling amount of FeI₂ must be suitable to avoid radiation energy insufficiency (quantity less) and self-absorption phenomenon (quantity excess), the spectrum output is in a ideal state. At the same time, FeI₂ will lead to the lamp voltage to rise, standard lamp voltage can be obtained through adjusting the quantity of mercury.

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LOW ENERGY D.C. TYPE ACCELERATORS
for RADIATION CURING

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BINP produces the high voltage d.c. ELV-type accelerators for industrial applications. Now we have delivered more than 60 accelerators that are installed in several countries. The total energy range of commercialised set of these accelerators is from 0.2 up to 2.5 Mev and the power of electron beam is 20 - 100 kW. Two models of ELV-type accelerator are used for radiation curing. They are ELV-mini and ELV-0.5. ELV-mini has energy range 0.2-0.4 MeV and power of electron beam - 40 kW, it is very compact. ELV-0.5 has energy range 0.4-0.7 MeV and power 25 kW. ELV-0.5 allows to cure more thick layers.

ELV-mini accelerator is shown on fig.1. It consist from high-voltage rectifier, accelerating tube and extraction device. High-voltage rectifier is placed inside of separate vessel and is connected to accelerating tubes with high-voltage cable. It consist of 2 column which are connected in parallel. So the high-voltage potential is on half of height of rectifier. The cable pass trough the top column. Insulation media is SF6 under pressure 0.7 atmosphere. The maximum output current of power supply source is 100 mA if maximum output voltage 400 kV and 200 mA if maximum voltage 200 kV. This source can supply up to 3 separated accelerating modules and current of each module can be controlled independently. It is very convenient for multistage radiation curing.

Accelerating module consist of accelerating tube and extraction device. Accelerating tube has length 30 cm. It is placed inside of pressure vessel with pressure 5 atmosphere. Due to small volume of this vessel total amount of SF6 is small.
Fig.1 - ELV-mini accelerator:
1- high-voltage power supply source, 2- high-voltage cables, 3- vessel with accelerating tube, 4- scanning magnets, 5- trajectories of beam in extraction device, 6- ion pumps, 7- bending magnet, 8- radiation shielding.

The beam current is controlled by heating 4 of cathode. Power supply for filament is provided through special transformer at frequency near 20 kHz.

Extraction device consist of scanning magnets, horn, output window and bending magnet. Output window can be produced in 2 versions: with air cooling Ti foil or with Al foil.
on water cooling grate. The maximum angle of deflection for electrons is 45 degrees. Bending magnet changes electron trajectory and they pass through the foil exactly perpendicular. So the loses of beam current in the foil are decreased. The maximum beam current through the foil window is determined by its length and for 90cm length is equal 40 mA.

Design when accelerating tube and extraction device are separated from high voltage rectifier is convenient for installation in local radiation shielding. The height of local shielding (if accelerator is equipped with 90 cm foil window) is no more 1.5 meter.

ELV-mini accelerator has some advantages in comparison with usual low energy accelerators which uses one high-voltage vacuum gap and long cathode due to : accelerating tube, simple cathode unit and scanning beam. Accelerating tube totally eliminates the vacuum discharge during operation and allows to increase voltage upto 400 kV. It is higher than in one-gap accelerators. Cathode units has biggest lifetime (up to 5000 hours) and can be changed by simple way. Scanned beam allows to form several required profiles of beam current distribution under the foil of output window. It is possible to change the length of scanning (if it is necessary in connection with changing the width of irradiated material) using keyboard of computer only.

ELV-05 accelerator has higher energy range. It is typical ELV-accelerator. It is shown on fig.2. Here accelerating tube is placed inside of high-voltage rectifier column. So the size of accelerator is small and it can be installed in local radiation shielding. But the size of shielding will be some more because of higher energy of electrons and some bigger dimenions of accelerator in comparison with ELV-mini accelerator.

The ELV-05 and ELV-mini accelerator use the same rectifiering sections. The difference is number of them. ELV-05 has single column, which contains 24 rectifying sections. Accele-
Fig. 2 ELV-05 accelerator with concrete shielding:
1- removable steel cover, 2- accelerator, 3- concrete shielding, 4- technological holes, 5- extraction device, 6- technological equipment.

The electron beam of the operating tube has a length of 90 cm. Extraction device for this accelerator has a 30 degree deflection of the electron beam. Due to this circumstance and higher energy of electrons, the additional bending magnet is not needed. Usually, we use air-cooling extraction windows with 50 mkm Ti foil but water-cooling grate or additional protection foil also are available.

Due to high-efficiency of high-voltage rectifier (more
than 92%) the total efficiency of installation is also high. The efficiency of facility is determined by frequency converter and can achieve (including all systems) 85% if thyristor converter is used.

Control system of these accelerators is based on IBM computer. It allows operation in "on line" regime. Controlling program can be adapt to any technologies and it is possible to control both accelerator and technologies line at the same computer.

ELV-05 accelerators are installed in technological line of curing and coating of wood and concrete plate in Russia and abroad (sites: Tashkent, Sterlitamak, Omsk, Alma-ata) and line for production thermostable polyethylene film (Angarsk).
ELECTRON BEAM TECHNOLOGY FOR PRODUCTION OF PREPARATIONS OF IMMOBILIZED ENZYMES

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ABSTRACT

Possibility of electron beam usage for proteases immobilization on 1,4-polyalkylene oxide (1,4-PAO) was studied to obtain biologically active complex for multi-purpose usage. It is shown that immobilization of Bacillus Subtilis protease is done due to free-radical linking of enzyme and carrier with formation of mycelium-like structures. Immobilization improves heat resistance of enzyme up to 60 centigrades without substrate and up to 80 centigrades in presence of substrate, widens range pH activity in comparison with non-immobilized forms. Immobilized proteases does not contain peroxides and long-live radicals. Our results permitted to create technologies for production of medical and veterinary preparations, active components for wool washing agents and leather fabrication technology.

INTRODUCTION

One of the serious problems in creation of novel effective enzyme preparations for hide softening and unhairing in technological process of raw hide treatment is increase of stability and duration of action of enzyme complexes. The stabilized enzyme complexes can be obtained using various technologies.

Appearance of powerful sources of ionizing radiation created in Budker Institute of Nuclear Physics on market enabled the development of the fundamentally new multi-purpose radiation technologies [1, 2].

We are using radiation technology successfully during years for production of immobilized proteinases designed for hide softening and unhairing and wool scouring [3, 4]. The electron accelerator enables one to perform an immediate immobilization of proteolytic enzymes and sterilization of the final products in packed form, which gives an obvious advantage both in technological and economical aspects in comparison with conventional technologies of chemical immobilization of enzymes.
Fig. 1. Thermal resistance in presence of substrate.
1 - bacterial proteases, immobilised on 1,4-PAO;
2 - free bacterial proteases in 1,4-PAO solution;
3 - free bacterial proteases in the water.
Maximum value of enzyme's activity was assumed as 100%.

MATERIALS AND METHODS

The industrial electron accelerator ILU-6 with electron energy 2.5 MeV and beam power 20 kW was used in present study. The production of immobilized enzymes is realized in two stages. The first stage is transformation of 1,4-PAO water solution of 1,4-PAO into gel by radiation induced crosslinking. Then the enzymes are added to gel and radiation induced immobilization of proteases on polymer carrier with simultaneous sterilization of reaction mixture is led. Proteases were obtained from highly productive industrial producer Bacillus Subtilis, strain CH-15. Both stages are done on the same underbeam transportation line.

Final product was compared with preparation of free proteases - trypsin ("Spofa", Cze.). Proteolytic activity was determined by casein hydrolysis according the formula

\[ PA = \frac{D(280)}{M \times V \times T}. \]

\( D(280) \) is optical density at wavelength 280 nm, \( V \) is volume of analyzed probe in ml, \( M \) is mass equivalent of substrate in grams and \( T \) is the time in hours.
Fig. 2. Dependence of proteolytic activity from pK of substrate.
1 - bacterial proteases immobilised on 1.4-PA0;
2 - free bacterial proteases;
3 - trypsin.
Maximum value of enzyme's activity was assumed as 100 %.

The acid-soluble products of hydrolysis were determined by spectroscopy measurements at wavelength 280 nm. For 1 unit was assumed the quantity of probe containing protease which during 1 hour at 37 centigrades transmits 1 mg of casein (substrate) into non-precipitating by 0.3 mol/l solution of threeclorvinegar acid state.

The thermal stability of free and immobilized proteases in presence of substrate was determined by incubation with 2 % casein solution during 1 hour at the temperatures 37, 45, 50 & 66 centigrades. The results were indicated in percents with respect to value at 37 centigrades [5].

RESULTS AND DISCUSSION

Complex of bacterial proteases in water solution of polymer under electron irradiation creates free-radical links forming mycellium-like structures enzyme-polymer. The radiation immobilization of proteolytic enzymes on polymer matrix imparted them qualitatively new properties. This treatment permits to increase the time of specific action of enzymes by a factor of a some tens while specific properties of substrate remain the same. The thermal stability, resistance to pH variation, storage time period in the liquid and jellylike form are increased (see Fig.1 & 2).
The proteolytic activity of immobilized proteases depends on initial activity of enzyme and mode of radical generation during electron irradiation. Our immobilization method permits to preserve from 40 to 60% of enzyme's initial activity.

Usage of radiation technology for free-radical cross-linking of proteinases with polymer matrices made it possible to produce various preparations and components, various cleaning means, active components for use in technologies connected with the processes of softening and unhairing of cattle, swine and sheep hides.

Duration of unhairing process depends on the kind of hide, treatment conditions and type of equipment. Usage of immobilized enzymes permits to remove the hair from hide and to obtain undamaged and clean wool with the increase of ecological safety due to reduction of water and chemical agents consumption.

Duration of unhairing process is for sheep hides 1-3 hours, for cattle hides - 6-8 hours. The yield of dried clean wool is 320-360 grams from cattle hide and 1000-1500 grams from sheep hide.

Action of immobilized proteases during hide softening permits to fabricate high quality leather products (see Table 1).

The advantage of radiation technological process for immobilization in comparison with the conventional methods turned out to be as follows:

1 - substantial reduction of the production cost;
2 - high rate of technological process;
3 - reduction of energy consumption and chemical contamination;
4 - reduction of chemical components required for the immobilization of proteases;
5 - a possibility to readjust the line for the solution of other problems like sterilization of water flows, solvents.

The industrial electron accelerator can provide the electron beam with following parameters for production of immobilized enzymes:

a) electron energy up to 4 MeV which permits to treat the products with surface density up to 1.5 g/sq.cm at unilateral irradiation and up to 4 g/sq.cm at bilateral irradiation;
   b) beam power 20 kW and irradiation dose 2.5 Mrad thus permitting to create technological line with production rate no less 1 ton of product per hour;
   c) continuous operation up to 24 hours per day;
   c) sterilization or pasteurization of packed preparations of biologically active substances, medical products, packed food items.
DESCRIPTION OF PREPARATIONS

The preparations "Biosib" and "Woolsib" were designed for treatment of wool and raw hides together with the technological processes.

The wool retains its natural properties while hard-separable proteins, pigment impurities and particulate matter are simultaneously removed. Components of washing solution "Biosib" are forming two-phase liquid system containing immobilized enzymes. Its main components are more safe after use than widely used sulphonates, sodium phosphate, ferro- and polyphosphates and water glass. "Biosib" can be recycled.

The used washing solution is transferred into separating column where it separates rapidly into three layers. The top layer contains large quantity of lanolin which can be extracted for use in cosmetic industry. The middle layer (about 85% of total volume) is pure washing solution ready for use. The bottom layer contains particulate matter removed from the raw wool. The recycling rate of "Biosib" washing solution depends on level of wool impurity.

Comparative data of wool before washing and after washing by described new technology and traditional technology are given below:

<table>
<thead>
<tr>
<th>Main parameters</th>
<th>Initial material &quot;Biosib&quot;</th>
<th>&quot;Biosib&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Traditional</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Relative tensile strength</td>
<td>8.7-9.3</td>
<td>9.6-9.9</td>
</tr>
<tr>
<td>Solubility in urea-bisulphate</td>
<td>5.2-5.6%</td>
<td>4.5-5.1%</td>
</tr>
<tr>
<td>Residual weight of lipide content</td>
<td>2.4-4.3%</td>
<td>0.3-0.5%</td>
</tr>
</tbody>
</table>

"Woolsib" is a name of a preparation and new technology designed for leather fabrication and additional obtaining of wool. Its use permits to shorten the unhairing process with simultaneous increase of ecological safety.

The unhairing can be performed by means of bath or smearing technique. The duration of unhairing process depends on the kind of hides, treatment method and type of equipment and is about 1-3 hours for sheep hides and 6-8 hours for cattle hides. The yield of absolutely dry clean hair from a sheep hide is 1000-1500 g and from a cattle hide is 320-360 g. Enzymatic soaking permits to realize production cycle without hide bating.

The "Woolsib" advantages are:
- possibility to increase the production rate without any quality lowering due to shortening of total duration of technological process;
- considerable reduction of calcium hydroxide and sodium sulfide in the sewage, prevention of economical losses connected with risk of fines for ecological harm;
- obtaining of additional profit due to reduction of expenses for sewage purification.

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Table 1.

Comparative property characteristics of bovine hides treated according traditional technology and new technology using immobilized enzyme agent "IPE".

<table>
<thead>
<tr>
<th>Leather parameters</th>
<th>Usual samples</th>
<th>Experimental samples</th>
<th>Standard values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Average thickness, mm</td>
<td>1.34</td>
<td>1.38</td>
<td>1.2-1.6</td>
</tr>
<tr>
<td>2. Tear resistance, MPa</td>
<td>18 +/- 4</td>
<td>19 +/- 3</td>
<td>13 +/- 2</td>
</tr>
<tr>
<td>3. Percentage elongation at load tension 10 MPa</td>
<td>27 +/- 5</td>
<td>35 +/- 5</td>
<td>30 +/- 10</td>
</tr>
<tr>
<td>4. Cracking resistance, MPa</td>
<td>18 +/- 2</td>
<td>19 +/- 2</td>
<td>11 +/- 1.5</td>
</tr>
<tr>
<td>5. Water content, %</td>
<td>13.7 +/- 1</td>
<td>13 +/- 1</td>
<td>14 +/- 2</td>
</tr>
</tbody>
</table>

The testing were led on the samples with dimensions 10*50 mm*mm on the load machine with maximum load 1.0 kN and elongation velocity 100 +/- 10 mm/min.

CONCLUSIONS

There are reasons to assume that widening of the application area of the radiation technologies developed on the basis of industrial electron accelerators is a profitable and ecologically verified way of manufacturing of a novel products and improvement of actually existing products.

REFERENCES


PRODUCTION OF THICK-FILM HIGH TEMPERATURE SUPERCONDUCTIVE ELEMENTS BY THERMAL-RADIATION TREATMENT

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ABSTRACT

Modern electron accelerators type ILU permit to organize the electron beam irradiation of different objects in air with beam current density up to 0.1 mA/sq.cm and electron energy up to 4 MeV. In these conditions dose power is about 4-5 Mrad/s and temperature of object decreases up to 1500 centigrades in some minutes. This treatment can be classified by its results as thermal-radiation for objects with mass thicknesses less than 2 g/sq.cm.

The fast heating in intensive irradiation field was used for obtaining of high temperature superconductive (HTSC) thick film elements based on Y1Ba2Cu3O7-X. Creation of such elements by standard technique of thick-film technology seemed to be unreal due to long duration (tens of minutes) and low process temperature (less than 1000 centigrades).

The thick film samples possessing HTSC properties with dimensions 10*1 mm*mm were obtained on aluminium oxide ceramics by stencil printing and following successive radiation-thermal firing of separating sub-layer and working layer formed from paste powder compositions. Maximum treatment temperatures were 900-1400 centigrades depending on the contents of composition, and duration varied within 10-300 seconds. The experiments were made using electron accelerator ILU-6, and mass production of elements can be made on installation ILU-BTP.

INTRODUCTION

The production of the thick-film elements possessing high temperature super conductivity (HTSC) properties is realized with the use of thick film thermal-radiation (ThR) firing method using electron beam extracted in air [1]. The ThR firing technology is based on the fact that during the object irradiation by an intensive electron beam (with the average current density about 100 mcA/cm) the object's temperature increases up to 1500 centigrades in few minutes. The kinetic energy of electrons is converted into a thermal energy with the efficiency close to 100%.
When thickness of object does not exceed the electron penetration depth in the substance, the heating is performed practically homogeneously over the entire thickness and there are no limits for the temperature growth rate. If a plate coated by the thick film paste compound is irradiated, the processes connected with the coating hardening (decomposition and release of an organic binding component, melting and crystallization of the glass, an oxidation of the functional material, etc.) proceed in the field of an intense radiation. It just determines substantial difference between the firing ThR process and the pure thermal firing, for example, as in the conveyor oven. An important difference is an approximately 50-fold decrease in hardening time of thick film-coating in the ThR firing process.

The technology of ThR firing of thick film coatings is developed on the beams formed by the pulse linear accelerators type ILU [2] providing the given density of beam current on the irradiated object at energy of electrons 0.7-4.0 MeV.

MATERIALS AND METHODS

The production of thick film component on the basis of Y1Ba2Cu3O7-X composition requires the solution of a number of problems on the compound composition, sublayer quality, and the film structure. The most important problems in providing the required composition is an attainment of homogeneity over film thickness and surface, overcoming principal disadvantage of the material thermodynamics, and so on. When selecting the material for a plate one should envisage its passivity with respect to the film material, to provide a possibility to arrange the buffer layers between the plate and film, to take into account the necessity that the coefficients of thermal expansion should coincide for the plate and the film. The film structure should be orthorhombic at axial orientation in the superconductive material. The material admixtures should not cause degradation of HTSC properties. Taking all this into account, the thick film components are produced on the plates made of alumina ceramic coated by buffer layer made of initial powders active with respect to backing.

Various powders were used for preparation of pastes. They are differed in the methods of their preparation and in the mean size of powder particles. Among them there are cryogenic one with the size of 3.7 μm (MSD); the ground powder PN with the size 7.7 μm (PF); a chemical sediment with the size 14.6 mm (CS); a powder obtained by the sole-gel method with the size 17.7 μm (PG); powder according to TFK 6-05-02-403-57 with the size 30.8 μm (PN); powder PN treated with attritor with the size 58:5 μm (AT). A paste composition includes binding substance in amount of 25-42%.
The quality of films was defined by visual inspection with the microscope (magnifying factor - to 1000) and electron microscope, by the adhesion (scratching with ceramic stick), by the resistance to electric current at room temperature and at temperature of liquid nitrogen, by the critical temperature measured by the microprobe method. The phase composition of layer determined by the diffraction of X-ray beams by means of the Dron-2 device and the mean size of the powder particles was determined with the meter device SK Laser Micron Sizer.

EXPERIMENTAL RESULTS

During the production of the buffer layer the best results were obtained for the paste on the basis of powder K33. The layer thickness was not lower than 20 mcm with a two-fold coating. The good adhesion of coating to the plate is reached at such regime of thermal-radiation treatment when the paste temperature reaches 1150 centigrades corresponding to the onset of powder melting. At process temperature 1000-1050 C adhesion is satisfactory. The weak adhesion of buffer layer to the plate was observed at process temperature 930-950 centigrades. The duration of thermal-radiation treatment during the formation of buffer layer is 30-200 s. The electric resistance of layer is few thousands Ohms if the treatment temperature does not exceed 950 centigrades and at higher temperature it drops down to 10 Ohm and lower.

If the buffer layers with good and satisfactory adhesion to the plate are coated by the active layers of the paste based on the powder K33 and then processed with the ThR method during 20-40 s with maximum temperature 950 centigrades resulting film has good or satisfactory adhesion and possesses HTSC properties without special procedure of oxygen saturation. However in this case an insufficient density of active film layer is observed. The films with higher quality are obtained by two fold printing of the buffer layer with ThR treatment at temperature 1160 C during 80-90 s and consequent two fold printing of active layer with its further treatment by ThR method to the temperature 950-1200 centigrades during 40-50 s. In this case, the samples with dimensions 10*1*0.03 mm possess the HTSC properties with critical temperature 75-80 K and critical current density 1-10 A/cm*cm without additional procedure of oxygen saturation.

Adhesion values of active layers obtained by ThR treatment at the temperature 980-1050 centigrades are different for the pastes made using different powders. The powders lined in the order of reduction of adhesion value give the following row: K33, PM, CM, PF, PN. On the other hand, if the buffer layer is obtained by treatment at temperature 1200-1250 centigrades, i.e. on the melting threshold or during the mixture melting, its adhesion to the sublayer is very good for all the powders. This evokes the interest to the search for the way of forming thick film elements possessing HTSC properties on the basis of Y1Ba2Cu3O7-X in the liquid phase.
During the process of thermal radiation treatment.

- **T** - sample temperature
- **C** - concentration of HTSC phase
- **T1 & T2** - baking and synthesis zones
- **T3 & T4** - melting zone
- **a** - mixture containing HTSC phase in initial state
- **b** - mixture without HTSC phase in initial state

**ONE MORE APPROACH**

It is known from literature that during baking process if the system reaches the melting state it deteriorates the HTSC properties, however this facilitates the material to get higher density [3]. On the other hand, it is known that the crystals with HTSC properties grown from liquid state have the high value of critical current [4]. In order to check influence of ThR treatment on the HTSC properties of material during its baking from the powders the following experiment has been performed. An initial powder of phase Y1Ba2Cu307-X possessing HTSC properties was compressed into the tablets 1.5 mm thick and 10 mm in diameter and then they were baked by ThR method. During baking the temperature was raised from room temperature to 900 centigrades and then the subsequent cooling down to temperature 800 C lasted 60 s. After cooling the baked tablets possessed the HTSC properties like the initial powders. So we can consider that if there is degradation of HTSC properties during ThR treatment, its level is negligibly low.

One can present two methods of formation of thick film elements with HTSC properties on the basis of given facts and considerations. Their principles are illustrated by Fig.1.
Temperature during ThR treatments of initial mixture are plotted along the horizontal axis, and the phase concentration in initial mixture Y1Ba2Cu3O7 possessing the HTSC properties are plotted along the vertical axis. One process is given by lines and zones marked by letter "a". As a result of heating during ThR treatment up to temperature close to melting onset temperature (required for obtaining good adhesion) the concentration of HTSC component in the initial mixture is totally or partly restored providing the HTSC properties for the fired (formed) thick film element. Another process is shown by lines and zones marked by letter "b". Here initial mixture does not contain HTSC component. With temperature growth due to ThR treatment the phase with HTSC properties appears in the synthesis zone and it can left at following cooling or it can disappear again in the melting zone. However, after cooling the HTSC component appears again thereby determining HTSC properties of the formed thick film element. Which of these methods is realized in practice depends on the requirements to thick film component, kind of plate material and powder, etc.

CONCLUSION

An objective evidence of the HTSC property presence in thick film element based on the system Y1Ba2Cu3O7-X is an existence of orthorhombic or tetragonal phase in material independently of the method of its obtaining either baking or crystallization from the melt. This data were obtained from analysis of the X-ray diffractogrammes of the samples under normal conditions without their cooling down to cryogenic temperature.

Thus, the success in producing of the thick film component with HTSC properties by thermal-radiation firing is determined by the possibility to achieve an acceptable adhesion of thick film element to the plate and to the buffer layer, and to obtain the orthorhombic phase in the system and to select the most active small fractional powder. For preparation of the component for specific purpose an optimization of ThR treatment by critical temperature and current density can be required. The production of thick film elements with HTSC properties on the basis of system Y1Ba2Cu3O7-X by the conventional technique of thick film technology is apparently impossible due to large duration (tens of minutes) and insufficiently high ultimate temperature (lower than 1000 centigrades) of the firing process (thermal treatment) in the conveyor type oven.

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THE INSTALLATION ILU-8TP FOR THE THICK-FILM INTEGRATED CIRCUITS ELEMENTS FIRING

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ABSTRACT

The ILU-8TP System is designed for curing thick-film paste by means of an electron beam in air as a part of a technological complex for screen-and-fire process HIC (Hybrid Integrated Circuit) production. It consists of an electron accelerator type ILU-8, local shielding, internal conveyors and associate support devices and performs the following processes: cleaning of plates by heating; drying of thick-film coating; curing of dielectric, conductive, supraconductive, resistive, gas-sensitive thick-film pastes; hardening of polymer thick-film coatings.

The ILU-8TP System can work with following thick-film plate matters: alumina ceramics, crystalline glasses, stainless steel, titanium.

INTRODUCTION

The non-vacuum Hybrid Integrated Circuit (HIC) thick-film elements production technology is based on thermal radiation effects of firing the paste compositions on the thermoresistant plates. Its creation is one of the outputs of long lasting (more than 30 years) line of the industrial accelerator's elaboration in the Institute of Nuclear Physics. The described installation is an example of both radiation and heat treatment of different materials by the electron beam in the microelectronics industry.

The Electron Beam (EB) with energy 0.6-1.2 MeV is warming up the thin surface layer (about 1 mm) of the plate (with density 2 - 4 g/cm3) practically homogeneously, and the efficiency of the beam kinetic energy conversion into the heat is practically equal to 100%. The necessary firing time is 10 - 100 seconds at usual beam current density 0.01 - 0.1 mA/cm2. The beam energy range is lower the threshold of photonuclear reactions so the plates do not acquire the induced activity. The fast underbeam warming up determines great differences in the element's structure, phase and chemical states in comparison with fabricated by slow firing process in the oven. This is the reason of change of mechanical and electrophysical properties of elements.
Fig.1. The installation ILU-STP for the non-vacuum Hybrid Integrated Circuit thick-film elements firing.

1 - electron accelerator’s cavity, 2 - HF generator, 3 - coaxial air-filled feeder, 4 - electron beam extraction device, 5 - local shielding, 6 - conveyor, 7 - movable protection wall, 8 - high-vacuum pumps, 9 - forevacuum mechanical pump, 10 - air collector, 11 - air filter, 12 - input tray, 13 - output tray.

DESCRIPTION OF ILU-STP INSTALLATION

The installation ILU-STP with the peripheral technological equipment realizes the production of thick-film Hybrid Integrated Circuits (HICs) by Electron Beam (EB) technology. Installation comprises the high frequency electron accelerator ILU-8, local shielding, beam extraction device, three computer controlled conveyors for the HIC plates transportation in the thermal radiation treatment zone with the input and output channels. The power supply and control systems, water and air cooling are also present. The semi-automated mechanic transportation system can be supplied by special request instead of computer controlled conveyors.

The installation drawing is shown on the Fig.1. The High Frequency (HF) power is supplied to the accelerator’s cavity 1 from the generator 2 through the coaxial air-filled feeder 3. The conveyors 6 are placed under the extraction device 4 with three extraction windows. The extraction window foils are cooled by the air flux moving from the aerial filter 11 through collector 10 to exhaust blower. The accelerator’s pumping is provided by the forevacuum mechanical pump 9 and the high-vacuum magnetodischarge pumps 8.

The accelerator is surrounded by the steel local shielding 5 for the biological protection of the staff. The wall 7 can be moved on the rails to permit the personnel enter and work with the installation. The HIC’s plates are pushed on the input 12 and the output 13 trays passing through the channels in the protection wall. These channels are formed arch-like to provide the complete radiation shielding.
The power supply source is mounted in three cabinets with dimensions 0.9*0.9*2 (height) m³ and placed in a separate room. The manual control system is mounted in the same cabinet, and the automatic control system comprises the set of electronic blocks (placed in a single CAMAC crate) and IBM PC compatible personal computer together with the keyboard and colour display.

The ILU-8TP parameters are:

- Cavity's working frequency: 180 MHz
- Electron's energy in the beam: 0.7 MeV
- Maximal average beam current: 30 mA
- Current pulse duration: 0.6 ms
- Maximal pulse repetition rate: 50 Hz
- Maximal consumed power: 80 kW
- Extraction window dimensions: 600*90 mm²
- Continuous working time: 2 shifts per day

PERIFERAL EQUIPMENT AND MODES OF FUNCTIONING

The peripheral equipment comprises Automatic Mask Printing Installations (AMPI), automated (and/or semi-automated mechanic) plate transportation, cooling and cassetting devices, etc. All three technological lines of this installation can work either as independent lines or as the stages of the consequent production cycle. It is depending on the peripheral equipment configuration.

The technological complex elements are shown on the Fig.2. The elements 1, 2, 4, 5, 6 & 11 refer to the ILU-8TP description. In the three independent lines mode the autonomous AMPIs are supplied by the reception cassettes permitting to load the plates with the wet printing. Every production line is supplied by the unloading gear for this cassettes and the line of the elements 7, 8 & 9 providing the cooling and the loading of the ready plates into the cassettes.

The central production line N 3 is designed for the precise treatment operations performance such as the resistors' firing. The sidelong lines N 2 & 3 are designed for the non-precise operations such as the bake-out of the plates, the printing's drying, the firing of the conductive and insulating pastes.

The EB pulse is scanned across each of the three extraction windows in any sequence according the technological needs. Moreover the beam can be scanned across the central extraction window in two or three lines permitting to control flexibly the treatment intensity across the conveyor.

In the case of the consequent production cycle the AMPI 13 of the technological line N 1 is supplied by the cassette device and the manipulator for the single-plate loading. The AMPIs 10 & 12 of the lines N 2 & N 3 are working with the plate transportation gear, picking up the plates one by one. After the line N 3 output the plates are going on the cooler 9 and then are loaded into the reception device cassette 8 by the manipulator 7.
The main elements of the technological complex ILU-STF.

1 - electron accelerator's cavity, 2 - local shielding, 3 - TV camera, 4 - electron beam extraction device, 5 - conveyor, 6 - HF generator, 7 - manipulator, 8 - cassetting device, 9 - plate transportation and cooling devices, 10, 12, 13 - automatic mask printing installations, 11 - movable protection wall.

The typical example of consequent production cycle is:
line N 1 - the conductive elements printing and firing
line N 2 - first resistor's layer printing and drying
line N 3 - second resistor's layer printing and firing of both resistor's layers

The computer program maintains the beam energy and current, pulse repetition frequency, the temperature in the irradiation zones, etc. The values of these parameters and their tolerances can be changed routinely. The main subject of stabilization is the temperature in the irradiation zones. Moreover, the computer is able to maintain the established value of the check resistor (or several resistors) on the fired plate after the resistor's layer firing. Each plate can be tested automatically after firing and the irradiation regime can be changed to obtain the precise resistor's values thus compensating the slow changing parameters of the paste or of the printing process (due to the wear-and-tear), etc.
The thermal inertia of the process is very small because the electron beam energy transfers into the heat directly in the plates. Due to this, the installation enters into the normal way of functioning in 10—20 minutes after switching on from the cold state (in the beginning of the working day and week), and the change of operating conditions takes about 1 or 2 minutes.

As the automated computer controlled transportation system is high technology equipment and is very complex, we have envisaged the possibility to use semi-automated mechanic transportation system. It is simple, cheap, and does not require highly qualified persons for operation and service. It can be preferable for some production lines or for laboratory scale production.

Parameters of technological complex with ILU-8TP system are:

- ceramic plates dimensions: 60*48*1 mm³
- maximal process temperature: 1000°C
- temperature maintenance precision: 1%
- number of simultaneously functioning productive lines: 3
- maximum common productive rate: 3000 plates/hour
- number of simultaneously functioning productive lines: 1
- maximum productive rate: 1000 plates/hour

CONCLUSIONS

Using ILU-8TP system instead of baking oven permits to:

- improve the quality of thick-film components;
- increase the density of thick-film elements;
- decrease the quantity of defective multilayer plates;
- make the resistance trimming process easier;
- use base-metal paste instead of a noble-metal system;
- use metal plates instead of ceramic plates;
- make the screen-and-fire process fabrication system highly automatic.

In addition, ILU-8TP system can produce semiconductor gas sensors, heating elements, temperature-sensitive resistors and capacitors, supraconductive elements.

REFERENCES


ABSTRACT

Compact electron accelerators with energy range 0.25-1.0 MeV and beam power up to 32 kW are described. The feeding high voltage is formed by converter (working frequency 20 kHz), coreless step-up transformer and a set of rectifying sections. The rectifying multiplier circuit used in rectifying sections permits to reach voltage gradient along accelerator's axis up to 14 kV/cm. The accelerators with vertical and horizontal position are described.

The accelerators can be produced together with local radiation shielding and various underbeam transportation systems for irradiation of different products. Such version can be installed in any room facing general requirements for electric equipment.

INTRODUCTION

The design of main accelerator's components was chosen like that of known ELV type accelerators [1]. It consists of coreless step-up transformer, high voltage rectifier, accelerating tube, extraction device, power converter and other auxiliary equipment. The coreless transformer and high voltage rectifier are placed inside the high pressure tank filled with compressed nitrogen with insufficient addition of SF6.

The secondary winding of transformer is divided into separate windings. The high voltage rectifier is performed as a set of rectifying sections containing the winding and rectifying multiplier circuit. Resulting rectified voltage of section is in 2 or 4 times greater than the amplitude of alternative voltage on winding (Fig.1). The sections are connected with each other in series.

The transferred electric power is proportional to the energy stored in the transformer and to the working frequency. The increase of working frequency permits to increase transferred power at fixed outer dimensions. And the quality of primary winding is also growing with the frequency increase so the efficiency became better.

Accelerators in run are pumped by magneto-discharge titanium vacuum pumps. The forevacuum mechanic pump is used only after opening of accelerator for preliminary pumping out of air.

The design and fabrication technology of accelerating tube are the same as that of ELV accelerators. Design of extraction device is practically similar to that of ELV accelerators but its effectiveness and reliability are improved due to additional bending magnets and second protecting foil.
Fig. 1. Electrical circuit of the HFELV accelerators.

Fig. 2. General view of the HFELV-3.
Fig. 3 Design of the HFELV—4 accelerator.

1. Bearing Frame.
2. High pressure tank.
3. Primary winding.
4. Rectifying sections.
5. Accelerating tubes.
6. Heating control unit.
7. Optic lines.
8. Bearing insulator.
9, 10. Magnetic circuit.
11. Extraction device.
12. Extraction window.
13. Bending magnet.
15. High vacuum pumps.
16. Gate valve.
This doubled construction has obvious advantages from high voltage insulation point of view - it is a symmetric coaxial construction, and the point of maximum potential is in the centre of tank. The spheric screen on high voltage end of rectifier is not needed. And the coreless transformer in this design has a symmetric coaxial construction, and its magnetic resistance (for magnetic flux) is lower. So total efficiency of construction is better in comparison with traditional construction in 1.2-1.3 times. The detailed description of these advantages is given in [2].

The accelerator HFELV-4 has the same accelerating tube as HFELV-3 (insulator length 660 mm). It has heated lanthanum hexaboride cathode with diameter 6 mm and beam current control is the same as in HFELV-2. It is built in right rectifier (see Fig.3). The horizontal position of HFELV-4 required the special construction elements for support of rectifier sections. It is done by special bearing insulator (8) and three insulating bars penetrating through rectifiers. Each section is attached to these bars.

Right high voltage rectifier with accelerating tube inside, right half of tank, extraction device and vacuum pumps are fastened on the bearing frame supplied with rollers. The left high voltage rectifier and left half of tank are fastened on the movable supporting frame which can be moved along bearing frame during the mounting and service works.

EXTRACTION DEVICE

From the accelerating tube the beam of accelerated electrons goes into extraction device where it is extracted into atmosphere through window covered with foil. Design of the extraction device is practically similar to ELV accelerators but its effectiveness and reliability are improved due to additional bending magnets and second protecting foil. This more thin foil is preventing the main titanium foil from contact with air in irradiation zone. The foils are cooled by air flux in the gap between them created by high pressure blowers. The electron beam is scanned over the surface of foil by deflecting coils in two directions. The main coil is deflecting beam along extraction window at an angle +/- 45 degrees with frequency 50 Hz. The additional coil is deflecting beam across the extraction window at an angle +/- 3.5 degrees with frequency 1075 Hz. A additional bending magnets permit to deflect the beam at an angle more than 60 degrees without increase of losses on the foil. Dimensions of extraction window for all modifications are 75*980 mm. The width of irradiation zone with high dose homogeneity is up to 900 mm.

CONTROL AND POWER SUPPLY SYSTEM

The accelerators are fully automated and controlled by IBM PC compatible computer. Manual operation mode is also envisaged. Energy and beam current are controlled and monitored. The underbeam transportation system can be synchronized with accelerator to organize industrial irradiation process.
The accelerator has control rack with dimensions 570*570*1600 mm. It comprises all control and monitoring circuits and most part of power supply system. The computer is installed in the same room and connected with control rack through cable. The accelerator is fed from standard three phase 220/380 V 50 Hz mains.

The development of technique of thyristor converters and industrial production of high-frequency rectifying units permit us to design new generation of compact electron accelerators. We have designed compact powerful controlled thyristor converter with working frequency 20 kHz and power up to 20 kW. It is built in the control rack, and its weight is only 10 kg. It also can be realized as a separate block and can be located near the accelerator or in other place because the length of output connecting cable can be up to 25 m. It has remote control and its output voltage is computer or manually controlled from 100 to 200 V. Its efficiency is high so air cooling is sufficient. Power supply blocks for magneto-discharge vacuum pumps are also air-cooled and very compact.

As all power supply system is very effective the need in cooling is very little. Nevertheless accelerator itself requires little water cooling. The primary winding of the step-up coreless transformer requires 1 l of water per minute. and magneto-discharge vacuum pumps consume 2 l per minute. The cooling water should be pure and have input temperature no more than 30 centigrades.

Gas filling post is used for filling of tank with gas mixture (nitrogen with 8-10% addition of SF6) up to working pressure about 12 at. It comprises two standard gas balloons with volume 40 litres each (one with compressed SF6, and other with compressed nitrogen), connecting pipes, valves (including protecting valve) and measuring devices. Its dimensions are 290*500*1800 mm and weight is 220 kg. The insulating gas mixture is not used again and after every opening the tank is filled by fresh gas mixture from these balloons. For HFELV-4 one balloon with SF6 can provide about 18 fillings of tank, and one balloon with nitrogen can provide about 2 fillings of tank. As HFELV-3 and HFELV-2 have lower volume of tank, the number of fillings for them is correspondingly higher.

CONCLUSION

The set of compact electron accelerators with energy range 0.25-1.0 MeV, beam power up to 32 kW and specific power up to 130 kW per cubic meter of high voltage generator are designed. Supplied with local radiation shielding they can be installed in any room like any other technological electric equipment.

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TECHNICAL TRENDS OF EXPOSING EQUIPMENT IN THE PCB MARKET IN ASIA
and APPLICATION OF THE UV TECHNOLOGY
TO THE RELATED ELECTRONIC INDUSTRIES

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SUMMARY

Exposing technologies for printed circuit boards (PCB) greatly depend on
improvement of photoresists in terms of material and the optical properties of a
light source used in exposing equipment and accuracies of peripheral devices, in
view of equipment. Where the same photoresist of high performance is used in
different exposing systems, results of pattern resolution performance may become
greatly different and to produce high-quality PCB, one of the most important
conditions is to select a high-quality exposing system.

INTRODUCTION

In the 1990s, foreign exchange rates of yen have risen and economy mainly
in Southeast Asia has drastically grown. Meanwhile, Japanese manufactures have
constructed many overseas plants and in association with prompt advancement of
production technologies in these countries (particularly in Taiwan), trends of
PCB production in this territory and Japan have significantly changed.

In Japan, production facilities for low-cost PCB have been shifted overseas
and then some middle-class goods have been returned to Japan while
consolidating and concentrating domestic production plants. In addition, types
of goods produced in Japan have been restricted to more sophisticated devices
through the development of high-grade production technologies. One of the most
important advantages of goods production in Southeast Asia (especially in Taiwan)
is overwhelming low manufacturing cost introducing many automatic exposing sys-
tems concentratedly into the manufacture of PCB for personal computers.

Another tendency in these countries is that manufacturers including
Japanese overseas corporations have been dedicated to the production of PCB for
consumer appliances. Furthermore, manufacturers in the countries want to or are
actually constructing production machines in each nation. In these circumstances
of changing as described above, the authors will describe key technologies in the production process of PCB, technical trends of exposing systems in patterning and the relationship between light sources and materials (photoresists), along with demonstrated test data.

**TRENDS OF EXPOSING SYSTEMS AND RELATED UV EQUIPMENT**

The elementary technologies in exposing systems are classified generally into 4 categories of light sources, controlling method of exposing energy, alignment and the structure of exposing frame. Light sources have been improved from high-pressure mercury lamps to mercury short-arc lamps via capillary typed superhigh-pressure mercury lamps, as a general trend in Japan. Although the controlling method of exposing energy has not been renovated greatly, that is, from timer control to integrated light meter, spectra of light sources and spectral sensitivities of photoresists must be taken into consideration. Regarding alignment, the trend of alignment method is visual (manual) alignment, pin alignment and automatic alignment by image recognitions. These 4 elementary technologies in ORC's exposing systems are shown in the following Fig.1 together with the relationship with similar products.

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<tr>
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<tr>
<td>VISUAL (MANUAL) ALIGNMENT</td>
<td>IMAGE RECOGNITION ALIGNMENT</td>
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<tr>
<td>MW-201 FAMILY (3kW ~8kW)</td>
<td>EXM-1500</td>
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<td>MANUAL</td>
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<td>: HT-102, HTE-102S, ETC.</td>
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<td>similar products</td>
<td>HTE-8000, YH-6080, ETC.</td>
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<td>HMW-680</td>
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**AUTOMATIC EXPOSING SYS.**

EXM-1050 --EXM-1280 --EXM-1350 --

FIG. 1 Chronology of ORC's exposing systems

As shown in Fig.1, other manufacturers have put similar models to those of ORC, one of the leading manufacturers in the market. We generally note that, in the U.S.A., Canada and even in the Southeast Asian market, users who have bought ORC's goods looking for the production of high-quality, high-value-added PCB, and users in the other territories or those who are not looking for the production of such PCB, seem to prefer goods from manufactures other than ORC, in many cases.

Relating to UV conveyors, some manufactures in Southeast Asian countries have already constructed UV conveyors in their own countries, and part of other manufacturers is going to produce the conveyors nationally. because very high
technologies are not required. UV conveyors are mainly used for producing low-cost consumer appliance PCB. Therefore, Japanese brand of UV conveyors are not always specified. So-called spot-UV equipment, used in UV bonding in a package process, was originally supplied from Japan, but recently, low-cost goods have been put on the market. Users seem to select Japanese goods where machinery will be applied to full-automatic lines, because numerous interfaces are demanded, and in other more simple production lines, simple and easy equipment and systems may possibly be introduced.

DEVELOPMENT OF NEW PRODUCTION TECHNOLOGY

Type of PCB are classified generally into those using supermulti-layer boards of about 40 layers, for supercomputers, multi-layer boards of about 6 to 18 layers, and others of front and rear surface layers only, for general consumer appliances. For each type, new production methods have been developed in every generation of renovation 1). New production methods recently developed include the modified build-up process and transprinting build-up process, improved from conventional build-up process; in the former process, an alkaline development type photoresist is used as an inner-layer insulation resin, and the latter process has been developed by combining a conventional build-up process with the transprinting process. Application of these processes to high-density PCB with IHV, MCL-L PCB, and etc. is proposed. Regarding the transprinting build-up process, reported particulars of a practical application include circuit line width and space of 125/150 μm for an inner-layer circuit and those of 40/40 μm in an outer circuit 2).

On the other hand, new photoresists have been continuously developed, and new high-follow-up type dry-film photoresists (dry-film) have been also developed, though conventional dry-film were considered to be inferior in PCB follow-up properties; reportedly 3), 40 μm and 15 μm thick resists could be resolved to 25/25 μm and 10 μm, respectively. In addition, new materials have been also developed, and dry-film are sometimes applied to chemical milling, though liquid photoresists were used conventionally. Results of such development work may bring about a favorable effect to manufacturing of COB boards in which part of patterns must be finest. This technology may possibly become a mainstream for packaging of devices in the future. Also in the category of exposing systems, conventional total exposing systems will possibly be advanced next generation.

EXPOSING TECHNOLOGY AND MATERIALS

Among light-source qualities that govern imaging, parallel rays are of
course much more superior than scattered rays in terms of resolving power. Those important key factors for good imaging are shone in Table 1.

<table>
<thead>
<tr>
<th>KEY FACTOR FOR GOOD IMAGING</th>
<th>EXPOSING EQUIPMENT</th>
<th>MATERIAL</th>
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<tbody>
<tr>
<td></td>
<td>LIGHT SOURCE</td>
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<td>SCATTERED LIGHT SOURCE</td>
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<td>UV-INTEGRATOR</td>
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<td>ALINGMENT MÉTHODE</td>
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<td>PIN-ALIGNMENT</td>
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Table 1 Classification of technical items for good imaging

The relationship between exposing light and materials has been discuss from numerous viewpoint, in regard to photoresist then available \(^4\)\(^5\). Normally, the relationship is presented with a parameter of a gap between a photomask and a photoresist, including vacuum adhesion and soft contact, for a maximum resolving power and a pattern shape after developing. In a practical manufacturing process, a theoretical minimum line width to be discussed next will not be applied directly, but a minimum practical line width seems to be about twice or more the minimum theoretical line width (at a maximum resolving power). Under the diversified conditions described above, only the relationship between resolution property and light-source qualities (scattered light or collimated light) discussed in the following. Three types of light sources were used: the first one generated parallel light (with a collimation angle of 2° and a declination angle of about 2°: corresponding to ORC MODEL EXM -1201) using a mercury short arc lamp that has been becoming a standard light.
source in Japan, and a conventional mainstream of scattered light: A (corresponding to ORC MODEL HMW-201) using a superhigh-pressure, high-luminance mercury lamp which arc size is about $2\text{mm } \phi \times 150\text{mm}$. And a metal halide lamp which arc size is about $20\text{mm} \phi \times 80$ to $150\text{mm}$ scattered light: B (corresponding to a model of OLEC, U.S.A.).

ED-PHOTO RESIST, DRYFILM PHOTORESIST, and LIQUID ETCHING RESIST were used for testing. An ORC's standard test pattern (minimum line width: $25/25$ $\mu\text{m}$) was used for exposing. Each light source was operated appropriately for vacuum-contact exposing and gap exposing. The test sample were developed under specified developing conditions of each photoresist. Fig. 2 shows one of the examples of SEM-Photos of dry-film ($50 \mu\text{m}$ thickness).

As shown in the SEM photos, obtained pattern shapes are significantly influenced by the light source. It is also revealed that considerable differences occurred between resolving powers where extremely large air gaps were provided for exposing. Exposing with collimated lights of course brought the best pattern reproducibility, and even by exposing with air gaps, acceptable resolving powers were demonstrated as shown in Fig. 3.
FIG. 3 Reproducibility in contact/air-gap exposing

SUMMARY

1) It was concluded that exposing performance is greatly affected by a light source.
2) It was suggested that the performance of the entire exposing equipment may greatly affect practical production.
3) To produce high-added-value PCB in high precision in the future, the introduction of reliable, long-proved system is recommended.

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ULTRAVIOLET MEASUREMENT INSTRUMENTS FOR PROCESS MONITORING

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ABSTRACT

Ultraviolet (UV) radiation is gaining widespread acceptance in industrial processes. Measurement of UV intensity and total energy falling on a work piece is very valuable as an aid to process control. This paper describes two UV measuring instruments and their characteristics. The instruments are designed for use in a production environment and are commercially available.

INTRODUCTION

In the past, ultraviolet radiation measurements have been restricted to the laboratory because of the bulky, awkward equipment required to make the measurements. Because of the increase in popularity and utilization of UV radiation in industry, a number of new developments in UV measurement has occurred. These instruments are designed to be used in the workplace and are aids to process control. This paper describes two of these instruments and their basic principles of operation. The instruments are:

- High Energy Integrating Radiometer
- UV Energy Mapping Device

BACKGROUND INFORMATION

The UV radiation spectrum comprises those wavelengths 200-450nm as shown in Figure 1. The UV spectrum is subdivided into UV-A, UV-B, UV-C and UV-V as indicated. UV-A, 320-450nm, is transmitted by ordinary glass and plastic. Glass and plastic pass wavelengths longer than 320nm and strongly attenuate below 320nm. If pure quartz is used in the light path all wavelengths from 200 to 400nm are passed. However, quartz is much more expensive. Further, the shorter wavelengths tend to produce ozone, which, if not removed, can cause operator discomfort and tends to deteriorate certain materials such as rubber and some plastics. As a result, some curing lamps are treated to suppress all but the UV-A and UV-V band.

In recent years, ultraviolet-visible, or UV-V, defined as the range from 400-450nm, has become more widely used, particularly in heavily pigmented materials because of its ability to penetrate thin layers of material.

UV imaging is typically conducted at relatively low intensities, seldom exceeding 50mW/cm². While UV curing is typically done at levels up to several watts/cm². Measurement at higher energy levels is more difficult because the infrared radiation associated with the source elevates the temperature in the curing area. Also, because the UV sources are usually mechanically shielded, access to the work area for measurement of UV with conventional lab instruments is inconvenient at best.

UV radiation sources typically use medium or low pressure mercury vapor lamps. The envelopes are quartz and the interior is a partial vacuum to which a small quantity of mercury and inert gases has been added. Radiation is produced by electrically exciting the mercury molecules in the tube. Excitation may be accomplished by electrically accelerated electrons or by microwave energy. Figure 2 is a spectral distribution from a typical mercury lamp. Note that not only is there energy in the UV portion of the spectrum, there is also a large amount of energy present in the
visible portion of the spectrum. The visible and infrared wavelengths are generally not of interest in the radiation curing process but their presence does complicate the measurement of UV. One of the basic objectives for any instrument that measures UV energy is for the instrument to measure only UV and reject visible and infrared energy.

Development of the high energy radiometer and the intensity mapping device was done to enable a user of UV radiation to have a small, simple to use instrument which can characterize the UV process environment. The characterization is made more difficult by a harsh industrial environment.

HIGH ENERGY UV INTEGRATING RADIOMETER

Figure 3 shows a high energy UV integrating radiometer. It is used to measure and display peak UV intensity and the total amount of UV energy impacting on the radiometer's top or measuring surface while it is in a UV system. This energy is the same amount of UV energy that would be impinged on a work piece while the work piece is in a UV system. The instrument is designed to be compact enough to fit the work area of most curing systems and is also thermally and optically designed to operate in the extremely hostile environment encountered during UV processes. It is battery powered so that no external power source or wires are required.

The radiometer is placed in operation by depressing a flush-mounted switch on its surface. The unit is then placed under the UV source with its quartz window (measuring) side toward the source. UV radiation intensity is measured, integrated and displayed on a self-contained digital display. When the unit is removed from the radiation it continues to display the integrated intensity, which is accumulated energy in mJ/cm², for a period of four minutes after the last radiation was received. By depressing the “Select” button total energy is replaced by peak intensity, in W/cm². The last values of energy and peak intensity are stored even while the instrument is off so that the last readings are available long after use. The radiometer can be used to measure UV energy received from a conveyorized curing system or a stationary source such as a curing chamber or sterilizer. Figure 4 shows a radiometer emerging from a conveyorized system. This is a very common application.
The radiometer is battery powered from user replaceable lithium cells which provide about 50 hours of use. A "LoBat" display indicates that the battery is near the end of its life. The electronics can tolerate 85° C; however, to avoid possible damaging temperatures, an audible and visible alarm is provided when the internal temperature exceeds 70° C. These two features are very important to avoid thermal damage during prolonged operation.

**TECHNICAL DESCRIPTION**

The instrument is housed in a stainless steel case which protects the microprocessor based electronics. A quartz window admits radiation on one side, (Figure 4) Two control buttons and a liquid crystal digital display are on the opposite side (Figure 3). Replaceable batteries under a cover are also accessible from this side.

The instrument is designed to measure individual UV bands, either A, B, C or V. In the instrument shown maximum accumulated energy is 250 Joules/cm\(^2\) Instrument range is finite. It has an upper intensity limit of 5W/cm\(^2\) and a measurement threshold, below which the instrument does not measure, of 5mW/cm\(^2\). Thus, the instrument is designed for high energy curing situations.

The optics of the instrument are carefully designed to provide maximum temperature stability and matching of spectral characteristics. Matching of optical characteristics has long been a problem in the industry. In the past, it was not unusual to place two instruments side by side and obtain results which differed by ±40% due to lack of optical characteristic matching between the two units. This instrument is designed to obtain results which differ, unit to unit, of no more than ±5% regardless of spectral characteristics of the illuminating source. Figure 6 shows numerical results obtained from two instruments under a "V" type lamp. It also illustrates the results obtained when varying conveyor speed. Since total energy varies inversely with speed, the resulting curve is a hyperbola. The good agreement between the two units is an excellent indicator of measurement quality.

The optics are also designed to provide cosine response to incident radiation because such response replicates how workpieces absorb energy as a function of angle of incidence. Cosine response is defined as the ability of the instrument to provide measured intensities as a function (1-cosine of the angle of incidence) of radiation. For example, rays which strike the instrument perpendicular to the measurement lens have a value of (1-cos 90°)=1. Rays which strike at 30° have a value of (1-cos 30°) = 0.5 and so on. Figure 7 illustrates theoretical cosine response and measured response for UV-A and UV-V channels on an actual instrument.
In addition, the optics provide at least 10,000:1 rejection of infrared (IR) and visible wavelengths compared to UV. This is very important because there are typically large amounts of IR compared to UV in a UV source.

APPLICATIONS

The instrument is used in many industrial processes that utilize UV including the printing, semiconductor, wood finishing, printed circuit board, and compact disc industries. It is used by both operators and supervisors as a process control monitor.

UV INTENSITY AND TEMPERATURE MAPPING INSTRUMENT

A UV Intensity/Temperature Measurement and Plotting Instrument (UVIMAP™), which provides the capability of measuring and plotting UV intensity and associated temperatures in a UV system is shown in Figure 8. It is fabricated from temperature and UV resistant materials.

In use, the measurement instrument is placed in the UV environment, such as the conveyor of a curing system, and is exposed to the same UV and temperature conditions that a work piece encounters. The instrument measures and electronically stores the UV and temperature data. Upon completion of the measurement the UVIMAP can be connected, via cable, to a small, self-contained printer/plotter which automatically plots the stored data and annotates the chart. Figure 9 shows the instrument and its associated printer plotter. Figure 10 is a sample plot. Note that the ordinate is simultaneously UV intensity, in mW/cm², and temperature in °C. The abscissa is the number of UV and temperature samples with the area between each mark representing 10 and 5 samples, respectively. Alternatively, the UVIMAP can be connected to an IBM PC or equivalent and the stored data transferred to the PC. The data can be presented in tabular form on the screen, printed and/or downloaded to hard or floppy disk for permanent storage.
TECHNICAL DESCRIPTION

UVIMAP comprises two separate assemblies, the data collection unit (DCU) and the printer/plotter. An IBM PC or PC clone may also be used as an alternative to the printer/plotter in connection with the DCU. Figure 11 is a simplified block diagram of the complete system. The function of the DCU is to measure, digitize and store UV and temperature data for subsequent display on the Printer/Plotter and/or display and storage by the PC.

The DCU has a quartz measurement window on one side which admits UV. The other side contains switches which allow selection of:

- Intensity range: 100mW - 5W full scale
- Sample rate: 1-40 per second
- Temperature range: 50-400°C full scale

Two switches located on the end of the unit allow selection of "ON/OFF" and "Record/Plot". These controls are visible in Figure 12. The DCU is rechargeable battery powered and will operate about 6 hours on a single charge.

In operation, the unit is turned on and UV and temperature data are measured, digitized and stored in DCU memory. The memory can accommodate up to 4096 separate measurements so that if a sample rate of 40 per second is chosen, data can be recorded for 100 seconds or 1-1/2 minutes. Alternatively, a sample rate of 1 per second provides 4000 seconds or about 60 minutes.

Stored data is plotted on a battery powered printer/plotter by connecting a cable between the DCU and printer/plotter and activating the PLOT switch on the DCU. The plotter can also be powered from AC sources. Data may be transferred to a PC in like manner.

TYPICAL APPLICATION

The instrument is designed to be inserted into environments where excessive thickness, protruding wires or sensitivity to heat or UV would preclude making measurements. Conveyorized and static UV curing systems are two such examples.

Figure (10) is a typical plotted result. It shows that the plot provides simultaneously, UV intensity and temperature. In addition, the instrument provides, in numerical form, total integrated UV energy, peak UV intensity and peak temperature. In Figure 10, total energy is 277mJ/cm², peak intensity is 170mW/cm², and peak temperature 83°C. Both the traces and the numerical data provide important information. Integrated energy is valuable as an indication of process conditions. Peak intensity is an indication of lamp and reflector condition. Shape of the intensity curve is indicative of lamp focus and reflector condition. The temperature trace is of value to determine if the product is receiving excess heat or if lamp cooling is inadequate. Data in tabular form provides valuable archival data.
Among the more common applications of the instrument is for process control monitoring in conveyorized systems. It is also commonly used to determine UV system maintenance requirements. The traces provide a valuable indication of lamp, reflector and cooling system condition and assists in determining if these elements require replacement, repair and/or modification.

CONCLUSION

UV radiometry and measurement instruments have gradually evolved in terms of flexibility and capability so that they have become very important factors in process control. This type of instrument is vital to Statistical Process Control efforts.
The Absorbed Dose Measurements of 0.3-0.6 MeV Electrons in Multilayer Media

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In this paper, an electron beam current densimeter has been described and used for dose measurement in EB radiation curing. Our emphasis is laid upon the dose distribution measurement and calculation of 0.3 MeV low energy electrons in multilayer media. In addition, the dose distributions of 0.4-0.6 MeV electrons in multilayer media have been calculated by the bipartition transport model. The calculation results are in agreement with the measurement data.

INTRODUCTION

The absorbed dose measurement in EB radiation cured coatings is an important problem, and it is difficult to solve the problem on 0.2-0.6 MeV electron dosimetry. To unify the methods of dose measurement and estimation, Japanese Low-Energy Electron-Dose Measurement Committee performed the first dose intercomparison in 1985 (Tanaka et al. 1989). The multilayer depth dose distributions can be evaluated by the Tabata's code EDMULT (Tabata et al. 1989). The dose measurement and calculation of 0.2-3 MeV electrons in EB radiation processing have been reported by us (Zhou et al. 1993). Luo's bipartition model of electron transport (Luo, 1982, 1985) has been used to calculate the electron energy depositions, and the dose distributions have been measured by FWT-60 nylon film dosimeter.

MEASUREMENT AND CALCULATION

An electron beam current densimeter has been used for beam current monitoring of 0.3-0.6 MeV electrons. The total beam current intensity I(A) is measured with a charge-collected plate made of aluminium. From the known quantities and I(A) measured here, the mean beam intensity \( \dot{i}_0(A) \) in irradiated product region can be calculated, and the charge-density \( q \) may be obtained by

\[
q = \frac{i_0}{\nu w} \quad (C/m^2)
\]

where \( \nu \) is conveyor speed (m/s); \( w \) is beam width perpendicular to the movement of conveyor at the product surface (m).

Using \( q \), the absorbed dose \( D \) can be given by following form (Okabe et al. 1989):
\[ D = Kq \quad \text{(kGy)} \]  
\[ K = \left( \frac{10^2}{x_s} \right) \int_{x_s+x_w}^{x_s+x_w+x_t} I(x, E_0) dx. \]  
\[ \text{where } K \text{ is absorbed dose coefficient (kGy m²/C), } x_s \text{ is coating thickness (g/cm}^2\text{), } x_w \text{ is Ti window thickness (g/cm}^2\text{), } x_t \text{ is air layer thickness (g/cm}^2\text{).} \]

\[ I(x, E_0) \text{ is energy deposition (MeV cm}^2\text{/g); } E_0 \text{ is initial energy (MeV); } x \text{ is depth in the multilayer absorber (g/cm}^2\text{).} \]

When the coating thickness\(\leq 50\mu\text{m}\), the form (3) may be simplified as following approximate relation:

\[ D = \frac{10^{i_t} f_s I(x_p, E_0)}{v w} \quad \text{(kGy)} \]  
\[ \text{where } f_s \text{ is the electron reflection coefficient of the charge-collected plate; } I(x_p, E_0) \text{ is the energy deposition (MeV cm}^2\text{/g) by electrons of the acceleration energy } E_0 \text{(MeV) at the depth } x_p \text{(g/cm}^2\text{) in the irradiated material; } x_p \text{ is the depth at which } I(x_p, E_0) \text{ reaches the maximum;} \]

\[ i_o, v, w \text{ are the same with that in form (1).} \]

The simplified bipartition model of electron transport was used to calculate the energy depositions \(I(x, E_0)\) and \(I(x_p, E_0)\) of 0.3 MeV electrons in multilayer media (An et al. 1993).

The absorbed dose distributions of electrons in irradiated materials have been measured with FWT-60 nylon flims. The calibrations of the nylon flims were performed with gamma rays and electron beams. The total uncertainty of the absorbed dose measured by the flim dosimeter is better than 8% at 95% confidence level.

**RESULTS AND DISCUSSION**

In this work, we have calculated the energy depositions of 0.3-0.6 MeV electrons in multilayer media, and measured the absorbed dose distributions of 0.3-0.4 MeV electrons in irradiated materials. The materials are nylon flims, MAR (polyester type multifunctional acrylic resin) and MFA (polyether type multifunctional acrylate). The substrates are Al, Fe and gypsum. The Ti window thickness is 30\(\mu\text{m}\). The air layer thickness is 6cm. In addition, the effects of Ti window and air layer on low energy electron transport have been considered. Thus, the electrons will penetrate through 3 or 4 layer materials. Some parameters of measurement and calculation are listed in Table 1.
Table 1. The parameters of Measurement and Calculation

<table>
<thead>
<tr>
<th>Materials</th>
<th>$Z_{eff}$</th>
<th>$Z'_{eff}$</th>
<th>density (g/cm$^3$)</th>
<th>thickness (mg/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nylon</td>
<td>5.67</td>
<td>32.15</td>
<td>1.125</td>
<td>28.1</td>
</tr>
<tr>
<td>MAR</td>
<td>5.97</td>
<td>36.64</td>
<td>1.16</td>
<td>30.0</td>
</tr>
<tr>
<td>MFA</td>
<td>6.69</td>
<td>44.76</td>
<td>1.20</td>
<td>30.0</td>
</tr>
<tr>
<td>Al</td>
<td>13</td>
<td>169</td>
<td>2.699</td>
<td>94.5</td>
</tr>
<tr>
<td>Fe</td>
<td>26</td>
<td>676</td>
<td>7.874</td>
<td>787.4</td>
</tr>
<tr>
<td>Gypsum</td>
<td>16.21</td>
<td>262.76</td>
<td>0.95</td>
<td>475.0</td>
</tr>
</tbody>
</table>

We have calculated the energy depositions of 0.3-0.6 MeV electrons in Ti-Air-Nylon-Gypsum, Ti-Air-MFA-Al, Ti-Air-MFA-Gypsum and Ti-Air-MAR-Fe. The calculation and measurement are as shown in Fig. 1-4.

Fig 1. The dose distributions of 0.3 MeV electrons in Ti-Air-Nylon-Gypsum and Ti-Air-semi-infinite Nylon.
— — our calculational results;
— • — our measurement results.

Fig 2. The energy dose distribution of 0.3 MeV electrons in Ti-Air-MFA-Al.
— — our calculational results;
— • — X — our measurement results.
The energy depositions $I(x_f, E_o)$ of 0.3-0.6 MeV electrons at the depth $x_f$ are given in Table 2.

Fig. 5 shows the dependence of energy depositions $I(x_f, E_o)$ with initial energy $E_o$ and effective atomic number $Z_{eff}$.

Table 2. The Energy Depositions $I(x_f, E_o)$ of 0.3-0.6 MeV Electrons (MeV cm$^2$/g)

<table>
<thead>
<tr>
<th>$Z_{eff}$</th>
<th>$I(x_f, E_o=0.3$ MeV)</th>
<th>$I(x_f, E_o=0.4$ MeV)</th>
<th>$I(x_f, E_o=0.6$ MeV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.67</td>
<td>4.42</td>
<td>4.34</td>
<td>4.27</td>
</tr>
<tr>
<td>5.97</td>
<td>4.54</td>
<td>4.46</td>
<td>4.39</td>
</tr>
<tr>
<td>6.69</td>
<td>4.88</td>
<td>4.79</td>
<td>4.72</td>
</tr>
</tbody>
</table>

Fig. 1-4 show that Ti window and air layer have a great effect on the dose distributions of 0.3-0.6 MeV electrons in the materials irradiated, such as Nylon, MAR, MFA. It can be seen that our calculational results are in good agreement with the measurement data of 0.3 MeV electron dose distributions in semi-infinite Nylon, Nylon-Gypsum and MFA-Al shown in Fig. 1-2. However, when the $Z_{eff}$ of substrates and irradiated materials are higher, the some difference presented between calculation and measurement.

Fig. 5. The dependence of energy depositions $I(x_f, E_o)$ with initial energy $E_o$ and effective atomic number $Z_{eff}$. 

Effective Atomic Number $Z_{eff}$
shown in Fig. 3 - 4. Therefore it is necessary to perform detailed transport calculation and dose distribution measurement of low energy electrons.

REFERENCE

DEGREE OF CONVERSION AND RATE OF POLYMERIZATION AS A FUNCTION OF LIGHT INTENSITY.

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ABSTRACT

Fundamental kinetic theory of free radical polymerization predicts an increase in double bond conversion with increasing light intensity. Experimental findings from FTIR spectroscopy, Laser Induced Polymerization (LIP), Raman Spectroscopy and extraction analysis clearly support this prediction. In this study we have measured the degree of double bond conversion as a function of light intensity at a constant dose of exposure and spectral distribution form the irradiation source. The difference in degree of conversion at a constant dose level is more pronounced at low average degrees of functionality in the polymerizing system. This is also expected from the theory of vitrification and rapid microgel formation, whereby the mobility in the system is greatly reduced even at low degrees of conversion. In the extension of the study it is shown that the concentration of the photoinitiator can be dramatically reduced by increasing the light intensity. In a model study this is confirmed both for curing in air and nitrogen.

INTRODUCTION

Free radical induced polymerization of Acrylates:

For free radical induced polymerization there is a simple proportionality between rate of polymerization, $R_p$, and the light intensity at half power $(I_0)^{0.5}$. At a constant dose of UV exposure, $I_0 \cdot t$, where $t$ is the time of exposure, this simple means that the rate of polymerization will be higher at a higher light intensity.

"Steady State Conditions"

At "steady state", where $R_i = R_t$, we have the following equations:

$$R_i = 2 I_a \phi f(1); \quad \dot{d}[R^*]/dt = R_t = k_t [R^*]^2 \quad (2) ; \quad R_p = k_p [R^*] [M] \quad (3)$$

Insertion of (1) and (2) in (3) gives the well known expression for $R_p$ under "steady state" conditions.

$$R_p = (R_i/k_t)^{0.5} k_p [M] = k_p 0.5 (I_a \phi f)^{0.5} [M] \quad (4)$$

"Non-steady State Conditions"

By integration of (2) we can follow the decay in radical concentration after a short light pulse or exposure time, where $t$ is the decay time after the light pulse.

$$1/[R^*]_0 \cdot 1/[R^*]_t = k_t t \quad (5)$$

After rearrangement: $R_p = k_p (1/[R^*]_0 + k_t t) * [M]_t \quad (6)$
For short exposure times, there are two different cases.
First, for high initial radical concentrations, \( \frac{1}{[R^*]} \) is dependent on the rate of
termination to the negative power of one. Secondly, for low initial radical concentrations,
\( \frac{1}{[R^*]} \) is now less dependent on the rate of termination. However, these general
assumptions are strongly dependent on the pulse length (exposure time).

\[
\begin{align*}
R_i & \text{, rate of initiation} \\
R_t & \text{, rate of termination} \\
k_t & = \text{termination rate constant} \\
k_p & = \text{propagation rate constant} \\
[M] & = \text{concentration of reactive functionality} \\
[R^*] & = \text{total concentration of free radicals, including chain growth, } [M^*]. \\
I_a & = \text{number of photons absorbed/sec., volume} \\
\Phi & = \text{quantum yield, i.e. the fraction of photoinitiator that yields initiator species} \\
f & = \text{cage factor, i.e. the fraction of initiator that initiates polymerization}
\end{align*}
\]

**Dependence on average functionality**

The functionality of the monomers affects both the reactivity as well as the ultimate
conversion of acrylate groups. Generally, the maximum polymerization rate of
multifunctional acrylates are much higher than for monofunctional acrylates but the final
degree of conversion of acrylic double bonds are much lower. This can be explained by the
crosslinking that accelerates polymerization of multifunctional monomers at lower
conversions (less than 30%)\(^5,6\). The main reason behind this is due to the formation of
microgels, giving an increased reactivity of pendant double bonds, i.e. a double bond in a
monomer in which the other acrylate group has already been polymerized. Eventually, at
higher conversions the radical chain and the monomer diffusion become restricted as the
crosslinking density of the matrix increases. A monofunctional monomer, acrylate ester,
does not crosslink and hence the mobility of the radical chain and the free monomer diffusion
is comparably higher allowing for a more complete conversion of the double bonds. As will be
discussed in the Results and Discussion section, a photo-DSC study of the laser initiated
polymerization (LIP) of mixtures of mono-, di- and trifunctional acrylates\(^7\) clearly shows the
inherent reactivity of such multifunctional systems. A study by Wight and Hicks\(^8\) revealed
the effect of a long spacer group between the acrylate groups. For instance, neopentylglycol
diacrylate reached 78% conversion, whilst two difunctional acrylated urethane oligomers and
one difunctional acrylated epoxy oligomer all reached between 98 - 100% conversion.
The more flexible oligomers yields a network with lower glass transition temperatures
compared to the low molecular weight diacrylate. Kloosterboer et.al\(^9\) used photo-DSC to show
that the highest conversion for difunctional acrylates were attained for monomers with three
or four ethylene glycol or propylene glycol units between the acrylate groups. More recently,
Decker\(^11\) and Moussa\(^10,12\) have developed an interesting method to study the kinetics and
degrees of conversion of the acrylate double bond (RTIR). The method is based on exposing the
sample to UV irradiation and at the same time recording the decay of the IR absorbance of the
acrylate double bond.

**EXPERIMENTAL**

**Materials**

Trimethylolpropanetriacrylate, TMPTA, Hexanedioldiacrylate, HDDA,
Ethyl-diglycol-monoacrylate, EDGA and Hexylacrylate, HA, were all obtained from
Scientific Polymer Products and in order to remove the inhibitor passed through a column of
\( \text{Al}_2\text{O}_3 \) before use.1-Hydroxy-cyclohexyl-phenyl-ketone (Irgacure184, CIBA), 2,2-Dimethoxy-
2-phenyl-acetophenone (Irgacure 651, CIBA) and 2,4,6-Trimethylbenzoyl-diphenylphosphine
-oxide (TPO, BASF) were used as photoinitiators.
Procedures

**LIP Apparatus**

Photopolymerizations are carried out in a Perkin-Elmer DSC-2B, modified to allow irradiation of the sample through a quartz window. The output of the polymerization exotherms are channelled through a microvolt meter into a IBM-PC via an A/D converter. The analysis is performed with a spread sheet for integration and non-linear regression analysis. The IBM-PC also controls the firing sequence and the total number of pulses delivered to the sample. The pulsed excimer laser (Questek model 2460, XeF - 351 nm) was operated in the single pulse mode where discrete pulses (15–30 pulses) are fired into the sample; each pulse is followed by a 15 second dark polymerization period before firing additional pulses.

**Raman Spectroscopy**

Raman Spectroscopy data were obtained by the use of a Perkin Elmer FTIR, 1700, IRDM Version 3.01, equipped with a Near infrared FT-Raman accessory with a 1760 X optical bench. Excitation was done with a Nd: YAG Laser, with an Yttrium Aluminium garnet crystal doped with ionized Nd. Excitation wavelength is 1064 nm.

**UV "Curing"**

Photopolymerization (UV curing) of films were carried out as draw-downs on glass plates at various film thicknesses and passed if needed several times under a Fusion 600 model and/or a Primarc system equipped with a medium pressure mercury lamp. The Primarc system giving an intensity of 180 mW/cm² and the Fusion F600 H system 880 mW/cm². The intensities were measured by means of an EIT® UV map instrument at conveyor speeds of 10 m/min. The given intensity values are, however, best regarded as relative rather than absolute due to the difficulty of measuring exact values. In each case the total dose delivered was kept constant.

**RESULTS AND DISCUSSION**

1. **LIP studies of Acrylates**

LIP studies on HA, HDDA and TMPTA have already been reported in numerous publications\(^1\) in which the effect of repetition rate on conversion was investigated. In Figure 1 are shown a typical thermogram and the corresponding time-cumulative conversion plot of a laser initiated polymerization of pure HDDA and TMPTA and a 47/53 mixture.

The photoinitiator is 2,2-dimethoxy-2-phenylacetophenone, at 2 % by weight. The reactivity of the system is reflected by the conversion of acrylate double bonds on the first laser pulse. Thus TMPTA shows the highest reactivity, giving 17 %, the 47/53 mixture 7 % and HDDA only 2 % conversion on the first pulse. See Table 1. The LIP of pure HA with the same conditions gives less than 1 % conversion on the first pulse. Neat HDDA required eight pulses before reaching the maximum rate of polymerization (reflected by the height of the exotherm). For the mixture three pulses were needed and for the pure TMPTA only one. None of the exotherm curves for TMPTA and the mixture reach the baseline until high conversion. An autoacceleration effect takes place immediately after the first pulse. HDDA, however, requires several pulses before this effect starts. As expected, the total conversion of acrylate double bonds was in this case highest for neat HDDA, 93 %, while neat TMPTA only reached 59 %, due to an earlier vitrification and reduced mobility of remaining double bonds. The very high reactivity of TMPTA cannot be explained simply by the increase of double bond concentration, since there is little correlation between the first pulse conversion and the total concentration of acrylate groups. The reason that an increase in TMPTA acrylate groups gives a higher reactivity, can be explained by a lower termination rate and / or an enhanced reactivity of pendant acrylate groups (i.e. after one of the acrylate groups has been polymerized, the other two become more reactive).
Table 1. Degree of conversion as a function of functionality.

<table>
<thead>
<tr>
<th></th>
<th>TMPTA</th>
<th>HDDA</th>
<th>DMPA</th>
<th>Conc.</th>
<th>TMPTA</th>
<th>Conv.</th>
<th>1st Pulse</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt%</td>
<td>wt%</td>
<td>wt%</td>
<td>M</td>
<td>mol %</td>
<td>%</td>
<td>%</td>
<td>%</td>
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<tr>
<td>0</td>
<td>98</td>
<td>92</td>
<td>2</td>
<td>8.94</td>
<td>0</td>
<td>93</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>93</td>
<td>93</td>
<td>2</td>
<td>9.04</td>
<td>6</td>
<td>90</td>
<td>2</td>
</tr>
<tr>
<td>9</td>
<td>89</td>
<td>90</td>
<td>2</td>
<td>9.13</td>
<td>11</td>
<td>87</td>
<td>3</td>
</tr>
<tr>
<td>24</td>
<td>74</td>
<td>70</td>
<td>2</td>
<td>9.46</td>
<td>27</td>
<td>76</td>
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</tr>
<tr>
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<td>49</td>
<td>2</td>
<td>9.99</td>
<td>53</td>
<td>74</td>
<td>7</td>
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<td>25</td>
<td>25</td>
<td>2</td>
<td>10.55</td>
<td>77</td>
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<td>12</td>
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<td>96</td>
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<td>0</td>
<td>2</td>
<td>11.15</td>
<td>100</td>
<td>59</td>
<td>17</td>
</tr>
</tbody>
</table>

Results of the laser initiated polymerization of mixtures of HDDA and TMPTA using 2,2-dimethoxy-2-phenylacetophenone (DMPA) as photoinitiator.

Short laser pulses 12 ns, 30 pulses, 15 s between pulses.

The concentration of monomers and the photoinitiator (Weight %).
The total concentration of acrylate double bonds (M).
The concentration of TMPTA acrylate double bonds (mol %).
The ultimate conversion and the conversion of the first pulse are given.

Figures 2 and 3 show the exotherms and the time-cumulative conversions for mixtures of HA/HDDA and HA/TMPTA. Interestingly, for the HA/HDDA mixture (Figure 2), the 25/75 ratio gives an "optimum" ratio between the two monomers. Although, the rate of polymerization follows the predicted order, the degree of conversion is considerably higher than expected. The corresponding ratio of the HA/TMPTA mixtures (Figure 3), shows the same behaviour. Thus, it appears as the "optimum" ratio for this mixture is much broader than for the HA/HDDA mixture. As mentioned in the previous section, the autoacceleration process takes place at a "lower" degree of conversion for TMPTA compared to HDDA. In order to promote further polymerization, there is a need for "small" mobile molecules, such as solvents or more preferred low molecular weight acrylates, i.e. HA, with high mobility to react with the "immobilized" pendant acrylic groups. Since this ongoing polymerization is a reaction between "more reactive" pendant acrylic double bonds and a "mobile" fraction of monoacrylate groups, the rate of polymerization is increased, due to restricted or decreased termination. This effect is more pronounced for TMPTA, since it is trifunctional and the distance between the acrylic groups is shorter than in HDDA.


Raman Spectroscopy was used to measure the degree of conversion as a function of light intensity. The Optical Density (O.D.) was adjusted to the corresponding film thickness and O.D. = 0.4 in all cases. An O.D. value of 0.4 was chosen due to the fact that this optical condition ensures the maximum photon absorption at the bottom of a film, regardless of the thickness of the coating. The only difference in the experiment is that the "high power" irradiator generates a light intensity of 780 mW/cm², whereas the "low power" irradiator generates 96 mW/cm². The recordings were taken at the same exposure time and should therefore be regarded as a relative comparison. As can be seen from Table 2, a significant difference in degree of conversion is obtained. For the 19 μm film, the conversion is increased from 17 % to 96 % and the corresponding values for the 90 μm film are 16 % versus 57 %. In alignment with the conversion results from the LIP studies we can conclude that a "low power" irradiator in combination with high acrylate functionality as "cure" compensation will introduce a high portion of unreacted acrylic double bonds in the polymerized matrix. This high portion of unreacted acrylates also implement a fraction of unreacted acrylates that are not chemically bonded into the matrix. It is important to conduct extraction measurements to calculate the ratio of Unreacted - But bonded versus Unreacted - Not bonded.
3. Conversion as a Function of Multiple Exposures.

In almost all industrial UV applications multiple exposures are used. Some of the reasons for this are obvious, such as one exposure will not give high enough conversion in order to obtain the mechanical properties needed for a certain application. Another important reason is that the final cure of the surface often need a separate high intensity exposure to overcome the oxygen inhibition. From the L.I.P. studies it is obvious that a single high intensity exposure will give higher degrees of conversion that multiple exposures at the same dose. This is due to the gelation effectand it is therefore much more pronounced in acrylate systems with higher functionalities. In Table 3 is shown the degree of conversion as a function of exposure frequency. A difunctional aliphatic urethane acrylate was given 520 - 550 mJ / cm$^2$ as a total dose. The results clearly illustrate the importance of exposure frequency. Especially in this case, where a low light intensity irradiator was used, $I_0 = 85$ mJ/cm$^2$. One exposure at 520 mJ / cm$^2$ gives a conversion of 44 %, whereas 10 times at 55 mJ / cm$^2$ only give raise to a 11 % conversion. As discussed in the Raman Spectroscopy section this effect will be less pronounced in the case of a high intensity irradiator.

<table>
<thead>
<tr>
<th>UV Source</th>
<th>$d$ (nm)</th>
<th>Dose (mJ/cm$^2$)</th>
<th>$I_0$ (mW/cm$^2$)</th>
<th>Dose / $I_0$ (sec)</th>
<th>Conv. (mol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 W/cmHg</td>
<td>19</td>
<td>535</td>
<td>96</td>
<td>5.6</td>
<td>17</td>
</tr>
<tr>
<td>100 W/cmHg</td>
<td>90</td>
<td>535</td>
<td>96</td>
<td>5.6</td>
<td>16</td>
</tr>
<tr>
<td>240 W/cmHg</td>
<td>19</td>
<td>565</td>
<td>780</td>
<td>0.7</td>
<td>86</td>
</tr>
<tr>
<td>240 W/cmHg</td>
<td>90</td>
<td>565</td>
<td>780</td>
<td>0.7</td>
<td>57</td>
</tr>
</tbody>
</table>

Optical density = 0.4.
Filmthickness = 80 μm.
Aliphatic urethane diacrylate

Degree of conversion for Ethyldiglycolmonoacrylate in the presence of 1-Hydroxy-cyclohexyl-phenylketone as photoinitiator.

CONCLUSIONS

The radiation curable acrylate based technology has been investigated from a photophysical and photochemical point of view. Especially, we have focussed our intentions on reactivity and degree of conversion. These two important parameters have been thoroughly examined by the use of Photo - DSC, LIP and Raman Spectroscopy. The overall findings show the importance and interrelated dependence of light intensity, optical density and average degree of acrylate functionality. At a constant dose of exposure, the results show higher degrees of conversion at higher light intensities. These findings are supported by fundamental theory and the experimental data also confirm that this dependence is more pronounced at lower average degrees of functionalities. The time of exposure and multiple exposures are crucial, especially when the exposure time is considerably longer than the time to reach a "staedy state" condition.

Table 2.

<table>
<thead>
<tr>
<th>UV Source</th>
<th>$d$ (μm)</th>
<th>Dose (mJ/cm$^2$)</th>
<th>$I_0$ (mW/cm$^2$)</th>
<th>Dose / $I_0$ (sec)</th>
<th>Conv. (mol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 W/cmHg</td>
<td>19</td>
<td>535</td>
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<td>5.6</td>
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<tr>
<td>100 W/cmHg</td>
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<tr>
<td>240 W/cmHg</td>
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<tr>
<td>240 W/cmHg</td>
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<td>565</td>
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</table>
REFERENCES


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HARDNESS MEASUREMENTS OF SILICON RUBBER AND POLYURETHANE RUBBER CURED BY IONIZING RADIATION

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ABSTRACT

This work investigates the hardness of both silicon rubber and polyurethane rubber cured by ionizing radiation. Shore A Hardness is used to characterize the subject elastomers in relation to the crosslinking process. Various formulations of both materials have been investigated in order to achieve the optimum cure conditions desired. A small amount of the curing agent has been incorporated in some formulations in order to reduce the required dose to achieve full cure conditions. Silicon rubber has shown improvements in hardness as absorbed dose is increased, whereas hardness remained constant over a range of absorbed doses for polyurethane rubber.

INTRODUCTION

Silicon rubber belongs to an important class of special-purpose synthetic rubber which is partly inorganic and partly organic. They contain the repeat unit as shown in (I), where the main chain consists of a sequence of -Si-O-- units which is inorganic in nature while the attached groups are organic in nature,

\[
\begin{align*}
\text{Si} & \quad \text{O} \\
\text{R} & \quad \text{R}
\end{align*}
\]

The attached groups are usually either methyl or phenyl, but some times a small amount of vinyl group is added in order to be able to vulcanize it by heating in the presence of sulfur and accelerators. In this work polydimethylsiloxane rubber (R=CH₃) was used, and it was cured by heating with organic peroxide. The rubber is vulcanized through hydrogen abstraction from methyl group by radicals derived from the peroxide. The initial hydrogen abstraction reaction will lead to the formation of the -CH₂ radicals which will combine to give crosslinks between polymer chains.

Polyurethane elastomers are manufactured in three different groups based on their processing characteristics derived from molecular weight and terminal end-group functionality and are liquids, millable rubber and thermoplastic elastomer. Of interest to this work is the liquid polyurethane which its process and detailed technology is presented elsewhere. Prepolymer liquids are processed to produce a small but positive excess of
NCO groups which are utilized in subsequent chain extension reaction. As the content of diisocynate is increased, i.e. higher OH/NCO block ratio, then more NCO will be available to promote the chain extension process. A unique feature of liquid urethane elastomers is that they can be processed to cover a range of hardness from 10-95 IRHD and (Shore A).

A type A "Durometer Hardness Tester" utilizes a truncated conical indenter as a probe. A schematic diagram of the Durometer A instrument used in this work is presented in fig-1.

![Schematic diagram of the Durometer A instrument](attachment:image.png)

**Fig-1** (a) A schematic diagram of the Durometer A instrument; (b) geometric details of the truncated cone indentor; (c,d) two different types of contact geometry for the "Durometer" indentation.

The correlation between the applied force $F$ and hardness number $H_A$ is as follows:

$$ F = 0.55 + 0.075 H_A $$

(1)

where $F$ is in Newtons and $H_A$ is hardness reading for the type A indentor. The associated hardness scale (linear) is defined by the following conditions:
\[ H_A = 0 \quad \text{when } y_1 = 0 \]
\[ H_A = 100 \quad \text{when } y_1 = 2.5 \text{ mm} \]

and \( y_1 + y_2 = 2.5 \text{ mm} \)

Considering Equation (1) and the boundary conditions, we determine the characteristic instrument spring stiffness as 3 N/mm and the minimum force \( F_{\text{min}} = 0.55 \), and maximum force \( F_{\text{max}} = 8.05 \). Combining the relationships we determine the instrument compliance as:

\[ F = 0.55 + 3(2.5-h) \quad (2) \]

where \( F \) in N, \( h \) in mm

In our measurements, the hardness number \( (H_n) \) of a sample is calculated from the point of intersection of the instrument compliance and the desired sample contact compliance (i.e., data points from Instron machine). Three data points were measured per sample. The speed of the universal testing machine was 1 mm/min.

**EXPERIMENTAL**

1. Materials:

   Commercially available polydimethylsiloxane elastomer known by Sylgard 184 (Dow Corning Corporation, U.K) and Diphenylmethane 4,4'-Diisocynate known by Diprane 54 prepolymer three component elastomer system (Kemira Polymers U.K.) were used. The preparation of Diprane 54 prepolymer involves the addition of C 54/55 (polyester polyol blend curative) which works as chain extender and Diprane C which is the curing agent (1,4 Butane Diol) (Polymed Ltd.). Diprane 54 prepolymer can be prepared in various formulations to give Shore A Hardness in the range of 55-95.

2. Sample preparation and irradiation:

   Sylgard 184 was thoroughly mixed by hand using a weight ratio of 10 parts of base elastomer to one part of curing agent. The mixture was then de-gassed by exposing to vacuum of 20 mm of mercury for 30 minutes and then allowed to stand for 10 minutes to remove the final air bubbles. The mixture was then poured into a 25 ml heated glass beaker which was treated with releasing agent for three times with heating in between. For chemical curing the mixture was heated for two hours at 100 °C, and for radiation curing the mixture was heated for one hour prior to irradiation. Three formulations were prepared for radiation curing, and one formulation was prepared for chemical curing as presented in table-1.

<table>
<thead>
<tr>
<th>Formulation Code</th>
<th>Ratio of Curing Agent/Silicon Rubber</th>
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</thead>
<tbody>
<tr>
<td>Si</td>
<td>0/10</td>
</tr>
<tr>
<td>Si-1*</td>
<td>0.5/10</td>
</tr>
<tr>
<td>Si-2*</td>
<td>0.25/10</td>
</tr>
<tr>
<td>SiC**</td>
<td>1/10</td>
</tr>
</tbody>
</table>

Note: * Samples were heated for 1 hour prior to irradiation at 100 °C.
** Samples were heated for 2 hours for chemical curing at 100 °C.
Diprane 54 prepolymer was mixed by considering the following optimum processing temperatures:

- Diprane C54/55 curative: 40 °C
- Diprane C: 25 °C
- Diprane 54 prepolymer: 25 °C

and the mixed components was poured into pre-released molds heated to 80 °C. After preconditioning the components to the recommended temperatures, the required quantities of Diprane C 54/55 and Diprane C curative were mixed together by hand. Then, the required amount of Diprane 54 prepolymer was added to the vessel and mixed thoroughly for approximately one minute. The mix was put under vacuum of 5 torr for 2 minutes until bubbling ceased. Finally, the mix was poured into a 25 ml heated glass beaker which was treated with releasing agent for three times with heating in between. Four chemically cured formulations were prepared to give hardness shore A measurements of 55, 60, 80, and 90 as presented in table-2.

Table 4 Formulations of Polyurethane Rubber Samples Prepared for different hardness values.

<table>
<thead>
<tr>
<th>Mixing Ratios:</th>
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<tr>
<td>Formulation Code</td>
<td>Pu-1</td>
<td>Pu-2</td>
<td>Pu-3</td>
<td>Pu-4</td>
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<tr>
<td>Hardness (Shore A)</td>
<td>55</td>
<td>60</td>
<td>80</td>
<td>90</td>
</tr>
<tr>
<td>Diprane C54/55</td>
<td>100</td>
<td>95.7</td>
<td>90.7</td>
<td>86.2</td>
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<tr>
<td>Diprane C</td>
<td>--</td>
<td>4.4</td>
<td>9.3</td>
<td>13.8</td>
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<tr>
<td>Ratio with 54 prepolymer:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diprane Curative blend</td>
<td>470</td>
<td>250</td>
<td>165</td>
<td>125</td>
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<tr>
<td>Diprane 54 prepolymer</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
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Note: The above ratios are in parts by weight and should be measured to an accuracy of ± 1%.

3. Irradiation:

Irradiation was carried out at the Nuclear Technology Group 17,866 Ci Co-60 source in the Imperial College of Science and Technology in London. The exact dose rate at the center of the source, at the time of irradiation, was determined by Fricke dosimetry in accordance with ASTM D1671-72. A series of irradiations were performed at different times and the average of five measurements was calculated to be 5.69 kGy/hr ± 1%.

4. Hardness Measurements:

Both of silicon rubber samples and polyurethane samples were indented by a "Durometer A" type indentor attached to the crosshead of an Instron Universal testing machine. No presser foot was used. The displacement...
was recorded through a sensor and the load was measured by the load cell of the instrument. Both measurements were recorded at 1 second interval as the indentor moved into the sample.

RESULTS AND DISCUSSION

In the case of silicon rubber, Shore A Hardness measurements for the radiation-cured formulations were determined as shown in fig-2. Si formulation was irradiated at four dose points and Shore A Hardness increased with absorbed dose. At 400 kGy the hardness was 25% higher than chemically cured formulation. An absorbed dose between 300-400 kGy will achieve full cure condition. Si-1 formulation was irradiated at five dose points and hardness again, increased with absorbed dose. The absorbed dose required to achieve full cure condition was lowered to almost 150 kGy. Si-2 formulation was irradiated at four dose points and hardness measurements were determined. No further reduction in the absorbed dose required for full cure condition was observed.

In the case of polyurethane rubber, Shore A Hardness measurements for chemically cured formulations are listed in table-3. All measurements are in agreement with supplier values. Three formulations were irradiated at various absorbed doses and hardness measurements were determined as shown in fig-2. Pu-1.NH formulation which was not heated after mixing, was irradiated at three dose points. Another Pu-1 formulation was irradiated at four dose points, and Pu-2 formulation was irradiated at three dose points. It is obvious from the graph that no curing took place during irradiation for all three formulations. It is possible that a simultaneous oxidation reaction of the samples was hindering the curing process. Further work has to be done on the irradiation of polyurethane formulations in inert atmosphere.

![Fig-2](image1.png)

![Fig-3](image2.png)
Table 3 Shore A Hardness measurements of various polyurethane rubber blends.

<table>
<thead>
<tr>
<th>Formulation Code</th>
<th>Hardness Shore A</th>
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<tr>
<td>Pu-1</td>
<td>50</td>
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<td>Pu-2</td>
<td>58</td>
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<tr>
<td>Pu-3</td>
<td>81</td>
</tr>
<tr>
<td>Pu-4</td>
<td>92</td>
</tr>
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CONCLUSIONS

Shore A Hardness measurements of four silicon rubber formulations cured by ionizing radiation were examined. Radiation curing demonstrated increased hardness with absorbed dose. An absorbed dose between 300-400 kGy achieved full cure condition. Doubling the content of the curing agent reduced the required absorbed dose for full cure to 150 kGy. Another three formulations of polyurethane rubber were irradiated at various absorbed doses and their hardness shore A were evaluated. A minor influence on shore A hardness was observed.

ACKNOWLEDGEMENT

This work was performed during a summer post-doctoral research program sponsored by the British Aerospace and organized by the British Council. The author would like to thank Dr. Peter Clay of the Nuclear Technology Group at the Imperial College of Science, Technology and Medicine in London for arranging the visit and for his efforts in facilitating this work. Also, I would like to thank professor Brian J. Brisco, Head of the Particle Technology Group, for giving me the opportunity to use his laboratories. Sincere appreciation to Mr. Savio Sebastian and Mr. Savvas for their help in conducting the experiments.

REFERENCES

THE USE OF RISO B3 FILM GAMMA DOSIMETER FOR MONITORING ULTRAVIOLET RADIATION

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ABSTRACT

The Riso thin B3 plastic film, which is essentially a gamma radiation dosimeter, has been successfully used for measuring integrated UV irradiance. The colorless flexible plastic film changed color to red upon exposure to UV-irradiation. The radiation-induced color was analyzed spectrophotometrically at the maximum of the absorption peaking at 554 nm wavelength. The film was found to respond faithfully to UV-B, UV-C and UV-A radiation, showing maximum sensitivities at 200, 298, and 366 nm wavelengths. Correlations were established between the absorbed dose of UV radiation and the change in absorbance (A554) measured from films exposed to the same UV irradiance. The effect of post-irradiation stability on the dosimeter performance was discussed. The results demonstrate that B3 film has a maximum sensitivity and suitability for use as a personal dosimeter for biologically effective solar UV-B and UV-C radiation, where most acute and chronic effects of sunlight exposure on biological systems believed to occur. Also, it can be used for monitoring of artificial ultraviolet radiation sources used for medical and industrial processes.

INTRODUCTION

Ultraviolet radiation occupies that portion of the electromagnetic spectrum from 100 to 400 nanometers (nm). This is commonly divided into three subregions: short wavelength (UV-C), varying from 100 to 280 nm; medium wavelength (UV-B), ranging from 280 to 315 nm; and long wavelength (UV-A), varying from 315 to 400 nm (1).

UV radiation is harmful to humans and ecosystems; the UV-A is relatively less harmful, but UV-B has many damaging effects, while UV-C is lethal to many forms of life. The biological effects of UV radiation in humans are limited to the skin and the eye because of its low penetrating properties in human tissues. The normal responses of the skin to UV radiation may be classified as either acute, e.g., erythema, melanin pigmentation, vitamin D production; or chronic, e.g., skin aging and skin cancer (2). Erythema (e.g., the reddening of the skin in sunburn) is a photobiological response of the skin normally resulting from overexposure to wavelengths in UV-C and UV-B regions (180-315 nm). Erythema induced by the longer UV-B wavelengths (295-315 nm) is more severe and persists for a longer period than that for shorter wavelengths (3).

Photobiological UV radiation sources are divided into two classes: natural and artificial. The sun is the most important natural source of UV light although much of its transmitted energy is in the longer wavelength subregion above 295 nm. The ozone layer in the stratosphere and troposphere around the Earth acts as a protective shield by cutting off UV-C radiation and reducing the amount of UV-B radiation reaching the Earth's surface. The reduction of ozone layer results in an increase in UV-B radiation, within a narrow 25 nm bandwidth, between 290 and 315 nm (4).

Artificial UV radiation is used in a wide variety of industrial and medical processes and for cosmetic purposes. Industrial applications include photocuring of plastics and inks (UV-A and UV-B), solar simulation (all UV), fade testing (UV-A and UV-B), and wastewater disinfection (UV-C), etc (1,5). Clinical medicine includes photochemotherapy, where proper UV-A radiation dosimetry is important in PUVA therapy, not only to prevent severe erythema, but also to determine the lowest effective radiant exposure to minimize long-term damage (6).

Many substances, in the form of dyes and undyed plastic films, exhibit a measurable change in their properties upon exposure to UV radiation have been investigated in the search for a UV badge dosimeter, e.g., polystyrene film (7,8), diazo films (9) and poly-vinyl chloride (PVC) films incorporating photosensitizing drugs (10,11). Recently, we have developed several thin plastic films for UV radiation measurements (12-14). To continue this work, it was decided to study several photoactive chemicals incorporated into polymeric matrix with a view to developing UV dosimeters.
The present work evaluates the B3 film as a UV radiation detector in terms of colour response range, spectral sensitivity down to short wavelengths, post-irradiation stability and uncertainties associated with dose measurement. Possible application of the B3 film for monitoring artificial and environmental UV radiation are also reported.

EXPERIMENTAL

The thin plastic film (150 μm) used in this investigation was the Riso B3, batch 343310 (made by Beiersdorf AG). The plastic film (polyvinyl butyral) contains ioucycyanide (pararosaniline), which can be made radiochromic upon exposure to ultraviolet light or ionizing radiation (15). Before use, all dosimeters were stored in the laboratory and protected against exposure to daylight and light from fluorescent lamps. Relative humidity in the laboratory was between 25 and 40% and the temperature was 21±2°C.

For calibration purposes and irradiation of samples, three UV radiation sources were utilized: a) A standard 8 watt mercury lamp (Desaga 131200) and monochromatic filters with a bandwidth of 5 nm (Oriel Corporation, Stratford, Ct, U.S.A) were used to provide the required irradiation wavelength. The filters were found to reduce the amount of light intensity falling on the film. Intensity meters for short and long wave ultraviolet lamps Model J-225x, UVP and J-221, UVP were used to measure the intensity of ultraviolet light of the mercury lamp (located at NCRRT). b) UVP ultraviolet Crosslinker model: CL-1000 was also used for irradiation of B3 films at 302 nm wavelength. The UVP CL-1000 is designed to measure and control the ultraviolet radiation within the exposure chamber. It is equipped with a UV sensor to measure the UV energy and automatically adjusts to variations in UV intensity that occur as the UV lamp ages (located at KACST). c) A XENOTEST 150 S (Heraeus Instruments), light and weatherfastness tester, where solar and global radiation is simulated by XENON arc radiation. Radioluux UV meter (Heraeus Instruments) was used to measure the irradiance and dose in the wavelength range 300-400 nm in the weathering device (Located at KACST). Perkin Elmer UV/VIS spectrophotometer Lambda 3B (KACST) and UVIKON 860 spectrophotometer (NCRRT) were used to measure the absorbance and absorption spectra of the irradiated and unirradiated films.

RESULTS AND DISCUSSION

1. Radiation-induced absorption spectra

Upon UV irradiation, the colorless B3 films showed a significant colour change to red. The red colour developed and the intensity of this colour increases with increasing doses of incident UV radiation. Figure 1 shows spectrophotometric scans of unirradiated film and films irradiated to a series of doses in the range from 0.75 to 55.5 kJ/m² at irradiation wavelength of 298.8 nm. The radiation-induced absorption spectra show that the largest change in absorbance occurs at 554 nm wavelength. Therefore, this wavelength was subsequently used to quantify the UV-induced changes in the film.

![Absorbance](image)

Fig-1 Variation in the absorption spectra with incident UV dose at 298.8 nm
2. Dose response

In order to study the response of the B3 film to UV radiation, irradiations were carried out using the standard 8 watt mercury lamp and the monochromatic filters to provide the required irradiation wavelength. The UV irradiations were carried out at exposure wavelengths of 254 ± 5 nm, 298.8 ± 5 nm and 366 ± 5 nm. The change in absorbance of the irradiated film \( \Delta A = A_f - A_0 \), where \( A_0 \) is the absorbance before irradiation and \( A_f \) is that after irradiation, were measured at 554 nm wavelength as a function of UV incident energy. The recorded variations in \( \Delta A_{554} \) as a function of UV exposure energy at different irradiation wavelengths are shown in Fig. 2. It is observed that the response at all three irradiation wavelengths is non-linear and tends to saturate at high doses. Statistical analysis of the results indicates that the radiation-induced changes in the B3 film may be expressed by the following general empirical relationship

\[
K(\lambda) D = 0.031 + 0.074 X + 7.74 X^2 - 3.5 X^3 + 3.24 X^4 \quad (r = 0.99995) \quad (1)
\]

where \( K(\lambda) \) is the wavelength response of the film normalized to unity at an irradiation wavelength \( \lambda = 298.8 \), \( X \) represents the change in absorbance measured at 554 nm ( \( \Delta A_{554} (D, \lambda) \) ) for a UV exposure energy \( D (\text{kJ/m}^2) \) at wavelength \( \lambda \). The expressions given by equation (1) are represented by the full lines in Fig. 2. These curves agree fairly well with experimental data points within 2.5 % and so Eq. 1 may be used to quantify the UV dose received by a B3 film for a given \( \Delta A_{554} \).

3. Spectral sensitivity

The wavelength response of the B3 film was established by applying a dose of 0.65 kJ/m² at various irradiation wavelengths in the range from 200 to 400 nm (3 films at each wavelength) and the radiation-induced absorbance was measured for all films at 554 nm wavelength (\( A_{554} \)). The relative responses \( K(\lambda) \) were evaluated at each wavelength by employing equation (1) and setting \( D = 0.65 \) kJ m⁻². The resulting \( K(\lambda) \) values were normalized to unity at the most effective irradiation wavelength (298.8 nm) and plotted as a function of irradiation wavelengths Fig. 3. It can be seen that the maximum sensitivity of the B3 film lies between 295 and 320 nm wavelength in the UV-B region, where most significant adverse health effects of exposure to UV radiation have been reported (16). This region of the spectrum has a relatively high penetrating power and can cause severe burns of the eyes and skin. Although maximum sensitivity occurs at 310 nm, there is still an easily measurable response at 254 and 366 nm. For wavelengths longer than 330 nm, extremely long exposure times would be necessary in order to reach a film response. It is clear from the work reported in this paper that B3 film can be used down to shorter wavelengths. Our results show that there is still a useful sensitivity at 254 nm but when used at short wavelengths, careful filtering would be required to exclude the much more reactive longer wavelengths. Compared to the spectral sensitivity (action spectrum) of the well known polysulphone plastic film dosimeter for biologically effective solar UV-B radiation (7), both films show a similar action...
spectrum in the important wavelength region between 295 and 315 nm, which is important for monitoring devices designed for natural ultraviolet radiation Fig. 4.

The principal limitation of the new dosimeter in the form used here is its sensitivity which extends to wavelengths of up to 340 nm, with a less sensitive region between 340 and 400 nm, where the biological effectiveness of UV radiation is negligible at wavelengths above 315 nm. This difference in spectral response can lead to significant errors in estimates of the biologically effective UV-B dose when the B3 film is used to monitor natural UV radiation, due to the rapid increase in the intensity of the solar spectrum between 315 and 350 nm. Similar effects have been reported for the polysulphone dosimeter. In this case the response of polysulphone was related to erythema effective UV-B radiant exposure by carrying out correction calculations which involve estimates of the action spectrum, the spectral sensitivity of polysulphone film, and the relative spectral power distribution of the incident radiation (6).

Similarly the B3 film spectral response bears a resemblance to the erythema action spectrum although it does extend too far into the UV-A. However, using appropriate filters in combination with the B3 film, the relative sensitivity of the film (Without UV-A sensitivity) can be adjusted for erythema induction (17).

4. Post-irradiation stability

B3 films irradiated to a dose of 1.13 kJ/m² were stored immediately after irradiation in the dark at a temperature of -22.7 °C and relative humidity of 30.6% (normal laboratory storage conditions). The films were read spectrophotometrically at 554 nm and at different intervals of time during the post-irradiation storage period of 200 hours. They were found to experience an increase in absorbance of -6% by the end of the storage period (see Fig. 5).

5. Assessment of uncertainties

The reproducibility of the measured (ΔA554) of the films exposed to the same UV irradiance was determined by considering two uncertainties. The first uncertainty is associated with the measuring process and the second is concerned with the measurements resulting from different films exposed to the same UV irradiance.

The uncertainty associated with the measuring process was determined by taking into consideration multiple readings of (ΔA554) of the same film (a hundred readings per film). From the data obtained, it was found that the average uncertainty was 0.7%, reflecting the precision associated with a single (ΔA554) measurement. However, the percentage uncertainty associated with the mean readings of different films exposed to the same dose varied from 0.6 to 2% with the mean of 1.3%. The combined effect of both errors was reflected by the uncertainty of all the measured ΔA554 values for all films exposed to a given dose. The obtained combined percentage uncertainties of ΔA554 values after irradiation (3 films at each dose point) over the useful dose range was found to be ±2.2%. In other words, it can
be said that the error associated with a single measurement of any film that has been exposed to radiation and the variations arising from the measuring process as well as those from the manufacturing of the film material were taken into consideration.

6. Application for monitoring environmental and artificial UV radiation

In order to test the efficiency of the B3 film for measurement of ultraviolet radiation emitted from artificial UV sources, two sets of B3 films were exposed to increasing doses of UV radiation from two different lamps. The first lamp was a type commonly used in weather fastness (XENOTEST 150 S). In this UV source, solar and global radiation (outdoor sunlight) is simulated by XENON arc radiation (see UV spectral distribution, Fig. 6). The second lamp (CL-1000 Crosslinker), in which the irradiation wavelength was set to 362 nm and the spectral emission of the lamp, according to the manufacturer, is shown in Fig. 7.

Fig-6 Spectral output of the XENOTEST in the UV region.

Fig-7 Spectral output of the UVP CL-1000.

Fig-8 Response of the B3 film to UV radiation emitted from the XENOTEST lamp. (Irradiance = 71.4 W/m²)

Fig-9 Response of the B3 film to UV radiation emitted from the UVP CL-1000 (Irradiance = 4 W/m²)
B3 film sets were exposed to different irradiation doses of UV radiation in the two lamps and the change of absorbance (ΔA_{554}) was measured for each film at each dose. The irradiance and irradiation doses were measured using the RADIALUX UV sensor (range 300-400 nm). The obtained responses of the B3 film are presented in Fig. 8. and Fig. 9. for XENOTEST and CL-1000 UV irradiations, respectively. The results indicate that the B3 film shows a higher sensitivity to the emitted UV radiation from the CL-1000 source compared to the other UV source. The higher sensitivity of the B3 film towards the spectral output of the CL-1000 can be explained by the similarity of the spectral response of the B3 film and the lamp emission spectrum (see Fig. 3 and Fig. 7). In fact determination of UV dose or irradiance are usually subject to some degree of uncertainty depending on both the UV sources and UV detectors used for monitoring the output of UV sources. Therefore, it is desirable to use a dosimeter which matches the UV source emission spectrum.

CONCLUSION

Riso B3 thin plastic films prepared from polyvinyl butyral and pararosaniline cyanide, as the radiation sensitive element are investigated for UV radiation measurement. When the colourless B3 films are exposed to UV radiation between 200 and 400 nm wavelengths, they exhibit a colour change to red and the optical absorption of the films increases. The increase in absorbance measured at a wavelength of 554 nm is proportional to UV dose, and so the film readily lends itself to application as a UV dosimeter. The dosimeter has a maximum sensitivity and suitability for use as a personal dosimeter for biologically effective solar UV-B and if suitably filtered it can provide the bases for a UV film badge with many medical and industrial applications in the UV-A and UV-C regions of the spectrum.

REFERENCES

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