The Second International Symposium on
RVNRL
(Radiation Vulcanisation of Natural Rubber Latex)
15–17 July, 1996
Kuala Lumpur, Malaysia

Jointly Organised
by

Malaysian Institute for Nuclear Technology Research (MINT)
International Atomic Energy (IAEA)
Rubber Research Institute of Malaysia (RRIM)
Kumpulan Guthrie Berhad
Malaysian Technology Development Corporation (MTDC)
Malaysian Rubber Gloves Manufacturers' Association (MARGMA)
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PREFACE

This is the proceeding of The Second International Symposium on RVNRL (Radiation Vulcanisation of Natural Rubber Latex) held in Kuala Lumpur, Malaysia from 15th. to 17th. July 1996.

A total of 31 papers and two keynote addresses were presented and discussed covering a wide spectrum of subjects on the latest advancement of research and development in RVNRL project. The general topic discussed include Preparation and Properties of RVNRL, Characterisation and Advantages of RVNRL, Scale Up RVNRL Preparations and Applications, RVNRL Pilot Plant Design and Operation and Property Improvement in RVNRL Products. A panel discussion with the theme "Towards Chemical-Free and Environment Friendly Latex Products" was the the final session of the two days on papers presentations. The final day of the Symposium was occupied with technical visit to RVNRL Pilot Plant in MINT, Bangi and Guthrie Medicare Products (NS) Sdn. Bhd. in Siliau, Negri Sembilan.

The Symposium would have not been successfully proceeded without the contribution from the authors of the papers, invited speakers, the Chairman of sessions, the panel members and of course the 99 registered participants from 17 countries. Their valuable effort in presenting papers and active participation in the Symposium are very much appreciated.

Special thanks are due to the International Atomic Energy Agency (IAEA) for funding the Symposium through the Government of Japan’s special contribution, the Rubber Research Institute of Malaysia (RRIM), Kumpulan Guthrie Berhad, the Malaysian Technology Development Corporation (MTDC), and the Malaysian Rubber Glove Manufacturers’ Association (MARGMA) for jointly organising the Symposium, the various sponsors, members of the various committees for their advice and assistance in running the Symposium. The assistance extended by the staff of the Human Resource Development Division, the Customer Services Unit and the Rubber Processing Group of MINT are also appreciated.

It is hoped that this proceeding will be an indispensable reference to those wishing to delve in research and development in radiation vulcanisation of natural rubber latex.

November 1996
Dr. Wan Manshol bin W. Zin
Executive Secretary
The Second International Symposium on RVNRL,
Kuala Lumpur, 1996
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Welcome Address

DR. AHMAD SOBRI HJ. HASHIM
Director General
Malaysian Institute for Nuclear Technology Research (MINT)
Chairman, Organising Committee, The Second International Symposium on RVNRL
(Radiation Vulcanisation of Natural Rubber latex), 15-17 July 1996, Kuala Lumpur, Malaysia

On behalf of the organizing committee, I wish to welcome everyone to this auspicious occasion, the Second International Symposium on Radiation Vulcanization of Natural Rubber Latex (RVNRL). It is indeed heartening to see that almost everyone related to natural rubber in one way or another; user, producer, researcher, and manufacturer are participating in this Symposium. Allow me ladies and gentlemen to take this opportunity to dwell a little bit on the evolution of the RVNRL project and the development of RVNRL technology that leads to this Symposium.

The RVNRL project was initiated in 1982 as a regional project under the auspices of the IAEA for the UNDP/RCA/IAEA Program for Asia and the Pacific Region. Many countries in this region including Bangladesh, China, India, Indonesia, Japan, Malaysia, Thailand, Sri Lanka and Vietnam are actively participating in this project. I am glad that these countries are represented here today. Even though the project was initiated 14 years ago, the actual R&D commenced in earnest only in 1986. For several years, JAERI of Japan has played a leading role in RVNRL R&D activities and in 1989 organized the First International Symposium on RVNRL in Japan. Since then, several developments that merit another occasion to discuss and exchange information on RVNRL such as this Symposium have taken place. Malaysia, in particular MINT, is indeed honored to host this Second International Symposium on RVNRL, the financial support of which is largely derived from the contribution of the Government of Japan to the IAEA. I also wish to record my appreciation and gratitude to the co-organizers of this Symposium, namely the IAEA, Kumpulan Guthrie Berhad, Rubber Research Institute of Malaysia, Malaysian Technology Development Corporation, and the Malaysian Rubber Glove Manufacturers’ Association for their contributions towards making this Symposium a reality.

For your information, this Symposium was actually planned to be held last year. However, MINT suggested it be postponed until after the commissioning of its semi-commercial RVNRL processing plant in Bangi in March this year. This would give the Symposium a better posture in introducing RVNRL to the market place and in showing that the technology is now available.

MINT’s involvement in RVNRL started at the initiation of RVNRL as an RCA/UNDP/IAEA project in 1982 together with the Rubber Research Institute of Malaysia (RRIM). MINT took an active role in this research in 1986 when it received its first gamma irradiation unit under the IAEA technical assistance program. The commissioning of MINT’s gamma irradiation plant, SINAGAMA, in 1989 that is also used by other research groups at MINT, boosted the capability of RVNRL research group to a new height. This capability has also enhanced our cognizance of the potential of RVNRL as a new and better product which, when successful, will be one of the significant developments in latex processing technology. At the same time, the increasing attention of the industries towards this technology strengthened our commitment to the research. Regularly, RVNRL was produced at a capacity of around 500 kg per batch and supplied to the industry, locally and abroad, for testing. The promising results have provided the much needed drive that leads to the construction of RVNRL pilot plant at MINT. The human aspect of the project is also an important determining factor for the success of the project. In this regard, the dedication, unwavering interests, and the strong sense of purpose of the researchers and others involved are very much appreciated.

Like other technologies, nuclear technology has both the good and the bad sides; but with the latter usually dominating the news and issues. This has shaped a misconception among the public, including the industrialists in most RCA member states, on the word “nuclear” and “radiation” and that to a certain
extent acts as a barrier to the eventual exploitation of its advantages. However, I believe that acceptability barrier is getting lower now.

Just last month, MINT Sterifeed plant for re-utilization of agro-industrial waste was inaugurated. The official opening of the MINT RVNRL Pilot Plant is scheduled to be held in the first quarter of next year, in conjunction with MINT’s Silver Jubilee celebration. In the medical sector, MINT has been producing and supplying radio-pharmaceutical kits to hospitals in Malaysia as well as establishing two tissue banks. The MINT Tissue Bank supplied hundreds of tissue grafts to the Philippines in the recent fire tragedy at a discotheque near Manila. Our contribution in the area of non-destructive testing and industrial plant quality assurance, especially in the petroleum industry, is already quite well-known in Malaysia. In radiation processing, our footstep in setting up a semi-commercial medical products gamma sterilization plant has been emulated to success by a private company. These are just some of the highlights that we feel worthy of note.

From those examples, it can be seen that the applications of nuclear science and technology cut across several sectors of national development and thus at time, it may appear that MINT is ubiquitous and seemingly encroaching into so many areas of R&D. It seems so only because MINT is always focused on its area of competency and embarks on R&D in which the application of this technology is relevant and advantageous. In fact, the complementary nature of some of the applications of nuclear technology makes inter-institutional collaboration and strategic alliances a very attractive arrangement. Such an arrangement should be encouraged, not only between institutions within a country but also inter-countries through bilateral or multilateral arrangements.

The current economic boom of the countries in this region and in particular Malaysia provides great opportunities for nuclear and related technologies to contribute effectively towards economic development of the country. The number of private sector concerns in contact with MINT and at various stages of negotiations for joint research, technology transfer, or for specialized services and consultancies increases every year. The 20 or so technical services offered by MINT are subscribed by close to 500 clients both from the public and private sectors. The Government’s policy of encouraging the commercialization of research and technology undoubtedly has greatly influenced this vibrant interests to acquire and apply technology by the private sector. The fact that it is experienced for nuclear technology too is indicative of its relevance and importance alongside other technologies in propelling progress in many sectors of national development.

I am optimistic that RVNRL, a product of this technology, will add to the lists of benefits of exploitation of nuclear technology. It is a very attractive alternative for latex dipped products manufacturing. Compared to sulphur vulcanization process, vulcanization by gamma radiation is a clean process; and the products made of RVNRL such as medical and household rubber gloves, catheters, balloons, and teats are free from some of the long-standing issues facing the same products based on sulphur vulcanized latex. Among the issues include skin allergy due to the use of accelerators which are necessary in sulphur vulcanization process; and this can give rise to nitrosamines which are reported to be carcinogens. The absence of sulphur RVNRL is expected to also attract the attention of the electronics industry when it is used to produce finger cots for use in the electronics manufacturing industry.

For the existing and prospective users of latex dipped-products to take advantage of these benefits, RVNRL needs to be made available in the market and manufacturers must be willing to use it. For this to happen, the RVNRL production process must be economically viable so that its price does not neutralize its advantages. The RVNRL pilot plant at MINT, with a reasonably large production capacity of around 6,000 tons/year to begin with, can be used to provide a rough estimate on the economics of the production process. This aspect of RVNRL production is the subject of one of the papers to be presented in this Symposium. There is, however, a more persuasive reason for the use of RVNRL in latex dipped-products manufacturing, that is the trend towards standardization of medical gloves in the industrialized countries in which the requirements for products free from zinc oxide, nitrosamines, and chemical accelerators may emerge. The supply of RVNRL samples from MINT to about ten latex producers, distributors, and manufacturers locally and abroad for market evaluation and product development have indicated positive
results of its suitability in meeting these requirements. I believe that the issue of standardization and supply availability is mutually supportive of each others cause. In this regard the current capacity of the MINT pilot plant can be utilized to prime the demand.

This Symposium will provide us with information on the latest development in RVNRL, its potential in fulfilling emerging needs with respect to latex products. what are the needs, and what is available right now. It includes visits to MINT RVNRL pilot plant and to a latex dipped product factory where the use of MINT RVNRL for rubber glove production will be demonstrated. I am sure everyone involved in arranging this Symposium has been hard at work to ensure everything is in order and I hope you will take this opportunity to learn more about RVNRL - a new product which I think is now at the advanced stage of entering the marketplace.

Finally, I wish everyone a fruitful deliberation and discussion. To those from abroad, I wish you a pleasant stay. Thank you.
Opening Address

Y.B. DATUK LAW HIENG DING
Minister of Science, Technology and the Environment, Malaysia

Terlebih dahulu saya mengucapkan berbanyak terima kasih kepada Jawatankuasa penganjur kerana memberi penghormatan kepada saya untuk merasmikan pembukaan simposium pada pagi yang bahagia ini. Saya berasa amat gembira dan bangga kerana dapat bersama-sama dengan sebegini ramai pakar-pakar dalam bidang radiation vulcanization of natural rubber latex dari dalam dan luar negara yang menghadiri simposium antarabangsa ini.

To our foreign participants, on behalf of the Government of Malaysia, I like to bid all of you “Selamat Datang” which simply means welcome to Malaysia. I wish your stay here will be both pleasant and memorable, and hope that you will find time to visit the places of interest and learn more about Malaysia.

It is indeed a great pleasure for me to welcome all of you to this Second International Symposium on Radiation Vulcanization of Natural Rubber Latex (RVNRL). For Malaysia, it is an honour to play host to this symposium, to be the venue for international experts, corporate figures, and business concerns to meet, and to discuss the latest development in rubber processing technology, and to also forge close friendship, cooperation, and partnership.

I was informed that the first symposium was held in Japan six years ago. I was also informed that this Symposium has attracted participants from 20 countries worldwide, comprising both public and private sector representatives. It is organized by agencies from the public sector, private sector, an international agency, and a non-government organization. If the number of “followers” or interested parties and the level of interest generated in technology can be taken as one of the indicators of progress, I am sure much progress have been made in RVNRL within the period between the two symposiums. For Malaysia, the progress of research and development in RVNRL has been remarkable. The commissioning of the RVNRL pilot plant at MINT just a few months ago brings this technology out of the laboratory scale production and testing to the next step which is closer to commercialization. I would like to take this opportunity to congratulate MINT and everyone who have contributed to this success. I applaud all that have been accomplished in this research work where I am sure a lot of effort have been put into at all levels.

This symposium will, among others, expound the advantages of RVNRL as a relatively “clean” process and product. The ever tightening grips of regulations on toxicity, carcinogenicity, and allergenicity of latex products being imposed by the international world, and the potential of RVNRL to solve these contemporary problems associated with latex products makes this symposium a meaningful one for latex processing technology. The theme, “Towards Chemical-Free and Environment Friendly Latex Products” befits RVNRL. Indeed this is what we should all strive for developing technologies that will also protect the environment. No doubt, one of the challenges we are facing today is sustainable development - meeting the needs of development while conserving the environment.

No matter how good a technology can be, it must operate in a commercial environment if it is to contribute to progress and development. Towards this end, team work by all parties is vital. research institutes can go so far as to develop and demonstrate the technological feasibility of technology, as well as creating awareness and interest in response to market needs. Success in commercialization, however, depends on the eventual adoption of the technology by the private sector, and this is influenced by economics as well as current trends. I am sure that the potential of RVNRL in solving problems associated with latex products mentioned earlier, makes it an attractive product for commercialization. It is timely, and only fitting, that now the public and private sectors work hand in glove with one another to make that objective achievable. Such a tie-up will also combine research facilities, technical capabilities, expertise, and marketing know-how in a team that will be capable of capitalizing not just on new technologies developed elsewhere but also to develop home-grown ones.
Malaysia is now embarking on the Seventh Malaysia Plan, in which the concept of a balanced development is being retained and re-emphasized. Under the Seventh Malaysia Plan, the promotion of science and technological innovation is given an even greater priority. The allocation for R&D has been increased by almost two times, from RM629 million under the Sixth Malaysia Plan to RM1.2 billion in the Seventh Malaysia Plan. In addition, there is also a provision of RM 2 billion for the development of related infrastructural facilities and services. Emphasis is placed on programs that will obviously increase indigenous technology capability, and the commercialization of R&D output from the public sector and universities.

Research agencies and universities are, therefore, encouraged to identify intellectual properties with commercial potential and to market them. For the private sector, full support from the Government in the form of a number of incentives, among which are the possibility of direct financial grants and long-term low interest loans, is available. But as I have mentioned before, joint efforts should be made the norm where technology is concerned.

It is heartening to know that steps are being taken by all parties involved in the latex industry to enhance its performance, improve present technology, and overcome current shortcomings. Given the expertise and skills acquired over the last fifty years, as well as the best technical back-up, I am sure we can still play the role of leader in the years to come. The level of support and cooperation given by the Government will be further enhanced to meet the goals of national development, and to sustain Malaysia's position at the forefront of the latex glove industry.

I believe RVNRL has the potential to compete in the world market, and I hope that the Symposium will pave the way for RVNRL to be exploited to its fullest bringing the process on par, if not better than the existing ones.

Last but not least, I wish you a stimulating and fruitful symposium in the three days ahead. I wish all delegates every success in their deliberations.

On that note, Ladies and Gentlemen, I have the pleasure now to declare “The Second International Symposium On RVNRL (Radiation Vulcanization of Natural Rubber Latex)” officially open.

Sekian, terima kasih.
Application of Radiation Technology for Industry and Environmental Protection

S. Machi
Deputy Director General
International Atomic Energy Agency
Vienna, Austria

Introduction

The world population today is 5.7 billion and increasing by 94 million per year. In order to meet the increasing consumption of food and energy due to the tremendous population growth, improved technologies which are environmentally friendly, are indispensable.

In this context, a number of advanced technologies have been brought about by the use of radiation and isotopes.

This paper highlights radiation technology applications in industry, environmental conservation, and agriculture.

1. Radiation Processing - Growing Application

Radiation can induce chemical reactions at any temperature in the solid, liquid and gas phase without using catalyst. This feature brings unique advantages of radiation processing, such as energy saving, and capabilities inducing reaction at room temperature and in solid state.

Radiation processing has been therefore increasingly applied in industries to improve the quality of products, energy efficiency, and to manufacture products with unique properties.

Worldwide, there are approximately 180 Co-60 gamma irradiators and 700-800 electron beam accelerators for industrial users as of today. For example, more than 280 electron beam accelerators in Japan as recently reported by the Science and Technology Agency are in operation both for commercial purpose and R & D work. The increase in the number of accelerators, as shown in Figure 1, reflects the growing of radiation processing application. About 100 accelerators are also used for research and development which are expected to bring new applications in the near future.
2. **Polymeric Products**

Radiation cross-linked polyethylene for insulation of wire and cable was first achieved in the 1950's and has been widely used in industry because of its excellent heat and chemical resistant properties. Since then many different types of polymeric products, as listed in Table 1, have been commercially manufactured by radiation processing.
Table 1: Industrial Products of Polymeric Materials Using Radiation Processing

<table>
<thead>
<tr>
<th>Products</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cross-linked wire and cable</td>
<td>Heat and chemical resistant insulation</td>
</tr>
<tr>
<td>Foamed polyethylene</td>
<td>Food packaging, insulation, protection for corrosion</td>
</tr>
<tr>
<td>Heat shrinkable tubing and sheets</td>
<td>Energy saving, environmentally friendly processing, Better quality products.</td>
</tr>
<tr>
<td>Curing of surface coating for wood panel, paper, roof tile, steel plate, gypsum tile, overcoat of printing, floppy disks and screen printing</td>
<td></td>
</tr>
<tr>
<td>Adhesive tapes</td>
<td>Curing of silicone coatings</td>
</tr>
<tr>
<td>Wood-plastic composites</td>
<td>Abrasion resistant, water resistant</td>
</tr>
<tr>
<td>Polymer flocculants</td>
<td>High molecular weight products</td>
</tr>
<tr>
<td>Automobile tires</td>
<td>Cross-linking of rubber</td>
</tr>
<tr>
<td>Teflon powder</td>
<td>Decomposition of used teflon</td>
</tr>
<tr>
<td>Contact lenses</td>
<td>Hydrogels</td>
</tr>
<tr>
<td>Water absorbents</td>
<td>Disposable diapers, etc.</td>
</tr>
<tr>
<td>Deodorant fiber</td>
<td>By radiation grafting</td>
</tr>
<tr>
<td>Cross-linked polyurathane</td>
<td>Cable insulation for antilock brake sensor</td>
</tr>
<tr>
<td>Cross-linked nylon</td>
<td>Heat and chemical resistant</td>
</tr>
<tr>
<td>Battery separators</td>
<td>AAc grafted polyethylene</td>
</tr>
<tr>
<td>Wound dressing</td>
<td>Hydrogels by crosslinking or grafting</td>
</tr>
<tr>
<td>Super heat resistant SiC fiber</td>
<td>Metal and ceramic composites, semi-commercial plant</td>
</tr>
</tbody>
</table>

(1) **Electron beam curing of surface coating**

Electron beam curing of surface coating is an important application growing in different products shown in Table 1, even including floppy disk manufacturing. An important feature of electron beam curing is the non-emittance of solvents into the environment during processing in contrast with conventional ones. This makes the processing more friendly to environment and workers. Due to this advantage and the excellent quality of products, EB curing of coatings is expected to grow first in the near future.
(2) **Super heat-resistant silicone carbide fiber**

A new super high-temperature resistant SiC fiber has been developed at the Japan Atomic Energy Research Institute (JAERI). The fiber was prepared from radiation cross-linked polycarbosilane (PCS) fiber followed by heat treatment at 1200°C. It has shown much better heat resistance than SiC fiber prepared from chemically cross-linked PCS (the conventional method). It can stand even at 1800°C in comparison to 1200°C for conventional ones.

The dose requirements for cross-linking is 10 MGy given by an electron beam accelerator. However, the cost of irradiation does not account for a large portion of the product price since the product has a very high value. A commercial plant to produce one ton of SiC fiber per month will be in operation in 1995. The product will be used for heat resistant composites with ceramics or metals for space shuttle, turbine blades, etc.

(3) **Absorbent fiber for uranium**

Radiation grafting is advantageously used for modification of polymeric materials. Sugo and his group have developed a new material which selectively absorbs uranium in water by grafting acrylamide on polyethylene hollow fibers followed by conversion of cyano group to amidoxime group. The grafting was carried out by a pre-irradiated method using electron beams\(^{21}\).

These hollow fibers were packed in column and tested for adsorption of uranium from seawater showing excellent efficiency. This material may provide an efficient recovery technology of uranium from seawater.

(4) **Radiation crosslinked natural rubber latex.**

The IAEA has been implementing an RCA/UNDP project to develop a new technology of crosslinking natural rubber latex by gamma radiation. In a conventional process crosslinking or vulcanization will be carried out by sulphur and heating. A small amount of a toxic substance, nitrosoamine, formed during vulcanization, therefore remains in the product. Radiation crosslinking without using sulphur can provide a clean latex not containing nitroamine. The latex is more safely used for manufacturing surgical gloves and other products.

The MINT (Malaysian Institute of Nuclear Technology and Research) has installed a large plant to produce 6,000 tons of irradiated latex per year which is now in operation.
Biomedical materials

Biocompatibility is the most important property of biomedical materials since they are used in contact with a living organism such as blood and tissues. Modification of surface properties improving the biocompatibility is advantageously carried out by radiation processing because of following points:

- absence of additives in products providing clean materials
- simple and reliable process and product quality control
- materials are simultaneously sterilized
- versatility of the process in terms of materials to be processed.

A number of papers have been published on the synthesis of biocompatible polymers, in particular tissue compatible polymers and anti-thrombogenetic polymers. However, there are only a few kinds of materials successfully developed to be used for clinical purpose.

Wound dressing

Two types of synthetic wound dressing have been produced by radiation processing for clinical use in commercial scale.

Mr. Rosiak and his group in Poland has developed a new hydrogel dressing used for temporary covering of a burned wound by radiation crosslinking and polymerization. Aqueous solutions of dressing components, polyvinylpyrrolidone, polyacrylamide or their monomers, polyethylene glycol and agar, are irradiated with a dose of 25 kGy to be converted into hydrogel with stable three-dimensional chemical network structure. The products are sterilized during irradiation. The hydrogel dressing products are used for healing wounds and especially burns, ulcers, bedsores and skin grafts. They are a good barrier for bacteria from outside and permeable for gases, drugs and water vapour. They have characters of good adhesion to wound and normal skin without stiching. Therefore, they can be removed painlessly. In 1993, for example, 5,000 m² of the product were sold.

Another type of wound dressing has been produced commercially in Israel, based on the studies by Mr. Behr and his group. The wound dressing, temporary artificial skin, is a thin flexible membrane of 40 μm thickness. This dressing is prepared by grafting hydrophilic monomers, such as acrylamide and hydroxyethylmethacrylate onto polyurathane film using radiation. The products are transparent and adhere well to the wound, and can be removed without pain. They prevent bacterial invasion, are highly permeable to water and prevent fluid accumulation. They are also permeable to drugs. Topical antimicrobials can be applied to their surface.
JAERI. Takasaki has recently developed a new hydrogel wound dressing by crosslinking of polyvinylalcohol (PVA) using electron beams. Treatment of casted PVA to form partial crystallization before crosslinking was found to significantly improve heat resistance and mechanical strength of the hydrogel. A plant for commercial production will be in operation in 2 years.

**Drug delivery system**

Radiation polymerization and crosslinking is a very convenient method to prepare a drug delivery system (DDS). Since polymer matrix used for DDS contacts directly with human tissues, the polymer matrix should not contain toxic residues from polymerization catalysts. Radiation polymerization can provide a most suitable method to prepare DDS because it does not need catalyst and heat which decompose drugs.

Mr. Yoshida successfully prepared testicular prosthesis with the controlled release of testosterone by radiation polymerization of HEMA and polyethylene glycol di-methacrylate. They were implanted in scrotum or in lower abdomen of 11 patients. The serum testosterone level was maintained at a level of more than 3.0 ng/ml for 2-5 years. By the implantation masculinization was observed for all patients. This successful method can solve problems associated with the treatment by injection.

(6) **Ion beam application for polymer modification**

Recently ion beam technology has been well advanced in the field of material science and technology. There are approximately 400 ion implantation units used for semiconductor manufacturing in Japan. However, modification of polymers by ion beam irradiation is quite a new field. It has been reported that cell adhesion property is obtained by ion beam irradiation of polystyrene and polyurathane. By adhesion of cells on the surface of these polymers, their biocompatibility is improved. The mechanism of these changes of polymer surface is not well known. It is understood that the morphology and structure of the surface may be changed by ion bombardment to be more biocompatible. The formation of micropores in polymer membranes by ion beam irradiation, followed by chemical etching is a promising application.

**3. Sterilization of Medical Supplies**

In developed countries 40-50% of medical products are sterilized by radiation processing. Radiation processing is better than the conventional ethylene oxide process with regard to safety for both workers and consumers, reliability of disinfection and simplicity of processing. This processing is also friendly to the environment because of non-emittance of toxic gases. This application of radiation processing will rapidly grow further in developing countries with the support of the IAEA. IAEA and UNDP have implemented the radiation sterilization plant projects in India, ROK, Chile, Hungary, Yugoslavia, Iran, Turkey, Peru, Bulgaria, Portugal, Syria, Ecuador and Ghana.
In developed countries, the ratio of radiation sterilization to the ethylene oxide method will further increase to the level of 80% in the future. Electron beam application for this purpose may grow at a higher rate than Co-60 in some countries due to possible economic advantages and better public acceptance, depending on the condition of countries.

The radiation sterilization of cosmetic products and raw materials of pharmaceuticals is also gaining wider acceptance.

4. Applications for Environmental Protection

(1) Cleaning of Flue Gases

Deterioration of the environment by pollution is the global concern. The emission of $SO_2$ and $NO_x$ into the atmosphere from coal- and oil burning power plants and industrial plants is one of the major sources of environmental pollution. These pollutants cause acid rain and also contribute to the "greenhouse effect".

Innovative technology using electron beams to simultaneously remove these pollutants by irradiation was first developed in Japan and followed by research groups in the United States, Germany, Poland and China. As shown in Figure 3, after the flue gas is cooled by water spray to 70°C, it is exposed to electron beams during passing through an irradiation chamber in the presence of a near stoichiometric amount of ammonia which has been added to the flue gas prior to the irradiation zone. The $SO_2$ and $NO_x$ are converted into their respective acids which are subsequently converted into ammonium sulfate and ammonium nitrate. These are then recovered by an electrostatic precipitator. The by-product is a useful fertilizer for agricultural purposes.

This innovative technology has been demonstrated by large pilot scale plants in Japan, USA, Germany, and Poland as listed in Table 2.
Table 2. Development of electron beam technology for cleaning flue gases.

<table>
<thead>
<tr>
<th>Institution/Year</th>
<th>Volume flow rate</th>
<th>Accelerator</th>
<th>SO_{2}/NO_{x} raw gas concentration (ppm)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JAERI 1981</td>
<td>900 Vh</td>
<td>1.5 MeV</td>
<td>1000/5000</td>
<td>80-150</td>
</tr>
<tr>
<td>Institute of Nuclear Chemistry &amp; Technology, Warsaw 1989</td>
<td>400 m³/h</td>
<td>775 KeV</td>
<td>0-1200</td>
<td>60-150</td>
</tr>
<tr>
<td>Karlsruhe Agate II 1989</td>
<td>1000 m³/h Crude oil</td>
<td>500 keV</td>
<td>400-1000</td>
<td>60-120</td>
</tr>
<tr>
<td>Ebara Fujisawa 1991</td>
<td>1500 m³/h Oil-fired and incineration gas</td>
<td>500 keV</td>
<td>300-1000</td>
<td>65</td>
</tr>
<tr>
<td>INC/INCT/Kaweczyn power plant 1992</td>
<td>20 000 m³/h Coal-fired</td>
<td>500-700 keV</td>
<td>200-600</td>
<td>60-120</td>
</tr>
<tr>
<td>NKK-JAERI Matsudo City 1992</td>
<td>1000 m³/h Incineration gas</td>
<td>900 keV</td>
<td>250</td>
<td>150</td>
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<tr>
<td>Ebara-JAERI Chubu 1992</td>
<td>12 000 m³/h Coal-fired</td>
<td>15 kW</td>
<td>NO_{x}-100</td>
<td></td>
</tr>
<tr>
<td>Ebara-Tokyo-EPA 1992</td>
<td>Auto-tunnel exhaust gas 50 000 m³/h</td>
<td>800 keV</td>
<td>HCL-1000</td>
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</table>

Flow diagram of electron beam process for flue gas treatment

Figure 2. Flow diagram of electron beam process for flue gas treatment
The pilot-scale plant being currently in operation in Warsaw was constructed through a joint project of the IAEA and Poland. The pilot plant has the capacity to clean 20,000 m$^3$ of coal-burning flue gases from the local heating plant.

Continuous operation of the plant for more than one month successfully removed 95% of the SO$_2$ and 80% of the NO$_x$ from flue gases. As an IAEA model project, a demonstration industrial-scale electron beam plant for cleaning emissions from coal-burning power stations is being implemented.

In Japan three pilot-scale electron beam plants for treating flue gases from coal-burning power stations, municipal waste incinerators and traffic tunnels, respectively, have been operated to remove efficiently SO$_2$ and NO$_x$ and other toxic gases.

The advantages of this technology over conventional processes for treating flue gases are:
- It is the only process to simultaneously remove SO$_2$ and NO$_x$.
- The by-product of the process can be used as agricultural fertilizer.
- It is a process which does not require large amounts of water.
- It can meet the stringent requirements for removal of SO$_2$ and NO$_x$.

The economics of the process have been studied for various kinds of fuels which have different SO$_2$ and NO$_x$ concentrations. It looks promising that the electron beam process is competitive with all existing SO$_2$ removal systems. When factoring in the cost of an SCR (Selective Catalytic Reduction) removal system for NO$_x$, it can be seen that the installed costs for the projected electron beam process make it one of the most economical systems to install and operate in a power station.

(2) Disinfection of sewage sludge and its recycling

Disinfection of sewage sludge by radiation has been studied at pilot- and full-scale plants in Germany, Japan, USA and India. Irradiated sludge is used on farm land as an organic fertilizer. In Japan, the technology of sludge irradiation followed by composting has been developed to produce disinfected compost for agriculture. The IAEA has started a new programme in 1995 to enhance the transfer of this technology to end users.

(3) Cleaning of water

Removal of organic pollutants by radiation in waste water and in drinking water also is being studied. A pilot-scale plant is being operated in the Laboratory of Gehringer in Austria for the treatment of drinking water using electron beams and ozone. In Miami, Florida, an engineering study has been carried out to evaluate the efficiency and cost-effectiveness of electron beam treatment for removing toxic pollutants in water streams such as groundwater, secondary effluents, and potable water.
5. **Food irradiation**

In the past 10 years the application of food irradiation has significantly increased. Currently more than 38 countries have approved one or more irradiated food items. Totally more than 120 items, for human consumption. In 27 countries irradiation processing of food has been commercialized.

Introduction of food irradiation can contribute to the reduction of post-harvest losses, increase export potential of certain food and reduce risks of food-borne diseases without using fumigation by chemicals, such as ethylene dibromide, methyl bromide and ethylene oxide. Chemical fumigation of food has been either prohibited or is being increasingly restricted in most advanced countries for health, environmental or occupational safety reasons. Under terms of the Montreal Protocol, adopted in 1989, chemicals which damage the ozone layer will have to be phased out by the year 2000. Food irradiation represents an alternative to treatment by chemicals in many cases.

The incidence of food-borne diseases increasingly affect adversely the health of populations. For example, in 1992, Salmonella and Campylobacter accounted for about 4 million cases of illness in the USA caused by food (at least half were attributable to meat and poultry). About 1,000-2,000 deaths thus resulted from Salmonella and 120-360 from Campylobacteriosis. Food irradiation is then being regarded more and more by health authorities as a means of reducing this health problem.

There is growing evidence from numerous consumer trials, including commercial market tests, that consumers are prepared to buy irradiated food.

The IAEA has implemented projects aiming at transferring the food irradiation technology to industry and developing countries. The IAEA General Conference in 1992 adopted a resolution to strengthen the assistance to developing countries in practical utilization of food irradiation. Following the resolution, a commercial irradiator will be constructed in Beijing by the Chinese Government in co-operation with the IAEA for treating rice and garlic in commercial quantities.
Fig. 3. Commercial irradiation of spices and vegetable seasonings in different countries. (From Loaharanu, IAEA Bulletin 36, No. 1. 30 (1994))

6. **Transfer of Radiation Technology to Developing Countries**

The IAEA is actively in charge of the technology transfer through:

- Technical cooperation projects
- Research contract programmes
- Provision of equipments, experts, fellowships
- Training of personnel
- Conferences, meetings and publications
- Laboratory services
- Information and data base services.
As shown in Figure 4, a large fraction of technical assistance funds is used for the transfer of technologies related to nuclear application in agriculture, industry and human health.

Fig. 4. Technical assistance co-operation disbursements by area of activity in 1994 (in thousands of dollars)

A number of irradiation facilities, such as electron accelerators and gamma irradiators have been provided to developing countries by IAEA and UNDP. The RCA/UNDP industrial projects on electron beam curing of surface coating and crosslinking of natural rubber latex have been implemented for member countries in South East Asia and Pacific. Since 1994 the project on environmental conservation by radiation technology has been started under the RCA/UNDP programme.
References


RADIATION Vulcanization of PHILIPPINE NATURAL RUBBER LATEX

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Abstract

The response of Philippine natural rubber latex to radiation vulcanization and the stability of the irradiated natural rubber latex (INRL) upon storage and aging were investigated. Commercially available high ammonia (HA) concentrated latices obtained from various rubber plantations in Mindanao Island were treated with 5 phr of n-butyl acrylate (nBA), and gamma-irradiated at the PNRI 60Co Irradiation Facility at a dose rate of 2.57 kGy/hr. Unirradiated cast latex films gave different green strength which varied from 2 - 11 MPa. Cast films from INRL exhibited maximum tensile strengths of 25 - 32 MPa at a radiation dose of 15 kGy. Higher tensile strengths were obtained from cast films with low Mg and high nitrogen contents. Thermal analysis using thermogravimetry (TG) revealed one major decomposition product at 374 °C. Its rate of decomposition decreased to a minimum at 15 kGy, then increased as radiation dose was increased. This trend correlated well with the tensile strength measurements. The stability of the INRL upon storage and aging is an essential parameter to the rubber latex industry. For storage studies, INRL was stored for various periods of time. It was found that the pH and total solids content of the stored INRL did not change significantly after 12 months of storage; the MST values remained at above 1900 seconds, and the viscosity decreased with time. The cast films exhibited a decline in tensile strength, modulus, and crosslinking density upon storage. While there were observed changes in the physical properties of the INRL during the storage period, the data indicate that these properties were within values acceptable to the latex industry. Tests on the aging properties of INRL films were undertaken. It was shown that among the chemical antioxidants presently used by the latex industry, TNP demonstrated the highest antioxidant property, followed by Antage DABQ and Vulcanox BKF. Our data indicate that the natural rubber latex produced and processed in the Philippines is suited for radiation vulcanization.

INTRODUCTION

Radiation vulcanization of natural rubber latex (RVNRL) is an emerging technology whereby radiation is used in place of sulfur in the conventional pre-vulcanization process for the manufacture of dipped natural rubber latex products (Minoura et al. 1961; Makuchibi et al. 1991). The radiation process involves the irradiation of NHL in the presence of sensitizers resulting in the improved properties of the latex. The products obtained have shown to have noticeable advantage over the conventionally vulcanized NHL due to the absence of the carcinogenic nitrosamines derived from the common accelerators of the sulfur vulcanized NHL, lower levels of cytotoxicity and allergic reactions, faster degradation in the environment, and absence of acid combustion gases (Gazeley et al. 1989; Nakamura et al. 1989; Tsuchiya et al. 1992; Makuchibi et al. 1992). The rise in the environmental consciousness among consumers has boosted the potential for RVNRL. This paper presents our data on the response of Philippine natural rubber latex to radiation vulcanization, the properties of irradiated NHL (INRL) and the effect of some antioxidants on the aging properties of the INRL.
Rubber plantations in the Philippines are found in Mindanao, the southern island of the country (Fig. 1). These plantations started as small-scale holdings before World War II. The area planted to rubber expanded gradually from 3,400 ha in 1950 to 88,100 ha in 1993 (Fig. 2) (PCARRD 1993; BAE 1980 to 1993). About 75% of the rubber farms are less than five hectares indicating that rubber farming is in the hands of smallholders (PCARRD 1993). Table I presents the rubber clones used in Mindanao. The annual rubber production has increased from 76,700 MT in 1980 to 181,150 MT in 1995 (BAE 1980 to 1995). Centrifuged latex, however, is produced in a limited scale of roughly 10% of the annual natural rubber production.

MATERIALS

Samples of locally processed, high ammonia (HA) concentrated latices with an average of 64% total solid content (TSC) and a mechanical stability test (MST) of 1000+ sec as well as HA latices imported from Malaysia and Thailand were obtained from the different industrial rubber producers/processors through the Philippine Rubber Industries Association (PRIA). Field latices with a TSC of 32% were obtained from Cotabato through the University of Southern Mindanao. The sensitizer, n-buty acrylate, was provided the Resins, Inc., and by Dr. K. Makuchini of TRCRE, JAERI. The antioxidants used in the aging experiments were provided by Dr. K. Makuchini of TRCRE, JAERI (TNPP, tris-nonylated phenylphosphite, and Antage DAHQ, 2,5-di-tert-amyhydroquinone), and by the local rubber manufacturing companies (Vulkanox BKF, 2,2'-methylene bis-(4-methyl-6-tertbutyl)phenol, Permanax HD/SE, alkylated diphenylamine, BHT, 3,5-di-tert-hydroxytoluene, and Aminox, of unknown structure).

METHODS

A. Characterization of Philippine Natural Rubber Latex

Percent TSC, dry rubber content (DRC) and volatile fatty acids were analyzed using the ASTM procedure Nos. D1076-88 (ASTM 1994). Elemental content of the samples was analyzed by AAS (ASTM D 1278). Kjeldahl analysis was used to analyze the nitrogen content of the rubber samples (ASTM D3533-90). The tensile strength and elongation at break of the cast films, cut into dumbbell pieces, were measured using the Instron testing machine (Model 1011). Thermal analyses were performed using the Shimadzu TGA-50 thermogravimetric analyzer.

B. Irradiation of NRL Samples

NRL was diluted to 50% TSC with NH₄OH and mixed with 0.2 phr KOH and 5 phr n-BA as sensitizer. NRL was irradiated at the PNRI °Co Irradiation Facility for different radiation doses (0, 5, 10, 15, 20, 30 kGy) at a dose rate of 2.57 kGy/hr.

C. Preparation of Cast NRL Films

Twenty five (25) mL of INRL was cast onto a glass plate, 19cm x 13cm, to make a film of 0.4 - 0.6mm thickness. The sample was air-dried. The film was removed from the glass plate, leached in 1% NH₄OH overnight, washed with tap water, air-dried for 24 hr, and cured at 70°C for two hr.

D. Permanent Set

A 10 cm distance (Li) was marked on film strips measuring 12L x 1W cm. The strips were fastened to a board with the 10 cm mark stretched to a 100 % distance for one hour. The strips were loosened and allowed to stand for 30 min. The final length (L) for the marked distance was then measured and the permanent set was computed as follows:

\[
PS = \frac{L_f - L_i}{L_i}
\]
E. Swelling Ratio and Crosslinking Density

A 0.1g film strip was immersed in toluene for 48 hr. The sample was taken out and blotted quickly with filter paper and weighed. The swelling ratio was computed using the following formula:

\[ Q = 1 + \frac{d_1}{d} \left( \frac{W_f}{W_o} - 1 \right) \]

where:
- \( W_o \) = weight of film before immersion
- \( W_f \) = weight after immersion
- \( d_1 \) = density of rubber latex
- \( d \) = density of toluene

Crosslinking density was computed using the Flory & Rehner equation:

\[ \chi = K Q^{-3/2} \]

where:
- \( \chi \) = crosslinking density
- \( K = 4.71 \times 10^8 \)
- \( Q \) = swelling ratio.

F. Aging Test

Antioxidant emulsions/dispersions were prepared using the formulation below and ballmilled for three days.

- Antioxidant 50%
- 20% emulsifier 10%
- 10% by wt casein in 10% by wt NH\(_4\)OH 10%
- Distilled water 30%

Different concentrations (0.0, 0.5, 1.0, 1.5, 2.0 and 2.5 par) of the antioxidant emulsion/dispersion were added to irradiated NRL and stirred for 2 hr. The latex was made into films and aged at 100°C for 22 hr using a Geer oven. Tensile strengths were measured before and after aging.

RESULTS AND DISCUSSION

A. Properties of Philippine NRL

Commercially available latices vary in their physico-chemical and mechanical properties depending on such factors as the rubber clone used, conditions of tapping and processing of latex, preservatives used, storage time, and non-rubber components of latex. These properties have been found to affect the response of NRL to radiation. Different sources of latices give distinct radiation responses as measured by the vulcanization dose, \( D_v \), and the tensile strength, \( T_b \). These variations in radiation response have been attributed mainly to the differences in composition and quantity of their non-rubber components (NRC). \( D_v \) is said to decrease with increasing green strength which is directly associated with protein content in the rubber phase (Panasa et al. 1987). Metal ions also affect RVNRL. Large amount of Mg decreases the tensile strength of radiation vulcanized natural rubber (Makunuchi et al. 1993). Mg and the volatile fatty acids (VFA) are known to have an adverse effect on the stability of NRL. Tensile strength of of NH\(_4\)OH-leached irradiated latex film increases upon the addition of latex serum proteins (Abad 1993). Thus, for a good RVNRL product, latex with higher green strength, low Mg content, and higher nitrogen content is the latex of choice for RVNRL.

Some physical and chemical properties of the Philippine NRL investigated are shown in Table II. The field latex from Cotabato exhibited higher NRC, which was expected, because these samples were not centrifuged. Centrifugation removes most of the NRC in NRL. The centrifuged latices varied in their NRC. The Mg contents of the latices from Zamboanga in Western Mindanao and Agusan in Northern Mindanao are 14-71 ppm and 12-13 ppm, respectively. For the same latex samples, the nitrogen contents are 0.18-0.71% and 0.32-0.71%, respectively. The VFA number is within the minimum set value of ISO 2004 which is 0.2 ppm. The latices are quite stable with MST of 1000+ sec, values greater than the minimum set limit of 800 sec. The green strengths of the latices (7-11 MPa) exceed the limit of 7 MPa except for Zam 2-1 which has only a green strength of 2 MPa. This low value could be attributed
to its nitrogen content which is only 0.18%.

B. Properties of Irradiated NRL (INRL)

The dose-effect response curves for the different Philippine latices are shown in Fig. 3. Cast films exhibited maximum tensile strengths of 25 - 32 Mpa at a radiation dose of 15 kGy. The tensile strengths decreased at higher radiation doses. Higher tensile strengths were observed from latices of Zam1-2 and Agu 1-2 with a Tb above 30 Mpa at this dose. The characteristics of latex Agu 1-2 indicate a low Mg content and a high nitrogen content. On the other hand, latex sample Zam-3-2 with the lowest green strength and nitrogen content exhibited a maximum tensile strength of 25 Mpa only. The data show that samples with lower green strengths gave lower tensile strengths at the vulcanization dose. The lower tensile strengths obtained could be due to high Mg content and/or low nitrogen content. The cast films formed from all latices would be able to meet the standard requirements of ASTM for the mechanical properties of examination gloves (21MPa) and finger cots (20MPa). The typical properties of the Philippine INRL and the cast films are shown in Table III.

The degree of radiation vulcanization was measured from the swelling ratio and crosslinking density of the cast films. As observed by other workers (Parinya et al., 1989), the swelling ratio decreased with increasing radiation dose while the crosslinking density increased with increasing dose (Table IV). It was further found that while the level of crosslinking in the rubber network continued to increase after 15 kGy, the tensile strength decreased indicating that there is an optimum number of crosslinks required to attain the maximum tensile strength of the INRL.

Thermogravimetric analysis (TGA) was used to study the thermal behavior of the INRL as a function of radiation dose. As shown in Fig. V, the TGA curves of the unirradiated and irradiated NRL revealed only one major decomposition product which underwent thermal degradation at 374° to 377°C. Its rate of decomposition, was affected by radiation dose as shown in Fig. 5 and Table V. Thermal decomposition decreased and reached a minimum at 15 kGy, then increased as radiation dose was increased to 30 kGy. This trend is consistent with the negative correlation between rate of decomposition and tensile strength up to 15 kGy. These observations indicate that the NRL irradiated up to the vulcanization dose of 15 kGy are more thermally stable than the unirradiated NRL and those irradiated above the vulcanization dose.

C. The Effect of Antioxidants on the Aging Properties of Philippine INRL

The thermal oxidative resistance of RVNR is inferior to that of the conventionally processed NR due to the absence of dihydrocarbonates that function as strong antioxidants. This aging property can be improved by the addition of some external antioxidants. The effectiveness of different antioxidants (TNPP, Vulcanox BKF, Permanox HD/SE, BHT, Antage DAHQ, and Aninox) was tested on the Philippine INRL. Table VI presents the chemical structures of the antioxidants and their respective effects on the aging properties of INRL. Figure 6 shows that among the antioxidants, TNPP was found to be the most effective. Percent retention was quite high (88%) even at a concentration of only 0.5phr. Vulcanox BKF and Antage DAHQ also demonstrated strong antioxidant properties with percentages retention of 85% and 76%, respectively, at 0.5phr. However, Vulcanox BKF leaves a red staining effect on the radiation vulcanized natural rubber. The effectiveness of the other antioxidants are quite poor with tensile strength retentions of less than 50%.

D. Storage Experiments

The storage stability of INRL would be an important factor to consider in the commercialization of RVNR. Table VII shows some of the physical and mechanical properties of INRL after a storage period of 12 months. The Philippine latex showed similar trends with the Malaysian and Thai latices. No significant changes have been observed with the MST, pH, %TSC, and Permanent Set for the three INRLs. Their viscosities decreased with time. This reduction may be due to the evaporation of n-BA which has been observed to increase the viscosity of natural rubber latex. The RVNR films formed from these latices indicated a decrease in Modulus min and tensile strength with time (Fig. 7). A sharp drop in Tb was observed after four months of storage from 27 MPa to 22 MPa for the Malaysian latex, 26 MPa to 22 MPa for the Thai latex and 26 MPa to 22 MPa which remains stable up to a period of 12 months for the Philippine latex. This decrease could be associated with the decrease in crosslinking density as seen in Fig 9. These values are, however, still within the acceptable limit for the mechanical properties of examination gloves and finger cots.
CONCLUSION

The Philippine latex is compatible for RVNRL. The cast films from the INRL have good mechanical properties which remain within acceptable limits even after storage of 12 months. The aging properties of the INRL can best be improved with the addition of TNFP as antioxidant. Improved handling and processing of the Philippine NRL can reduce the Mg content and VFA of the latices for an even better quality INRL.

ACKNOWLEDGMENT

The authors wish to thank the International Atomic Energy Agency (IAEA) for the technical assistance for the project under the TC Project PHI/8/013, the Philippine Council for Advanced Science and Technology Research and Development (PCASTRD) of the Department of Science and Technology, and the Philippine Nuclear Research Institute (PNRI) for financial assistance, the Philippine Rubber Industries Association (PRIA), the Reedex, Inc. and the University of Southern Mindanao for excellent collaboration and cooperation. The authors thank Dr. K. Makuuchi, TRCRE, JAERI, and Mr. Marga Utama, CAIR, BATAN for their technical advice.

REFERENCES

Table I. **RUBBER CLONES IN MINDANAO**

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<td>XII</td>
<td>RRIM 600, TJIR-1, PB-86, PB-300</td>
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*Philippine Industrial Crops Research Institute, 1991*
Table II. Characterization of Philippine Natural Rubber Latex

<table>
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<tr>
<th>Samples</th>
<th>% TSC</th>
<th>% DRC</th>
<th>% Nitrogen Content</th>
<th>Crosslink (Mpa)</th>
<th>% Ash</th>
<th>Mg</th>
<th>Ca</th>
<th>Cu</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zam 1-1</td>
<td>60.90</td>
<td>60.00</td>
<td>0.71</td>
<td>7</td>
<td>0.27</td>
<td>26.31</td>
<td>11.02</td>
<td>0.77</td>
<td>n.d.</td>
</tr>
<tr>
<td>Zam 2-1</td>
<td>62.00</td>
<td>61.50</td>
<td>0.18</td>
<td>2</td>
<td>0.34</td>
<td>13.98</td>
<td>15.78</td>
<td>1.12</td>
<td>n.d.</td>
</tr>
<tr>
<td>Zam 3-2</td>
<td>66.00</td>
<td>--</td>
<td>0.36</td>
<td>10</td>
<td>0.28</td>
<td>77.27</td>
<td>12.15</td>
<td>0.93</td>
<td>n.d.</td>
</tr>
<tr>
<td>Agu 1-1</td>
<td>64.27</td>
<td>62.95</td>
<td>0.32</td>
<td>10</td>
<td>0.25</td>
<td>12.19</td>
<td>7.24</td>
<td>0.94</td>
<td>n.d.</td>
</tr>
<tr>
<td>Agu 1-2</td>
<td>64.65</td>
<td>62.30</td>
<td>0.32</td>
<td>11</td>
<td>0.26</td>
<td>13.48</td>
<td>10.14</td>
<td>1.39</td>
<td>n.d.</td>
</tr>
<tr>
<td>Cot 1-1</td>
<td>31.65*</td>
<td>26.10</td>
<td>1.11</td>
<td>--</td>
<td>0.28</td>
<td>72.39</td>
<td>32.69</td>
<td>2.21</td>
<td>n.d.</td>
</tr>
<tr>
<td>Cot 1-3</td>
<td>33.17*</td>
<td>27.55</td>
<td>1.73</td>
<td>8</td>
<td>0.45</td>
<td>--</td>
<td>21.80</td>
<td>1.07</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

* not centrifuged
n.d - not detected

<table>
<thead>
<tr>
<th>Samples</th>
<th>MST</th>
<th>VFA Number</th>
</tr>
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<tbody>
<tr>
<td>A</td>
<td>1600</td>
<td>0.1724</td>
</tr>
<tr>
<td>B</td>
<td>1740</td>
<td>0.0187</td>
</tr>
<tr>
<td>C</td>
<td>1851</td>
<td>0.0294</td>
</tr>
</tbody>
</table>
Table III. Typical Properties of Philippine Irradiated Natural Rubber Latex

<table>
<thead>
<tr>
<th>Latex</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Solids Content (TSC)</td>
<td>50.03 %</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dry Rubber Content (DRC)</td>
<td>49.08 %</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-rubber Component (TSC-DRC)</td>
<td>1.05 %</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Viscosity</td>
<td>25.0 Cp</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>10.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mechanical Stability Time (MST)</td>
<td>1000+ sec</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cast Film</th>
<th></th>
<th></th>
<th></th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Before Aging</td>
<td>*After aging</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Modulus 300% (MPa)</td>
<td>1.5</td>
<td>0.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile Strength (MPa)</td>
<td>28.0</td>
<td>25.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Elongation at Break, %</td>
<td>990</td>
<td>990</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Permanent Set, %</td>
<td>4.32</td>
<td>3.57</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Swelling Ratio in Volume</td>
<td>7.63</td>
<td>7.14</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* aging was done at 100°C for 20 hours in a Geer oven
Table V. Thermal Stability of INRL vs Radiation Dose

<table>
<thead>
<tr>
<th>Temp. Rate (°C/min)</th>
<th>Degradation Rate (mg/min)*</th>
<th>Dose (kGy)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>-0.577</td>
<td>-0.691</td>
</tr>
<tr>
<td>15</td>
<td>-0.977</td>
<td>-1.110</td>
</tr>
<tr>
<td>20</td>
<td>-1.265</td>
<td>-1.329</td>
</tr>
</tbody>
</table>

* Obtained from the TGA Curves

Table IV. Swelling Ratio, Crosslinking Density and Tensile Strength vs Radiation Dose

<table>
<thead>
<tr>
<th>Dose (kGy)</th>
<th>Swelling Ratio</th>
<th>Crosslinking Density x 10^2</th>
<th>Tensile Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>45.3</td>
<td>0.08</td>
<td>13.1</td>
</tr>
<tr>
<td>5</td>
<td>9.87</td>
<td>1.04</td>
<td>21.2</td>
</tr>
<tr>
<td>10</td>
<td>7.49</td>
<td>1.64</td>
<td>28.6</td>
</tr>
<tr>
<td>15</td>
<td>7.20</td>
<td>1.75</td>
<td>30.3</td>
</tr>
<tr>
<td>20</td>
<td>6.63</td>
<td>2.01</td>
<td>29.0</td>
</tr>
<tr>
<td>30</td>
<td>3.32</td>
<td>6.37</td>
<td>28.7</td>
</tr>
</tbody>
</table>
Table VI. Effect of different antioxidants on Philippine Irradiated Natural Rubber Latex

<table>
<thead>
<tr>
<th>Antioxidants</th>
<th>Chemical Name/Structure</th>
<th>Concentration (phr)</th>
<th>% Tb Retention</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNPP</td>
<td><img src="image" alt="Tris-nonylated phenyl phosphate" /></td>
<td>0</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>88</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.0</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5</td>
<td>100</td>
</tr>
<tr>
<td>Vulcanox BKF</td>
<td>![2,2'-methylene bis-(4-methyl 6-tert-butyphenol)]</td>
<td>0</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.0</td>
<td>96</td>
</tr>
<tr>
<td>Permanox HD/SE</td>
<td><img src="image" alt="Alkylated diphenylamine" /></td>
<td>0</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.0</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0</td>
<td>35</td>
</tr>
<tr>
<td>BHT</td>
<td><img src="image" alt="3,5-di-tertiary butyl-4-hydroxy toluene" /></td>
<td>0.5</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.0</td>
<td>50.10</td>
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2.5 di-tertiary butyl-4-hydroxy toluene
Table VI. Effect of different antioxidants on Philippine Irradiated Natural Rubber Latex (continuation)

<table>
<thead>
<tr>
<th>Antioxidants</th>
<th>Chemical Name/Structure</th>
<th>Concentration (phr)</th>
<th>% Tb Retention</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antage DAHQ</td>
<td><img src="image.png" alt="Structure" /></td>
<td>0</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.0</td>
<td>88</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5</td>
<td>91</td>
</tr>
<tr>
<td>2,5-Di-tert-amylhydroquinone</td>
<td></td>
<td>0</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>56</td>
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<td></td>
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<td>61</td>
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<td>2.0</td>
<td>58</td>
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<td></td>
<td></td>
<td>2.5</td>
<td>56</td>
</tr>
<tr>
<td>Aminox</td>
<td></td>
<td>1.0</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.0</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5</td>
<td>56</td>
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</table>
### Table VII. Storage Studies on Philippine Irradiated Natural Rubber Latex

**A. Latex Parameters**

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>Viscosity (cps)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Storage Interval (month)</td>
<td>Storage Interval (month)</td>
</tr>
<tr>
<td></td>
<td>0  2  4  6  8  10  12</td>
<td>0  2  4  6  8  10  12</td>
</tr>
<tr>
<td>with TNPP</td>
<td>10.02 9.95 9.56 9.83 9.54 9.58 9.45 20.0 15.8</td>
<td>--  -- 15.0  --  --  --</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>% TSC</th>
<th>% DRC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Storage Interval (month)</td>
<td>Storage Interval (month)</td>
</tr>
<tr>
<td></td>
<td>0  2  4  6  8  10  12</td>
<td>0  2  4  6  8  10  12</td>
</tr>
<tr>
<td>with TNPP</td>
<td>49.5 49.4 49.7 49.5 47.2 48.2 47.8 47.6 47.8 48.3 47.7 46.1 47.1</td>
<td></td>
</tr>
<tr>
<td>w/o TNPP</td>
<td>49.6 49.8 49.6 49.9 47.9 47.9 47.7 47.8 48.2 48.7 46.3 46.0</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>MST (sec)</th>
<th>VFA Number</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Storage Interval (month)</td>
<td>Storage Interval (month)</td>
</tr>
<tr>
<td></td>
<td>0  2  4  6  8  10  12</td>
<td>0  2  4  6  8  10  12</td>
</tr>
<tr>
<td>with TNPP</td>
<td>1820 846 1152 1221 1183 1082 938 0.345 0.429 0.356 0.444 0.331 0.364 0.339</td>
<td></td>
</tr>
<tr>
<td>w/o TNPP</td>
<td>1850 756 1155 1127 1033 938 885 0.401 0.19 0.360 0.518 0.361 0.389 0.386</td>
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</tr>
</tbody>
</table>
### B. Film Parameters

#### Tensile Strength

<table>
<thead>
<tr>
<th>Sample</th>
<th>0</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>A</td>
<td>B</td>
<td>A</td>
<td>B</td>
<td>A</td>
</tr>
<tr>
<td>with TNPP</td>
<td>32</td>
<td>21</td>
<td>26</td>
<td>21</td>
<td>26</td>
<td>20</td>
<td>22</td>
</tr>
<tr>
<td>w/o TNPP</td>
<td>28</td>
<td>---</td>
<td>26</td>
<td>13</td>
<td>26</td>
<td>17</td>
<td>20</td>
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</table>

#### % Elongation at Break

<table>
<thead>
<tr>
<th>Sample</th>
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<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>A</td>
<td>B</td>
<td>A</td>
<td>B</td>
<td>A</td>
</tr>
<tr>
<td>with TNPP</td>
<td>985</td>
<td>950</td>
<td>950</td>
<td>950</td>
<td>1000</td>
<td>1046</td>
<td>1000</td>
</tr>
<tr>
<td>w/o TNPP</td>
<td>989</td>
<td>---</td>
<td>970</td>
<td>950</td>
<td>1000</td>
<td>1050</td>
<td>1000</td>
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</table>

#### Modulus (M

<table>
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<tr>
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<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>A</td>
<td>B</td>
<td>A</td>
<td>B</td>
<td>A</td>
</tr>
<tr>
<td>with TNPP</td>
<td>1.10</td>
<td>0.63</td>
<td>1.15</td>
<td>0.59</td>
<td>1.12</td>
<td>0.72</td>
<td>0.43</td>
</tr>
<tr>
<td>w/o TNPP</td>
<td>1.47</td>
<td>---</td>
<td>0.54</td>
<td>0.44</td>
<td>1.61</td>
<td>0.54</td>
<td>0.72</td>
</tr>
</tbody>
</table>
### Permanent Set

**Storage Interval (month)**

<table>
<thead>
<tr>
<th>Sample</th>
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<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>A</td>
<td>B</td>
<td>A</td>
<td>B</td>
<td>A</td>
</tr>
<tr>
<td>with TNPP</td>
<td>3.5</td>
<td>--</td>
<td>4.0</td>
<td>3.0</td>
<td>3.0</td>
<td>4.0</td>
<td>5.0</td>
</tr>
<tr>
<td>w/o TNPP</td>
<td>4.5</td>
<td>--</td>
<td>3.0</td>
<td>5.0</td>
<td>4.0</td>
<td>4.0</td>
<td>5.0</td>
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</table>

### Swelling Ratio

**Storage Interval (month)**

<table>
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<tr>
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<th>4</th>
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<th>8</th>
<th>10</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>A</td>
<td>B</td>
<td>A</td>
<td>B</td>
<td>A</td>
</tr>
<tr>
<td>with TNPP</td>
<td>7.56</td>
<td>7.85</td>
<td>8.00</td>
<td>8.62</td>
<td>7.44</td>
<td>8.00</td>
<td>8.00</td>
</tr>
<tr>
<td>w/o TNPP</td>
<td>7.71</td>
<td>--</td>
<td>8.00</td>
<td>9.26</td>
<td>7.44</td>
<td>8.00</td>
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</tr>
</tbody>
</table>

### Crosslinking Density x 10^9

**Storage Interval (month)**

<table>
<thead>
<tr>
<th>Sample</th>
<th>0</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>12</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>A</td>
<td>B</td>
<td>A</td>
<td>B</td>
<td>A</td>
</tr>
<tr>
<td>with TNPP</td>
<td>16.2</td>
<td>15.2</td>
<td>14.7</td>
<td>13.0</td>
<td>16.6</td>
<td>14.7</td>
<td>14.7</td>
</tr>
<tr>
<td>w/o TNPP</td>
<td>15.7</td>
<td>--</td>
<td>14.7</td>
<td>11.5</td>
<td>16.6</td>
<td>14.7</td>
<td>14.7</td>
</tr>
</tbody>
</table>
Figure 2. AREAS AND YIELD OF RUBBER IN THE PHILIPPINES (1980-1995)
Figure 3  Dose Response Curves of the Philippine NRL
Figure 4. Thermal degradation curve of INRI at different doses
Figure 5. Thermal degradation rate of INRL at different doses
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Figure 7: Tensile Strength of INRL with Storage Time
Figure 8  Crosslinking Density of INRL with Storage Time
STUDY OF VIETNAM LATEX FOR RADIATION VULCANIZATION

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Abstract
Radiation vulcanization of 6 different centrifuged latexes was studied. Sensitiser was n-BA of 5 phr and irradiation was carried out on gamma Co-60 source at 12kGy, dose rate 3.4kGy/h. Viscosity of latex and tensile strength of rubber films were measured. Result showed that the stability of LA type latex against the addition of n-BA was better than that of HA. Of 6 concentrated latexes studied, only two were suitable for radiation vulcanization process regarding tensile strength and stability.

INTRODUCTION
The advantages of radiation vulcanization natural rubber latex (RVNRL) were reported elsewhere (Makuuchi 1990, 1993; Wan manshol et al. 1995). However, some of the commercially available centrifuged NR latexes are not suitable for RV process due to low stability against the addition of sensitiser n-Butyl acrylate (n-BA) and low tensile strength of vulcanisate. For this reason, selection of centrifuged NR latexes and/or development of new ones that give consistent properties after radiation vulcanization is of great importance. This paper describes radiation vulcanization results of 6 different centrifuged latexes in Vietnam.

EXPERIMENTAL
Natural rubber latexes were commercially available HA 1: HA 2, double-centrifuged HA (DC-HA) and LA-TZ. Highly stable HA (HS-HA) and highly stable LATZ (HS-LA) centrifuged latex was produced follow the procedure recommended by the Sri Lanka Research Group (Nadarajah 1991). All natural rubber latexes studied have the MST value of 900-1200s and VFA No. of 0.01-0.03. Latex formulation and rubber films preparation were adopted as described elsewhere (Wan Manshol et al. 1995). Irradiation was carried out by gamma Co-60 source for the dose of 12kGy, dose rate of 3.4kGy/h. Volumetric swelling ratio (Q) was measured using benzene as solvent (Parinya and Makuuchi, 1990) and viscosity of latex was checked with the standing time before and after irradiation by Brookfield Viscometer Model RTV, Spindle 1. Tensile strength (Tb) was measured according to national standard (TCVN 1592-87).
RESULTS AND DISCUSSIONS

Table 1 shows that the Tb of films vulcanisates is not appropriate to the Q value. This could partly be due to random distribution of either grafted or crosslinking bridge poly (n-BA) to rubber molecules. HS-LA and DC-HA gives the highest and the lowest Tb respectively.

<table>
<thead>
<tr>
<th>Latex</th>
<th>Tb. kg/cm²</th>
<th>Q</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA1</td>
<td>220</td>
<td>6.94</td>
</tr>
<tr>
<td>HA2</td>
<td>250</td>
<td>6.88</td>
</tr>
<tr>
<td>DC-HA</td>
<td>180</td>
<td>6.55</td>
</tr>
<tr>
<td>HS-HA</td>
<td>240</td>
<td>6.14</td>
</tr>
<tr>
<td>LA-TZ</td>
<td>205</td>
<td>7.56</td>
</tr>
<tr>
<td>HS-LA</td>
<td>260</td>
<td>7.32</td>
</tr>
</tbody>
</table>

It was observed in Table 2 that the viscosity of DC-HA, LA-TZ and HS-LA was fairly stable. After irradiation, the viscosity of HA1 and HS-HA increased steadily from 20cP to about 40cP. HA2 showed the poor stability. It was also seen in Table 2 that the stability of LA latex type against the addition of sensitizer n-BA was better than that of HA except DC-HA

<table>
<thead>
<tr>
<th>Storage (hrs)</th>
<th>VISCOSITY (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>HA1 before irr.</td>
<td>16</td>
</tr>
<tr>
<td>HA1 after irr.</td>
<td>20</td>
</tr>
<tr>
<td>HA2 before irr.</td>
<td>23</td>
</tr>
<tr>
<td>HA2 after irr.</td>
<td>27</td>
</tr>
<tr>
<td>DC-HA before irr.</td>
<td>17</td>
</tr>
<tr>
<td>DC-HA after irr.</td>
<td>17</td>
</tr>
<tr>
<td>HS-HA before irr.</td>
<td>17</td>
</tr>
<tr>
<td>HS-HA after irr.</td>
<td>20</td>
</tr>
<tr>
<td>LA-TZ before irr.</td>
<td>18</td>
</tr>
<tr>
<td>LA-TZ after irr.</td>
<td>19</td>
</tr>
<tr>
<td>HS-LA before irr.</td>
<td>17</td>
</tr>
<tr>
<td>HS-LA after irr.</td>
<td>17</td>
</tr>
</tbody>
</table>

From the results given in Table 1 and Table 2 it can be concluded that among the latexes studied, HS-HA and HS-LA were most suitable for RV as regards tensile strength and viscosity stability. Further study is still needed to develop new type of centrifuged NR latex that is typical for RV, for example medium ammonia preserved latex or new HS-LA latex (Nadarajah 1991).
CONCLUSION

The behaviour of centrifuged NR latex to RV can be preliminarily tested by measuring the Tb of vulcanisate and the viscosity of irradiated latex at dose of around 12 kGy. Of 6 different latex studied, only two namely HS-HA and LS-LA that newly produced follow modified procedures can be used for RV.

ACKNOWLEDGEMENT

The authors wish to thank the Director of the Nuclear Research Institute Dalat, Dr. Tran Ha Anh for permission and encouragement to conduct this research work. The authors would like also to appreciate the contributions of the scientists and co-workers at the Binhlong Rubber Company, the Dongnai Rubber Company and the Rubber Research Institute of Vietnam.

REFERENCES


STUDY ON IRRADIATION CONDITION IN RADIATION VULCANIZATION OF NATURAL RUBBER LATEX

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ABSTRACT

The effect of γ-rays irradiation dose rates on RVNRL preparation was studied using Malaysian latex added with 0.2 phr of KOH and 5 phr of n-BA. The results showed, to ensure the tensile strength of the latex film meet the requirement, when applying vulcanisation doses, Dv of 20 kGy 20 and 15 kGy, irradiation dose rates should not be greater than 0.49 kGy/hr and 1.6 kGy/hr respectively. Its was found that within the storage time of 20 days there was no change in the physical properties of the latex films.

INTRODUCTION

RVNRL aims to produce the latex products with low proteins and free from nitrosamines. Research studies on RVNRL started in 1960's. It was not until 1980's that the commercialisation on RVNRL was made possible when the cost of its production was reduced to an acceptable value following the improvement in its formulation.

The purpose of this experiment was to investigate the effects of irradiation dose rates and storage time on the physical properties of RVNRL films.

EXPERIMENTAL METHOD

Materials

Industrial grade n-BA, analytical grade KOH supplied by Wako Junyaku Chemical Co. Ltd. and commercially available high ammonia natural rubber latex (IOTEX DRC 60%) from Malaysia were used in the radiation vulcanization studies.

Preparation of RVNRL

The latex of 60% drc was first diluted to 50% drc using 1% ammonia solution. It was then followed by the addition of 0.2 phr of KOH and 5 phr of n-BA with continuous stirring. After the addition of the stabiliser and sensitisier, the stirring was continued for another half an hour before the latex was irradiated to the required dose at a known dose rate using γ-rays from Cobalt-60 source.
The Preparation of RV Latex Film

The films were prepared by casting RV latex on a glass plate (12x18 cm²). The films thickness were about 0.8 mm. The films were left to dry in air at 25°C until transparent before they were leached in 1% ammonia solution for 24 hours. At the end of leaching period the films were washed with distilled water and left to dry at room temperature until transparent before they were finally heated in an oven at 70°C for an hour. The films were then cut into dumbbell shape and conditioned at 25°C over night before they were subjected to tensile test measurements.

Physical Properties Test

The dumbbell shaped test pieces were measured for the tensile strength (TB) and elongation at break (EB) using tensile machine.

RESULTS AND DISCUSSIONS

Effect of Dose on RVNRL

Figure 1 shows the effect of irradiation dose on TB of the RVNRL films irradiated at dose rate of 5 kGy/hr. The TB rapidly increased to a maximum value of 27.9 MPa at an irradiation dose of 20 kGy before it started to decrease again. Whereas the EB remained constant up to an irradiation dose of 10 kGy before it started to decrease when the samples were irradiated to higher doses. Though the mechanical properties of RVNRL seems to be influenced by irradiation dose, however, within the dose range employed the properties still met the requirement (TB > 24 MPa, EB of 700%). From the results, it seems that the optimum dose of vulcanisation, Dv was in the range of 15 - 20 kGy.

![Figure 1: Effect of dose on mechanical properties of RVNRL film.](image-url)
2. Samples with 0.2 phr of KOH and 4.5 phr of n-BA were irradiated to 20 kGy at different dose rates. Results are shown in Figure 2. It is shown that, the higher the dose rate the better were the properties of RVNRL films. TB and EB increased with the increased in irradiation dose rate. At the point of required TB (24 MPa), the dose rate was 0.49 kGy/hr. This was the critical dose rate for Dv of 20 kGy.

Results of similar trend were obtained for Dv of 15 kGy. This is shown in Figure 3. However, the critical dose rate had increased to 1.6 kGy/hr.

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Figure 2: Effect of dose rate on mechanical properties of RVNRL film (Dose: 20 kGy)

Figure 3: Effect of dose rate on mechanical properties of RVNRL film (Dose: 15 kGy)
Wan Manshol et al. reported on the effect of standing time on the properties of RVNRL films. He found that extended standing times reduced the mechanical properties of the RVNRL films. It was probably due to the hydrolysis of n-BA in alkaline latex. Especially in the condition of low dose rate, longer irradiation time was needed to reach the optimum vulcanization dose, this was because the hydrolysis of n-BA got more obvious and its content was reduced. Thus the film properties were poor.

These results suggest that for commercial production of RVNRL, the dose rate must be greater than the critical value.

**Effect of Storage Time on RVNRL**

Figure 4-7 were the results of TB and EB evaluated on RVNRL stored for 0, 2, 5, 10 and 20 days. It seems that within the storage times employed in the studies, there were no significant effect on TB and EB of the samples. In contrast, it was reported elsewhere there were cases where RVNRL showed an increased in TB and EB with storage times.

![Figure 4: Relationship between storage time and TB of RVNRL film (Dose: 20 kGy)](image-url)
Figure 5: Relationship between storage time and EB of RVNRL film (Dose: 20 kGy)

Figure 6: Relationship between storage time and TS of RVNRL film (Dose: 15 kGy)
4. Effect of Lower Dose Rate on RVNRL

Figure 8 shows the relationship of TB and EB to irradiation dose for RVNRLs prepared at an irradiation dose rate of 0.21 kGy/hr. It is shown that within the irradiation dose range employed 10-35 kGy, the TB and EB could not meet the requirement. At the maximum irradiation dose of 35 kGy, the TB and EB were only 12.3 MPa and 687 % respectively. This means to prepare RVNRL of higher mechanical properties, the irradiation should be carried out at higher dose rate.

Figure 8: Effect of dose on the mechanical properties of RVNRL film under low dose rate irradiation
CONCLUSION

1. For the latex formulated with KOH as the stabiliser and n-BA as the sensitiser, vulcanisated at the dose of 15 and 20 kGy, the critical dose rates were 1.6 kGy/hr and 0.49 kGy/hr respectively.

2. There was no change in the mechanical properties of RVNRL stored up 20 days.

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This paper was completed in Takasaki Radiation Chemistry Research Establishment when I was there as a visiting scientist. I hereby thank Dr. K. Makuuchi and F. Yoshii for their helpful instruction.

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DEVELOPMENT OF AN EFFICIENT PROCESS FOR RADIATION VULCANIZATION OF NATURAL RUBBER LATEX USING HYDROPEROXIDE WITH SENSITIZERS

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Abstract
An attempt was made to reduce radiation dose for radiation vulcanization of natural rubber latex. One of the best methods found was to co-vulcanize the latex using partial radiation vulcanization at 4 kGy with 5 phr n-butyl acrylate as sensitizer and 0.1 phr t-butyl hydroperoxide (BHPO) as co-sensitizer followed by redox vulcanization using either 4 phr fructose at temperature of 60°C for 3 hours or 0.2 phr BHPO and 0.4 phr tetra-ethylene pentamine (TEPA) at room temperature for 1 hour. The rubber films obtained had tensile strength of about 25 MPa, modulus 300% of 0.9 MPa and cross link density of about 1.5x10¹⁹ crosslink/cm³. It was noted that the crosslink density of rubber films from the co-vulcanization was the average value of the values obtained by radiation vulcanization and redox vulcanization.

INTRODUCTION
Radiation dose for radiation vulcanization of natural rubber latex is normally 12-25 kGy using 5 phr of n-butyl acrylate (n-BA) as sensitizer (Makuuchi 1985, Gazeley 1990). Several studies had been made to reduce the vulcanization dose by using polyfunctional monomers as sensitizer (Makuuchi 1984) using hydrogen peroxide as additive (Yanti 1990) using hydroperoxides as co-sensitizer (Parinya 1990). Vulcanization dose could be reduced somewhat by using hydrogen peroxide or hydroperoxide with some improvement of the tensile strength of the rubber films. Polyfunctional monomers although reduce the vulcanization dose to the lowest value, its toxicity inhibit the practical use. The present study intends to prepare radiation vulcanized latex with low vulcanization dose by partial crosslink via irradiation at a certain radiation dose with n-BA and t-butyl hydroperoxide (BHPO) and bring to full vulcanization by redox process.

EXPERIMENTAL
Materials
HA latex was from Jana Co.Ltd. Thailand. n-BA was technical grade from Formosa Plastic Co. Ltd. BHPO, fructose and tetra-ethylene pentamine (TEPA) were Purum grade from Fluka. The latex was diluted with 1% NH₃ solution to 50% DRC. 2 phr of 10% KOH solution was added as stabilizer and finally 0.1 phr of BHPO and 5 phr of n-BA were added and mixed by a magnetic stirrer for one hour before irradiation.
Irradiation

The mixture was irradiated in Gamma Cell 220 (Nordian International Co.) 16 kCi of Co-60 at a dose rate of 15 kGy per hour.

Combination of radiation and peroxide pre-vulcanization (co-vulcanization)

Peroxide prevulcanization formulation with fructose was adapted from Azemi, 1993 and with TEPA was adapted from Iskandar, 1994. The mixture after irradiation at 4 kGy was added with 1-4 phr fructose (20% fructose in water) and heated at 60 °C for 3 hours. Same procedure was repeated using 0.1-0.4 phr of TEPA but without heating and stand for 1 hour.

Determination of crosslink density

Crosslink density of the rubber film was determined by swelling ratio method based on Flory and Rehner equation:

\[ V_o = K \times Q^{5/3} \]

\[ V_v \] = crosslink density, C.L./mL
\[ K \] = 3.39 x 10^{20} for toluene/NR system
\[ Q \] = volume swelling ratio

RESULTS AND DISCUSSION

Figure 1 shows relationship between dose and properties of rubber film prepared from latex irradiated with 5 phr n-BA, 0.1 phr BHPO. It is noted that at maximum tensile strength, the crosslink density of the rubber film is approximately 2.0x10^{19} C.L./mL. The optimum dose or the vulcanization in this case is 8 kGy.

![Figure 1: Crosslink density and tensile strength of rubber films at different doses](image-url)
Table 1 shows a typical latex prevulcanization experiment using 5 phr n-BA, 0.1 phr BHPO and 4 phr fructose at 60 °C. The crosslink density at maximum tensile strength is $1.13 \times 10^{19}$ C.L./mL, somewhat lower than that of from RVNRL. This seems to agree with an earlier work if compared to that of from sulphur-prevulcanized latex (Ma’zam Md Said, 1990).

<table>
<thead>
<tr>
<th>prevulcanization time (hour)</th>
<th>$T_b$ (MPa)</th>
<th>$E_b$ (%)</th>
<th>C.L./mL x $10^{19}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>9.16</td>
<td>912</td>
<td>0.808</td>
</tr>
<tr>
<td>2</td>
<td>8.39</td>
<td>759</td>
<td>1.035</td>
</tr>
<tr>
<td>4</td>
<td>13.27</td>
<td>849</td>
<td>1.089</td>
</tr>
<tr>
<td>6</td>
<td>16.66</td>
<td>790</td>
<td>1.141</td>
</tr>
<tr>
<td>8</td>
<td>15.03</td>
<td>712</td>
<td>1.147</td>
</tr>
</tbody>
</table>

Table 2 shows results of latex co-vulcanization using 5 phr n-BA as sensitizer, BHPO as co-sensitizer and as an oxidant for the redox process with 1-4 phr fructose after irradiation at 4 kGy. The maximum $T_b$ of the rubber films was achieved at concentration of 0.1 phr BHPO with 4 phr fructose. The crosslink density at highest $T_b$ fall between the values obtained by RVNRL and peroxide prevulcanization.

<table>
<thead>
<tr>
<th>BHPO (phr)</th>
<th>fructose (phr)</th>
<th>$T_b$ (MPa)</th>
<th>Modulus (MPa)</th>
<th>$E_b$ (%)</th>
<th>C.L./mL x $10^{19}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.1</td>
<td>22.78</td>
<td>0.908</td>
<td>7.438</td>
<td>773.5</td>
</tr>
<tr>
<td>0.2</td>
<td>0.2</td>
<td>22.21</td>
<td>0.939</td>
<td>7.712</td>
<td>762.1</td>
</tr>
<tr>
<td>0.3</td>
<td>0.3</td>
<td>21.34</td>
<td>0.889</td>
<td>6.871</td>
<td>774.4</td>
</tr>
<tr>
<td>0.4</td>
<td>0.4</td>
<td>25.36</td>
<td>0.891</td>
<td>6.645</td>
<td>774.3</td>
</tr>
</tbody>
</table>

Table 3 shows results of latex co-vulcanization using 5 phr n-BA, BHPO at dose of 4 kGy followed by redox pre-vulcanization using fructose at 60 °C for 3 hours.

<table>
<thead>
<tr>
<th>BHPO (phr)</th>
<th>TEPA (phr)</th>
<th>$T_b$ (MPa)</th>
<th>Modulus (MPa)</th>
<th>$E_b$ (%)</th>
<th>C.L./mL x $10^{19}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.1</td>
<td>16.0</td>
<td>0.949</td>
<td>8.732</td>
<td>705.2</td>
</tr>
<tr>
<td>0.2</td>
<td>0.2</td>
<td>18.69</td>
<td>1.417</td>
<td>7.976</td>
<td>728.2</td>
</tr>
<tr>
<td>0.3</td>
<td>0.3</td>
<td>19.54</td>
<td>0.747</td>
<td>4.751</td>
<td>785.4</td>
</tr>
<tr>
<td>0.4</td>
<td>0.4</td>
<td>22.03</td>
<td>0.788</td>
<td>5.974</td>
<td>781.6</td>
</tr>
</tbody>
</table>

Table 3 shows results of latex co-vulcanization using 5 phr n-BA, BHPO irradiation at 4 kGy followed by redox vulcanization with TEPA at room temperature for 1 hour.

The maximum $T_b$ of the rubber film was achieved at concentration of 0.2 phr BHPO with 0.4 phr TEPA.
Table 4 shows the tests for tear strength according to JIS 6301 and trouser tear strength according to ASTM D 624R of rubber films from RVNRL, peroxide pre-vulcanization and co-prevulcanization. Tear strength of the films from three methods of prevulcanization are not different but the trouser tear strength of the films from co-prevulcanization shows much improvement when compared to that of from RVNRL.

Table 4: Results of tests for tear strength (JIS 6301) and trouser tear strength (ASTM D 624R) of rubber films from RVNRL, peroxide pre-vulcanization and co-prevulcanization.

<table>
<thead>
<tr>
<th>Means of prevulcanization</th>
<th>Tear strength kN/m</th>
<th>Trouser tear strength N/mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>RVNRL</td>
<td>22.45</td>
<td>5.76</td>
</tr>
<tr>
<td>Peroxide</td>
<td>22.58</td>
<td>13.48</td>
</tr>
<tr>
<td>Co-vulcanization</td>
<td>21.24</td>
<td>14.60</td>
</tr>
</tbody>
</table>

CONCLUSION

From the experiment results, it can be concluded that a combination of radiation vulcanization and peroxide vulcanization is effective. The radiation dose can be reduced to a much lower value when compared to RVNRL. The maximum tensile strength of the film from co-vulcanization increased slightly and there was much increasing of the trouser tear strength of the film. The trouser tear strength and the maximum tensile strength that increased may result from the more monogeneity of the vulcanization from the two prevulcanization processes.

REFERENCES


THE EFFECT OF LACTAMIN ON THE CHARACTERISTICS OF RVNRL FILMS IN THE PRESENCE OF N- BUTYL ACRYLATE

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ABSTRACT

The utilization of lactamin (pepton) and n-butyl acrylate (n-BA) as a sensitizer system for radiation vulcanized natural rubber latex (RVNRL) was studied. The concentration of 0.2 phr (parts of hundred rubber) of lactamin and 5 phr of n-BA was suitable for RVNRL. Effects of the concentrations of lactamin and irradiation doses on tensile strengths of RVNRL films were investigated. Relationships between swelling ratios and the concentrations of lactamin, the irradiation doses were determined. The swelling ratios drop sharply while irradiation doses increase with using a combination of 0.2 phr of lactamin and 5 phr of n-BA in comparison with 5 phr of only n-BA. In addition, a determination of nitrogen content of RVNRL films, which contained lactamin, was carried out after the films leached in soap water. The effect of residual nitrogen content on allergicability of the RVNRL films is negligible and permits of the industrial applications in production of health care products, such as catheters, gloves,...It was revealed that the optimum vulcanization dose of RVNRL films can reduce from 18 kGy for utilizing only 5 phr n-BA to 13 kGy for using the combination of the 5 phr n-BA and the 0.2 phr lactamin.

INTRODUCTION

It was indicated that protein content in the latex effects on the radiation vulcanization dose of natural rubber latex (NRL). The maximum tensile strength increases with raising nitrogen content in the latex. About 0.12-0.18 % casein added is suitable to attain a maximum tensile strength (Chyagrit et al.1990). Protein and some amino-acids forwards some improvements in properties such as modulus, stress-relaxation,... if compared with purified natural rubber (Othman et al.1988). The cover of linked protein layers around the rubber particles is considered as an unchangeable condition for the stability of the rubber particles (Nadarajah 1991). It was understood that the tensile strength of deproteinized latex vulcanized by radiation was very low in comparison with the once-centrifuged, double-centrifuged, triple-centrifuged, creamed latexes (Norjanah et al.1990). It was reported that the allergicability of protein in dried latex films vulcanized by radiation was negligible (Binh et al. 1996).

This paper presents the ability of extra-acceleration of lactamin, nontoxic broken protein, for radiation vulcanized process of NRL in the presence of n-BA sensitizer.
PROCEDURE

Material and methods

A high ammonia type centrifuged NRL was supplied by Binhlong Co., Vietnam. NRL was diluted by 1% ammonia solution. Benzene, n-BA, lactamin, KOH were of analytical grade. All chemicals was used without further purification. Diluted latex (53% TSC) was added with 0.2 phr of 10% KOH while stirring together with 5 phr of n-BA for 30 minutes.

Effect of lactamin concentration

The latex was mixed up 10% lactamin in 1% ammonia at different concentrations (0, 0.05, 0.1, 0.15, 0.2, 0.5, 1.0 phr). The latex was stored 1 hr at room temperature. The prepared latex was irradiated in the gamma source (3.3 kGy/hr) at an irradiation dose of 10 kGy. RVNRL was cast on glass plates, dried at ambient temperature, leached in soap water, powdered, redried, and heated at 80°C for 1 hr. 0.1g sample pieces were immersed in benzene for 48 hrs to determine swelling ratio.

Effect of irradiation dose on the tensile strength, elongation at break, and swelling ratio

Procedures prepared were the same item “material and methods” in which 0.2 phr of 10% lactamin was used. The latex was irradiated at 0, 5, 10, 15, 20, 25 kGy. RVNRL films were obtained as above. The physical properties were measured with a Tensile Tester FY-15/D (Hungary) according to TCVN-84 national standard. About 0.1g of the films was put into benzene for 48 hrs to measure swelling ratio.

Relation between irradiation dose and remain nitrogen content in the RVNRL films

The remain nitrogen in the RVNRL films was analyzed by micro-Kjeldhal method.

RESULTS AND DISCUSSION

Figure 1 shows effect of various concentrations of lactamin on swelling ratios and tensile strength of RVNRL films at an irradiation dose of 10 kGy. It was indicated that at a 0.2 phr concentration of lactamin, the lowest swelling ratio of around 7.29 can be obtained. The lactamin concentration is higher than 0.2 phr, adverse effect of crosslinking can be incurred. The reason to explain this is that lactamin content higher than 0.2 phr might form a very thick cover of protein around rubber particles; subsequently penetration of n-BA molecules into crosslinking reaction centers of rubber particles is very difficult. At that time hydrogen links can occur between n-BA molecules and functional groups of lactamin. Otherwise, at the same concentration of lactamin, the maximum tensile strength of the RVNRL film is about 17-18 MPa for an irradiation dose of 10 kGy as shown in Fig. 1.
Figure 1. Effect of various concentrations of lactamin on swelling ratios and Tb of RVNRL films, 10 kGy

Figure 2 indicates changes of tensile strength and elongation at break of RVNRL films with or without 0.2 phr lactamin in irradiation doses. In the presence of 5 phr n-BA and 0.2 phr lactamin, the tensile strength can be attained 27-28 MPa with shortening the irradiation dose from 18 kGy to 14 kGy and there is no remarkable change in Eb if compared with using only 5 phr n-BA.

Figure 2. Changes of Tb and Eb of RVNRL films with or without 0.2 phr lactamin, 5 phr n-BA

It was found that the extra-crosslinking role of lactamin is extremely important in Fig. 3 shown that the swelling ratio drops sharply when 0.2 phr lactamin is used.
Figure 3. The swelling ratio of RVNR films versus irradiation dose.

Figure 4 shows the relationship between the remain nitrogen content and the irradiation dose. The remain nitrogen content in dried RVNR films leached reduces with increasing the irradiation dose. The retaining content of nitrogen of the film irradiated at 15 kGy is about 0.206% like that without adding lactamin (0.205%).

Figure 4. Relationship between the remain nitrogen content and the irradiation dose.
CONCLUSION

The RVNRL using 5 phr n-BA and 0.2 phr lactamin is a practical application both to reduce the irradiation dose and to obtain a desired physical property. The RVNRL film gives a tensile strength of 27 MPa, a elongation at break of 950%, a swelling ratio of 6.5, and a remain nitrogen content of 0.206% at an irradiation dose of about 13 kGy.

REFERENCES


THE EFFECT OF LATEX MATURITY ON THE ABSORBED DOSE FOR PREPARING RVNRL OF OPTIMUM TENSILE STRENGTH

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Malaysia

ABSTRACT

This paper presents the results of the studies on the effects of using latex of different maturity periods, between 0 to 15 weeks on gamma irradiation dose required to prepare RVNRL of optimum tensile strength. Absorbed dose to prepare RVNRL of optimum tensile strength, molecular weight between cross-links and cross-link density were found to be influenced by the maturity of the latex used in the studies. With respect to optimum tensile strength and absorbed dose, latex of about six weeks maturity was found most suitable and economical for radiation vulcanization process. Using latex either with or without added secondary preservative the optimum tensile strength was determined at an absorbed of 8 kGy. However, the optimum tensile strength of RVNRL prepared from latex contained added secondary preservative was found to be higher than the optimum tensile strength of RVNRL prepared from latex without secondary preservative.

INTRODUCTION

In previous paper (Wan Manshol et al., 1993), it was reported how the time lapse between the latex formulation stage and irradiation stage may affect the efficiency of the sensitizer used in vulcanization process. Where it was found that any time lapse of more than two days, higher irradiation dose was required to prepare RVNRL of optimum tensile strengths.

Through observation, it was noticed that there were some differences in the mechanical properties of RVNRL film vulcanisates as an effect of its preparation using latex initially stored for different periods. To confirm the observation, studies on the influence of latex maturity periods on the absorbed dose required for preparing RVNRL of optimum tensile strength were carried out. The results are discussed in this paper.

MATERIALS AND METHODS

Materials

The high ammonia natural rubber latex used in this studies was obtained from Kumpulan Guthrie Berhad (with and without added secondary preservative).

Prior to the studies, the latex was analysed for its total solid content (t.s.c.), dry rubber content (d.r.c.), MST, pH and viscosity. Their methods of determinations were as previously described (Wan Manshol, W.Z., 1995a). Other materials involved were similar to those described in the previous report.
Methods

Freshly prepared latex concentrate was formulated for RVNRL preparation according to the method as previously described (Wan Manshol et al., 1993; Wan Manshol et al., 1995b). The latex mixture was placed into one-litre screw-capped bottles and irradiated with γ-rays from cobalt-60 source for six different absorbed doses ranging from 8 kGy to 30 kGy. After irradiation at which stage the latex is called RVNRL was tested and evaluated for their properties. Using the same batch of latex, the studies were repeated at three weekly intervals. The studies were carried out using latex contain no added secondary preservative and latex contained added secondary preservative.

PROPERTIES OF RVNRL

The RVNRL were analysed for their physical properties like t.s.c, d.r.c, viscosity, MST and pH. The technique of analysing the samples were as previously described (Ibid).

Mechanical properties were determined on RVNRL film vulcanisates prepared by coagulant dipping method. RVNRL films vulcanisates were leached in distilled water overnight at room temperature, followed by drying at room temperature before the films were given heat treatment in an air convection oven at 70 °C for an hour. RVNRL films vulcanisates were cut into five dumb bell-shaped test pieces according to BS 6746. The properties of the vulcanisates were determined as per relevant ASTM standards.

Cross-link density of the film vulcanisates were determined by swelling measurements method. From each film vulcanisates, three specimens of approximately 3 mm side were cut. The specimens were weighed and immerse in hexane at 25 °C until swollen to equilibrium. Removed from hexane, the samples were dried with filter paper and transferred into weighing bottles and reweighed. Finally, the samples were deswelled under vacuum at 50 °C to a constant weight. The difference between the swollen and deswelled weights gave the weight of hexane absorbed. From knowledge of the density of rubber and hexane at 25 °C, the volume of rubber rubber and of solvents were calculated and the swelling ratio were determined. Using the Flory-Rehner equation, the molecular weight between cross-links and hence cross-link density were calculated.

RESULTS AND DISCUSSIONS

The properties of RVNRL prepared using latex contained no secondary preservative and the properties of RVNRL prepared using latex contained secondary preservative are summarised in Table 1 and Table 2 respectively.

<table>
<thead>
<tr>
<th>Absorbed Dose, kGy</th>
<th>0.00</th>
<th>8.34</th>
<th>10.60</th>
<th>13.51</th>
<th>15.39</th>
<th>22.60</th>
<th>28.90</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total solid content (t.s.c.), %</td>
<td>53.90</td>
<td>51.60</td>
<td>52.40</td>
<td>52.00</td>
<td>53.00</td>
<td>52.40</td>
<td>52.90</td>
</tr>
<tr>
<td>Dry rubber content (d.r.c), %</td>
<td>50.00</td>
<td>50.80</td>
<td>51.07</td>
<td>51.00</td>
<td>51.40</td>
<td>51.60</td>
<td>50.90</td>
</tr>
<tr>
<td>Viscosity, cps</td>
<td>44.60</td>
<td>30.50</td>
<td>29.08</td>
<td>27.80</td>
<td>27.00</td>
<td>25.00</td>
<td>25.00</td>
</tr>
<tr>
<td>MST, s</td>
<td>1275</td>
<td>2692</td>
<td>2361</td>
<td>2428</td>
<td>2698</td>
<td>2565</td>
<td>2916</td>
</tr>
<tr>
<td>pH</td>
<td>10.16</td>
<td>10.29</td>
<td>10.23</td>
<td>10.18</td>
<td>10.25</td>
<td>10.27</td>
<td>10.26</td>
</tr>
<tr>
<td>Tensile strength, MPa</td>
<td>3.63</td>
<td>25.31</td>
<td>24.46</td>
<td>22.57</td>
<td>22.41</td>
<td>16.36</td>
<td>17.79</td>
</tr>
<tr>
<td>Modulus @ 500 % Elongation</td>
<td>0.44</td>
<td>2.06</td>
<td>2.17</td>
<td>2.84</td>
<td>3.10</td>
<td>3.12</td>
<td>2.95</td>
</tr>
<tr>
<td>Modulus @ 700 % Elongation</td>
<td>1.38</td>
<td>6.92</td>
<td>6.99</td>
<td>7.16</td>
<td>10.85</td>
<td>11.21</td>
<td>11.10</td>
</tr>
<tr>
<td>Elongation at break, %</td>
<td>1120</td>
<td>1100</td>
<td>1060</td>
<td>1020</td>
<td>1000</td>
<td>840</td>
<td>860</td>
</tr>
</tbody>
</table>
Figure 1: Effect of absorbed dose on the tensile strength of RVNRL film vulcanisates using latex contained no added secondary preservative.

Figure 2: Effects of absorbed dose on the modulus at 700% elongation of RVNRL film vulcanisates prepared using latex contained no added secondary preservative.
From Table 1.0 and Table 2.0, it seems that the physical properties of RVNRL, for example t.s.c., d.r.c., MST, viscosity, pH were not significantly affected by the changes in the absorbed dose. This was shown by both samples, whether it was prepared from the latex contained added secondary preservative or without secondary preservative.

In contrast, the mechanical properties of RVNRL film vulcanisate were determined by the absorbed dose. The typical effects of absorbed dose on the tensile strengths of RVNRL film vulcanisates are given in Figure 1 and Figure 4. As shown in these figures, with increasing absorbed dose the tensile strengths goes through a maximum before decreasing.

The moduli at 700 % elongation increases with absorbed dose, refer to Figure 2 and Figure 5. On the contrary, the elongation at break decreases with absorbed dose, refer to Figure 3 and Figure 6.

Table 2: Properties of RVNRL prepared using latex contained added secondary preservative.

<table>
<thead>
<tr>
<th>Absorbed Dose, kGy</th>
<th>0.00</th>
<th>8.34</th>
<th>10.60</th>
<th>13.51</th>
<th>15.39</th>
<th>22.60</th>
<th>28.90</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total solid content (t.s.c.), %</td>
<td>52.80</td>
<td>52.50</td>
<td>54.00</td>
<td>52.80</td>
<td>53.10</td>
<td>52.10</td>
<td>53.00</td>
</tr>
<tr>
<td>Dry rubber content (d.r.c.), %</td>
<td>49.40</td>
<td>50.20</td>
<td>50.40</td>
<td>50.60</td>
<td>50.80</td>
<td>50.80</td>
<td>50.90</td>
</tr>
<tr>
<td>Viscosity, cps</td>
<td>60.50</td>
<td>33.40</td>
<td>32.30</td>
<td>31.30</td>
<td>31.80</td>
<td>31.50</td>
<td>30.70</td>
</tr>
<tr>
<td>MST, s</td>
<td>1296</td>
<td>1801</td>
<td>1849</td>
<td>1946</td>
<td>1974</td>
<td>1964</td>
<td>2028</td>
</tr>
<tr>
<td>pH</td>
<td>9.96</td>
<td>10.60</td>
<td>10.12</td>
<td>10.05</td>
<td>9.93</td>
<td>10.16</td>
<td>10.05</td>
</tr>
<tr>
<td>Tensile Strength, MPa</td>
<td>4.87</td>
<td>26.03</td>
<td>26.20</td>
<td>25.98</td>
<td>25.69</td>
<td>23.40</td>
<td>22.83</td>
</tr>
<tr>
<td>Modulus @ 500 % Elongation</td>
<td>0.58</td>
<td>1.78</td>
<td>1.93</td>
<td>2.08</td>
<td>2.38</td>
<td>2.47</td>
<td>2.81</td>
</tr>
<tr>
<td>Modulus @ 700 % Elongation</td>
<td>1.03</td>
<td>5.37</td>
<td>6.13</td>
<td>6.97</td>
<td>8.38</td>
<td>9.19</td>
<td>10.09</td>
</tr>
<tr>
<td>Elongation at Break, %</td>
<td>1110</td>
<td>1100</td>
<td>1120</td>
<td>940</td>
<td>910</td>
<td>890</td>
<td>850</td>
</tr>
</tbody>
</table>

Figure 3: Effects of absorbed dose on the elongation at break of RVNRL film vulcanisates prepared using latex contained no secondary preservative.
Figure 4: Effects of absorbed dose on the tensile strengths of RVNRL film vulcanisates prepared using latex contained added secondary preservative.

Figure 5: Effects of absorbed dose on modulus at 700 % elongation of RVNRL film vulcanisates prepared using latex contained added secondary preservative.
Table 3: The molecular weight between cross-links, $M_c$ and cross-link density, CLD of RVNRL film vulcanisates using latex of different maturity periods.

<table>
<thead>
<tr>
<th>Maturity Periods, Weeks</th>
<th>0</th>
<th>3</th>
<th>6</th>
<th>9</th>
<th>12</th>
<th>15</th>
</tr>
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<tbody>
<tr>
<td>Contained No Secondary Preservative</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molecular weight between cross-links, $M_c$ ($x 10^4$)</td>
<td>1.98</td>
<td>1.07</td>
<td>1.33</td>
<td>1.13</td>
<td>1.05</td>
<td>1.12</td>
</tr>
<tr>
<td>Cross-link density, CLD ($x 10^5$)</td>
<td>1.89</td>
<td>4.66</td>
<td>4.87</td>
<td>4.54</td>
<td>4.75</td>
<td>4.46</td>
</tr>
<tr>
<td>Contained Added Secondary Preservative</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molecular weight between cross-links, $M_c$ ($x 10^4$)</td>
<td>1.75</td>
<td>1.45</td>
<td>1.07</td>
<td>1.07</td>
<td>8.71</td>
<td>9.32</td>
</tr>
<tr>
<td>Cross-link density, CLD ($x 10^5$)</td>
<td>2.85</td>
<td>3.44</td>
<td>4.78</td>
<td>4.69</td>
<td>4.68</td>
<td>5.52</td>
</tr>
</tbody>
</table>

The estimated values of molecular weight between cross-links, $M_c$ and cross-link density determined on RVNRL film vulcanisates of optimum tensile strength prepared using latex of different maturity periods are given in Figure 7 and Figure 8. In general the molecular weight between cross-link decreases with storage period and cross-link density increase with maturity periods. However, more significant increased in cross-link density with latex maturity periods was shown by the RVNRL prepared using the latex contained added secondary preservative.

The effect of latex maturity periods on the absorbed dose to obtain RVNRL of maximum tensile strength is summarised in Table 4, and graphical representation of the result is given in Figure 10.
Figure 7: Effects of latex maturity periods on molecular weight between cross-links of RVNRL film vulcanisates.

Figure 8: Effects of latex maturity periods on cross-link density of their RVNRL films vulcanisates.
Table 4: Tensile strengths of film vulcanisates from RVNRL prepared by using latex at different latex maturity periods.

<table>
<thead>
<tr>
<th>Latex Maturity, Weeks</th>
<th>0</th>
<th>3</th>
<th>6</th>
<th>9</th>
<th>12</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Contained No Secondary Preservative</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Optimum dose, kGy</td>
<td>10.60</td>
<td>8.34</td>
<td>10.60</td>
<td>13.51</td>
<td>13.59</td>
<td>13.59</td>
</tr>
<tr>
<td>Tensile Strength, MPa</td>
<td>23.22</td>
<td>25.31</td>
<td>27.43</td>
<td>25.77</td>
<td>24.97</td>
<td>24.29</td>
</tr>
<tr>
<td><strong>Contained Added Secondary Preservative</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Optimum dose, kGy</td>
<td>10.60</td>
<td>10.60</td>
<td>8.34</td>
<td>8.34</td>
<td>15.39</td>
<td>14.15</td>
</tr>
<tr>
<td>Tensile Strength, MPa</td>
<td>25.46</td>
<td>26.60</td>
<td>30.47</td>
<td>28.55</td>
<td>25.75</td>
<td>23.18</td>
</tr>
</tbody>
</table>

Figure 9: Effects of latex maturity on the optimum tensile strength of their RVNRL film vulcanisates.

From figure 9, it seems that within the maturity periods studied the optimum tensile strength of RVNRL film vulcanisates are influenced by the maturity of the latex used in its preparation. With increasing maturity periods the optimum tensile strengths goes through a maximum before decreasing. Similar trends were shown by both sets of studies either using the latex free from secondary preservative or using the latex contained added secondary preservative. However, as shown in Figure 9 using latex contained added secondary preservative produces RVNRL of higher tensile strength.
Figure 10: Effects of latex maturity on absorbed dose for the optimum tensile strength of their RVNRL film vulcanisates.

From Figure 10, irradiation dose required to produce RVNRL of optimum tensile strength decreases with the latex maturity period before starts to increase again. Similar trend was shown by both sets of results, using the latex with no secondary preservative or using the latex with added secondary preservative. With respect to absorbed dose and the maximum tensile strength, within the maturity periods employed in the studies, latex of about six weeks maturity was found most suitable and economical for RVNRL preparation.

CONCLUSION

The results from this study show that in RVNRL preparation the absorbed dose for optimum tensile strength is influenced by the latex maturity.

Latex maturity seems to effect the optimum tensile strength of RVNRL film vulcanisates. At a fixed maturity period, the latex added with traces amount of secondary preservative seems to exhibit higher optimum tensile strength than the latex contain no added secondary preservative. For large scale RVNRL preparation using latex of the required dose and hence its production capacity.

REFERENCES


EFFECT OF HETEROGENEOUS DISTRIBUTION OF CROSSTLINK DENSITY ON PHYSICAL PROPERTIES OF RADIATION Vulcanized NR LATEX FILM

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Abstract 

Thus a study has been carried out to investigate the effect of particle to particle variation in crosslink density on physical properties of radiation vulcanized NR latex film. NR latex was irradiated in small bottle by γ-rays without vulcanization accelerator to provide latex rubber particles having homogeneous distribution of crosslink density. The doses were 30, 50, 100, 250, 300, 400, 500 and 600 kGy. Weight swelling ratio, gel fraction, tensile strength and elongation at break of the latex film from the mixed latex were measured. The vulcanization dose of this latex was 250 kGy. Then the two different latexes were mixed in a such way to adjust the average dose of 250 kGy to prepare a latex consisting of rubber particles having heterogeneous distribution of crosslink density. Tensile strength of the latex film was depressed by mixing. The reduction increased with increasing the decrease of gel fraction by mixing. However the reduction was not serious when the dose difference of two latexes was less than 200 kGy. 

INTRODUCTION 

The radiation vulcanization of NR latex in a big container by γ-rays without stirring leads to particle to particle variation in crosslink density. In other words, crosslink density of each particle differs according to the absorbed dose. Similar phenomena will occur in vulcanization by electron beams. The effect of the heterogeneous distribution of crosslink density among rubber particles in on the physical properties of NR latex film is interesting from basic science and application sides. This study can be performed only by means of radiation vulcanized NR latex. For instance solid crosslinked rubbers are unable to be blended homogeneously. Additional chemical crosslinking is unavoidable during film formation in sulfur vulcanized NR latex. In this paper radiation vulcanized NR latexes with various doses were mixed and their physical properties were evaluated to analyze the heterogeneous distribution of crosslink density among rubber particles.
EXPERIMENTAL

Materials and irradiation

A commercial high ammonia natural rubber latex (IOTEX dry rubber content, DRC 60%) from Malaysia exposed to γ-rays from Co-60 at a dose rate of 10 kGy/h in one liter plastic bottle. Irradiation doses were 30, 50, 100, 160, 250, 300, 400, 500 and kGy.

Blending of the irradiated latex

The following two series of blended latex were obtained.

(a) Blending two latexes with the same weight ratio, refereed as blended latex (1:1)

(b) Blending two latexes with the weight ratio so as to achieve 250 kGy of average dose, refereed as blended latex (250 kGy)

Measurements of physical properties

The film of about 0.7 mm thickness was prepared by casting about 20 g of latex onto a glass plate (12X18 cm). The films were dried in air at room temperature (about 20°C) until they became transparent and then immersed in 1 % aqueous ammonia solution (leaching) for 24 hours followed by drying at room temperature until transparent. Subsequently, the films were heated at 80°C for an hour. After cooling, the films were cut to dumbbell shape and conditioned at 20°C over night in a desiccator. The tensile strength of film was measured according to JIS K 6301 with Strograph-R1 tension meter (Toyoseiki Co. Ltd.). Gel fraction and was measured by the weight change after boiling the disk (φ 20 mm) of the film in toluene for 24 hours. An antioxidant (TNPP) was added to toluene to prevent oxidative degradation during boiling. Weight swelling ratio was measured by the weight increase of the dry gel after soaked in toluene for 24 hours. Number average molecular weight of chains between crosslinks was calculated from the data of weight swelling ratio.

RESULTS AND DISCUSSIONS

Mechanical properties of blended latex

Tensile strength (Tb), elongation at break (Eb), gel fraction (Gel), weight swelling ratio (Sw) and number average molecular weight of chains between crosslinks (Mc) were plotted against the dose in Figures 1 - 5, respectively. The optimum dose for the NR latex used in this experiment is around 250 kGy. Generally the Tb of blended latex (1:1) deviated from a plot of Tb of non-blended original latex. The deviation of the Tb of the blended latex (250 kGy) was more remarkable than the Tb of blended latex (1:1). These were also
observed in Gel, Sw and Mc. However, negligible deviation was detected in plot of Eb against dose.

From these results it can be concluded that the physical properties of the blended latex can not be predicted by the absorbed average dose. Also it is clear that the blending of high and low quality latexes can improve the physical properties of low quality latex.

**Optimum gel fraction and swelling ratio**

Tb was plotted against Gel and Sw in figures 6 and 7, respectively, to estimate the optimum gel fraction and swelling ratio to achieve high tensile strength. Even the blended latex (250 kGy) high Tb can be achieved if Gel is around 96% and Sw is within 600 - 700%.

**Effect dose difference in blended latex**

Two latexes irradiated to lower and higher dose than 250 kGy were mixed so as to attain the average dose of 250 kGy. Physical properties of the blended latex differ, even the average dose is the same. Figure 8 shows the effect of higher dose on Tb. The Tb decreases with increasing higher dose. This means that Tb decreases with increasing the dose difference between lower and higher dose.

**Improvement of physical properties by blending**

Table 1 shows the effect of blending of low dose irradiated latex to the over-vulcanized latex on Tb. It can be seen that the blending is effective to improve the physical property of the over-vulcanized latex. This technique will be useful when the latex is irradiated to much due to dosimetry failure.

**CONCLUSION**

Blending of NR latex is the common technique in NR latex industry to minimize batch to batch variations in properties. In this paper the effect of the blending of radiation vulcanized NR latex was investigated and the following two important results were obtained.

1) Blending of high and low quality latexes tends to cause worsening of the physical properties of high quality latex.

2) However, blending of lower dose irradiated latex will be useful for improvement of the physical properties of over-irradiated latex.
Figure captions

Fig. 1 Relationship between dose and tensile strength
Fig. 2 Relationship between dose and elongation at break
Fig. 3 Relationship between dose and gel fraction
Fig. 4 Relationship between dose and weight swelling ratio
Fig. 5 Relationship between dose and number average weight of chains between crosslinks
Fig. 6 Relationship between gel fraction and tensile strength
Fig. 7 Relationship between weight swelling ratio and tensile strength
Fig. 8 Effect of higher dose on tensile strength of blended latex
Table 1  Improvement of physical property of over-irradiated latex by blending with lower dose irradiated latex

<table>
<thead>
<tr>
<th>100 kGy</th>
<th>300 kGy</th>
<th>400 kGy</th>
<th>500 kGy</th>
<th>600 kGy</th>
<th>Tb (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100%</td>
<td>27.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25.0%</td>
<td>29.5</td>
<td>100%</td>
<td>24.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50.0%</td>
<td>26.8</td>
<td>50.0%</td>
<td></td>
<td>20.7</td>
<td></td>
</tr>
<tr>
<td>62.5%</td>
<td>25.4</td>
<td>37.5%</td>
<td></td>
<td>18.0</td>
<td></td>
</tr>
<tr>
<td>70.0%</td>
<td>24.6</td>
<td>30.0%</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
- Original Latex
- Blended Latex (1:1)
- Blended latex (250 kGy)

Tb (MPa)

Dose (kGy)
Original 250 kGy Latex
Blended lower dose latex

- 0 kGy
- 30 kGy
- 100 kGy

Tb (MPa)

Higher Dose (kGy)

250 kGy
The graph shows the relationship between gel percentage (%) and tensile modulus (Tb, MPa) for different types of latex:

- **Original Latex**
- **Blended Latex (1:1)**
- **Blended Latex (250 kGy)**

The data points indicate a nonlinear increase in tensile modulus as the gel percentage increases.
PREPARATION OF HIGHLY STABILISED NATURAL RUBBER LATEX FOR RADIATION VULCANISATION

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ABSTRACT

There is a bright future for radiation vulcanised natural rubber latex (RVNRL) but there are problems in manufacturing it as the centrifuged latex to be used for radiation has to be kept for at least a month or sometimes even three to six months before adding the sensitisers and even then the latex sometimes coagulates on adding the sensitisers.

This paper describes a process by which the latex can be stabilised by addition of an anionic soap before centrifuging so that it has a high mechanical stability and hence can be used even within one week of the manufacture of the centrifuged latex.

INTRODUCTION

At present it is not possible to use any centrifuged latex available in the market and produce RVNRL having consistent and acceptable physical properties in the films made from it. Hence it appears very necessary to change the process of manufacture of centrifuged latex so that consistent and acceptable physical properties such modulus at 300%, tensile strength and elongation at break are obtained from it.

Normal centrifuged latex has to be matured for at least 3 to 4 weeks before using it to make latex based products using conventional sulphur vulcanisation. For radiation vulcanisation, it has been reported that stabilised natural rubber (NR) latex between 3 to 6 months after production should be used for radiation vulcanisation. This very long storage of latex is a serious disadvantage for the commercial implementation of radiation vulcanisation of natural rubber latex.

This paper describes the preparation of special types of centrifuged natural rubber latex which can be used even a few days after manufacture, has a very much higher stability than the normal centrifuged latex available in the market, is stable after adding 1,6-hexanediol diacrylate(A-HD) and/or n-butyl acrylate (n-BA) or carbon tetrachloride (CC14) addition, is stable after radiation vulcanisation.
EXPERIMENTAL

Material

Field latex was received from Rubber Research Institute of Sri Lanka. Technical grade n-BA, A-HD, CCl₄, and ammonia were used. Industrial grade lauric acid, zinc oxide (ZnO), sodium di ethyl carbonate (SDEC) and DAHP were used. All chemical were supplied by the established companies in the country and used without further purification.

The gamma cell installed at University of Colombo was used. The activity of Co-60 was 2900ci and dose rate was 0.6 Mrad/h.

Preparation of centrifuged latices:

a. Preparation of highly stable LA-TZ: (HS-LATZ)

The field latex was treated with 0.35% ammonia, with the required amount of DAHP, with 0.025% tetramethyl thiuram disulphide (TMTD)/ZnO (1:1) and with ammonium laurate at 0.2% on latex. The latex was allowed to stand for 48 hr and 0.025% TMTD/ZnO (1:1) added.

b. Preparation of highly stable LA-SZ: (HS-LASZ)

The field latex was treated with 0.35% ammonia, with the required amount of DAHP, with ZnO at 0.01% and with sodium diethyl dithiocarbanate (SDEC) at 0.05% on latex and with ammonium laurate at 0.2% on latex. The latex was allowed to stand for 48 hr and centrifuged, the ammonia content brought up to 0.2% and ZnO at 0.01% on latex and SDEC at 0.05% on latex added.

c. Preparation of highly stable HASZ: (HS-HASZ)

This latex is the same as No.(b) but having an ammonia content of 0.7% instead of 0.2%.

d. Preparation of LA-TZ:

Commercially available low ammonia centrifuged latices were used.(LATZ(1) & LATZ(2))

The latices were used after diluting with distilled water to rubber content of 50%. The sensitisers were added neat.

Irradiation

Measured weights of the sensitiser were added to weighed amounts of NR latex and mixed with a magnetic stirrer for 20 minutes. The mixture then kept standing for over night at room temperature. About 50-100 ml of the mixture was irradiated in a glass bottle with a screw cap in an environment of air.

The irradiated latices were dried on glass plates at room temperature for about 3 days till the films were clear. The films were leached in distilled water for 24 h. Then the films were dried in air till the films were clear and were then dried further at 80 C for 1 h. The tensile properties of the films were measured. The crosslinking density was measured after the specimens were immersed in toluene at room temperature for 24 h.
Stability of the various latices after adding sensitisers

A combination of 2.5 phr n-BA and 2.5 phr A-HD were added to the various latices (50% drc) given in Table 1 in neat form. Observations on the stability of the latices after adding the sensitisers, after radiation and details of film are given in Table 2.

Table 1: Properties of centrifuged latices used.

<table>
<thead>
<tr>
<th>Type of latex</th>
<th>Total solids %</th>
<th>Dry rubber content %</th>
<th>MST in sec.</th>
<th>Ammonia content %</th>
<th>Viscosity</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>HS-LASZ</td>
<td>63.2</td>
<td>62.0</td>
<td>&gt;1200</td>
<td>0.17</td>
<td>40.0</td>
<td>9.6</td>
</tr>
<tr>
<td>HS-HASZ</td>
<td>62.5</td>
<td>62.1</td>
<td>&gt;1800</td>
<td>1.0</td>
<td>37.5</td>
<td>10.2</td>
</tr>
<tr>
<td>HS-LATZ</td>
<td>60.6</td>
<td>61.7</td>
<td>&gt;1700</td>
<td>0.22</td>
<td>42.5</td>
<td>9.6</td>
</tr>
<tr>
<td>LATZ(1)</td>
<td>61.6</td>
<td>59.7</td>
<td>920</td>
<td>0.20</td>
<td>32.5</td>
<td>9.70</td>
</tr>
<tr>
<td>LATZ(2)</td>
<td>59.3</td>
<td>60.2</td>
<td>150</td>
<td>0.20</td>
<td>10.5</td>
<td>9.8</td>
</tr>
</tbody>
</table>

Table 2: Effect of adding sensitisers in latex (2.5 phr n-BA + 2.5 phr A-HD added neat)

<table>
<thead>
<tr>
<th>Type of Latex</th>
<th>Stability of latex after 18 h of sensitisers addition</th>
<th>Stability of latex after irradiation</th>
<th>Drying</th>
<th>Clarity</th>
<th>Transparency</th>
</tr>
</thead>
<tbody>
<tr>
<td>LATZ(1)</td>
<td>gives clumps on stirrer</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>*LATZ(1)</td>
<td>stable</td>
<td>stable for 21 days</td>
<td>bad</td>
<td>bad</td>
<td>bad</td>
</tr>
<tr>
<td>LATZ(2)</td>
<td>gives clumps on stirrer</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>*LATZ(2)</td>
<td>stable</td>
<td>stable for 21 days</td>
<td>slow</td>
<td>good</td>
<td>good</td>
</tr>
<tr>
<td>HS-LATZ</td>
<td>stable</td>
<td>stable for 40 days</td>
<td>fast</td>
<td>good</td>
<td>good</td>
</tr>
<tr>
<td>**HS-HASZ</td>
<td>stable</td>
<td>stable for 21 days</td>
<td>fast</td>
<td>good</td>
<td>good</td>
</tr>
<tr>
<td>HS-LASZ</td>
<td>stable</td>
<td>stable for 40 days</td>
<td>fast</td>
<td>good</td>
<td>excellent</td>
</tr>
</tbody>
</table>

*After adding 0.35% potassium laurate
**Latex diluted and irradiated

RESULTS & DISCUSSION

The properties of the centrifuged latices used by us are given in Table 01. It can be noted that LATZ (2) has a very low MST, whilst all the highly stabilised latices have a very high stability.

Table 02 shows the effect of adding sensitisers in latex. Of the five latices tested, four were low ammonia and one was high ammonia and it is HASZ. Only the high ammonia latex gives thickening. An explanation of this may be as follows.

It is known that the higher pH of high ammonia latex will cause more hydrolysis of the lipids and proteins than the lower pH of low ammonia latex. The KOH no is a measure of breakdown of lipids and proteins during storage. Thus if high NH₃ latex is stored for 3 months, it has been reported that KOH no. rises by 11 units. i.e. from 0.47 to 0.58 whilst if LATZ latex is stored for three months, the KOH number rose by only 3 units. i.e. from 0.49 to 0.56 (John et al 1976). When sensitiser is added to centrifuged latex it diffuses into the latex particle and swells it and it is the protein layer surrounding the latex particle which prevents the latex particles from coalescing and this protein layer must be kept intact to have a stable compound latex. Even though the MST of this latex is over 1800 (i.e. it has enough soap in it) it was unstable on adding the sensitisers. In the case of LATZ latices though there was some instability by clumps forming on the stirrer on adding the sensitisers, this was corrected by adding potassium laurate.
The important observation of Table 3 is that HS-LASZ and HS-LATZ latices were more stable latices compared to others after irradiation and the drying was fast, the film clarity was good and transparency was good. Tensile strength of the films made from HS-LASZ & HS-LATZ latices were 27.4 Mpa and 30.6 Mpa at 1.4 Mrad with 2.5 phr A-HD & 2.5 phr n-BA as sensitisers respectively. Hence these latices we would recommend for use in RVNRL.

Table 3: Relationship between MST of latex and Tensile Strength of film at radiation dose 1.4 Mrad, Sensitiser dosage 2.5 phr A-HD & 2.5 phr n-BA.

<table>
<thead>
<tr>
<th>Type of latex</th>
<th>MST in sec.</th>
<th>Crosslink density (no. of crosslinking moles per unit volume x 10^-4)</th>
<th>Modulus 300% in MPa</th>
<th>TS in MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>LATZ(1)</td>
<td>920</td>
<td>0.95</td>
<td>0.80</td>
<td>23.2</td>
</tr>
<tr>
<td>LATZ(2)</td>
<td>150</td>
<td>0.77</td>
<td>0.74</td>
<td>16.4</td>
</tr>
<tr>
<td>HS-LATZ</td>
<td>&gt;1700</td>
<td>1.16</td>
<td>1.11</td>
<td>30.6</td>
</tr>
<tr>
<td>HS-LASZ</td>
<td>&gt;1200</td>
<td>1.48</td>
<td>1.31</td>
<td>27.4</td>
</tr>
<tr>
<td>HS-HASZ</td>
<td>&gt;1800</td>
<td>1.41</td>
<td>1.25</td>
<td>27.7</td>
</tr>
</tbody>
</table>

Table 3 shows the relationship between MST of latex and Tensile Strength of films at 1.4 Mrad, with 2.5 phr & 2.5 phr n-BA sensitisier system. The higher the MST of the latex the higher the stability of the compound latex and higher the tensile strength. It will be noted that LATZ(1) and LATZ(2) gave tensile strength below 25 Mpa whilst all the other highly stabilised latices gave a tensile strength of above 25 Mpa.

Table 4: MST of latices with sensitisers after 24 hr.

<table>
<thead>
<tr>
<th>Type of latex</th>
<th>MST in Secs. 2.5 phr A-HD + 2.5 phr n-BA</th>
<th>MST in Secs. 1.5 phr A-HD + 2.5 phr n-BA + 0.5 phr CCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>HS-LA-TZ</td>
<td>501</td>
<td>782</td>
</tr>
<tr>
<td>HS-LA-SZ</td>
<td>695</td>
<td>592</td>
</tr>
<tr>
<td>HS-HA-SZ</td>
<td>coagulated</td>
<td>coagulated</td>
</tr>
</tbody>
</table>

The different latices with 2.5 phr n-BA and 2.5 phr A-HD and also with 2.5 phr n-BA, 1.5 phr A-HD and 0.5 phr CCl₄ were tested for MST after 24 hr after adding sensitisers. The results are given in Table 4. It confirms that HA latex even if highly stabilised is not suitable to add sensitisers in a neat form but LA latex if highly stabilised is suitable. Further the MST was done at 55% drc. Hence the modified LA latices can be irradiated at 55% drc instead of 50% drc.

A combination of 2.5 phr n-BA and 1.5 phr A-HD and 0.5 phr CCl₄ was added to highly stabilised LATZ latex (HS-LATZ) and the results are given in table 05. It is seen that the addition of the 0.5 phr CCl₄ gives a better stability to the latex after addition and good drying properties even at very low radiation doses.
Table 5: Effect of adding sensitisers in HS-LATZ latex. (2.5 phr n-BA + 1.5 phr A-HD added neat)

<table>
<thead>
<tr>
<th>Dose (Mrad)</th>
<th>Stability of latex after 18 h. of sensitiser addition</th>
<th>Stability of latex after irradiation</th>
<th>Drying</th>
<th>Clarity</th>
<th>Transparency</th>
</tr>
</thead>
<tbody>
<tr>
<td>without CCl₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.35</td>
<td>Stable</td>
<td>Stable for 21 days</td>
<td>good</td>
<td>good</td>
<td>excellent</td>
</tr>
<tr>
<td>0.7</td>
<td>Stable</td>
<td>Stable for 27 days</td>
<td>good</td>
<td>good</td>
<td>excellent</td>
</tr>
<tr>
<td>1.04</td>
<td>Stable</td>
<td>Stable for 30 days</td>
<td>good</td>
<td>good</td>
<td>excellent</td>
</tr>
<tr>
<td>1.4</td>
<td>Stable</td>
<td>Stable for more than 35 days</td>
<td>good</td>
<td>good</td>
<td>excellent</td>
</tr>
<tr>
<td>with 0.5 phr CCl₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.35</td>
<td>Stable</td>
<td>Stable for more than 35 days</td>
<td>good</td>
<td>good</td>
<td>excellent</td>
</tr>
<tr>
<td>0.7</td>
<td>Stable</td>
<td>Stable for more than 35 days</td>
<td>good</td>
<td>good</td>
<td>excellent</td>
</tr>
<tr>
<td>1.04</td>
<td>Stable</td>
<td>Stable for more than 35 days</td>
<td>good</td>
<td>good</td>
<td>excellent</td>
</tr>
<tr>
<td>1.4</td>
<td>Stable</td>
<td>Stable for more than 35 days</td>
<td>good</td>
<td>good</td>
<td>excellent</td>
</tr>
</tbody>
</table>

**CONCLUSION**

On improving the stability of the centrifuged latex so that it can be used to produced RVNRL even within a week of its manufacture.

Highly stabilised latices (HS-LATZ and HS-LASZ) are very stable after adding sensitisers in neat form to the latex and films made out of this HS latices have good physical properties specially tensile strength over 25 MPa.

**ACKNOWLEDGEMENT**

We thank the Chairman Atomic Energy Authority of Sri Lanka (AEA); the Chairman, Advisory Committee of AEA, the Director, Rubber Research Institute of Sri Lanka, the Chairman, Ceylon Institute of Scientific & Industrial Research for encouragement to carry out this project.

**REFERENCES**

NATURAL RUBBER LATEX. PAST, PRESENT AND FUTURE IN LATIN AMERICA

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Abstract

The origin of the *Hevea brasiliensis* tree was the Amazonian region in South America, particularly the Brazilian jungle. The rubber expansion at the end of 19th century brought prosperity and determined the borders of Amazonian countries. In spite of that, the Brazilian government has failed in establishing a successful policy for improving the NR production in the jungle. However, rubber plantations were successfully introduced recently near marginal areas of the humid forest in the Amazon due to the absence of the fungus *Microcyclos ulei*. Both, extraction of wild rubber and plantation have a key role in the maintenance of the forest health.

The market for dipping products is small but is growing very fast and is expected to follow this pattern as the sanitary conditions are improved by the health authority. The history of the Brazilian NR products industry is contemporary and is based on the policy of market protection and on the lack of investments due to extremely high interest rates. As a result, the industry was not competitive.

It was concluded that, in order to cope with the future challenge, the industry is required to invest in very modern technologies to produce first class goods with international acceptance. Latin America would follow the world trend for nitrosamine and protein free products. The radiation vulcanization of natural rubber latex could prove itself as a profitable solution and not only a quality solution. It was also concluded that both wild rubber and rubber plantations in Brazil have their future coupled with the future of a regional dipping industry. Moreover, the buildup of the dipping industry will be beneficial to the protection of the humid forest and the recovery of degraded areas.

INTRODUCTION

The Brazilian NR (natural rubber) production was the biggest in the world from 1850 to 1910. Nowadays, it is considered obsolete or it is completely unknown. This paper reviews the past and present of NR industry in Brazil. It encompasses all NR industry, i.e., the native extraction, plantation, solid rubber industry and in particular the dipping industry. The assessment of the future of the NR industry is the first objective of this work. It also demonstrates that the Brazilian industries of dipping products could overturn the trend of decline by applying the RVNRL (radiation vulcanization of natural rubber latex) process. The final objective is to prove that NR industry could promote the care of the forest and the recovery of degraded areas in the margins of the jungle.

PAST AND PRESENT OF NATURAL RUBBER IN BRAZIL

Natural Rubber Extraction

The *Hevea brasiliensis* was native to the America tropical region, particularly the Amazon basin, where it is still found in the greatest natural concentration. The NRL (natural rubber latex) was known from the pre-Colombian age for the production of kettles, clothes and footwear by the natives. During the Colonial period, wild rubber had no importance for the economy, however it was explored together with other natural products (nuts, fruits, fibers, etc) and they were the base of survival for the settlers in the Amazon.
After the invention of the vulcanization process by Goodyear in 1842 and with the expansion of many kinds of industries, the NR industry started to be of utmost importance for the industrialized world. As consequence, in 1860, the first intense exploration cycle started in the east Amazon region (Para state). This boom was soon transferred to the inner Amazon jungle and at the beginning of the 20th century, the central Amazon and west region, near Bolivia, were the source of NR. On that occasion, a border conflict took place with Bolivia, which was soon solved with the cession of Acre territory to Brazil.

In 1874, while the Amazon region was experiencing the economic boom of NR, based on the extraction procedure, Henry Alexander Wickman took 70,000 seeds of Hevea brasiliensis from the Amazon to Kew Garden (Nadler 1976). Only 2,397 germinated, but enough to set up large plantations in Southeast Asia.

Table 1 shows the increasing share of the oriental rubber in the international market (Mendes 1910; Nadler 1976). The tremendous expansion of the Asian plantations was followed by the contraction of NR extraction in South America. Before the World War II, the South American production was already less than 3% of the total.

<table>
<thead>
<tr>
<th>Year</th>
<th>Asia (1,000 kg)</th>
<th>South America</th>
</tr>
</thead>
<tbody>
<tr>
<td>1905</td>
<td>145</td>
<td>34,000</td>
</tr>
<tr>
<td>1910</td>
<td>8,500</td>
<td>41,000</td>
</tr>
<tr>
<td>1914</td>
<td>71,400</td>
<td>49,000</td>
</tr>
<tr>
<td>1937</td>
<td>1,000,000</td>
<td>27,200</td>
</tr>
</tbody>
</table>

**Natural Rubber Plantation**

Many attempts were made to transform Brazil into a big producer of NR again. The first official program started in 1906 and was improved in 1912 by offering a global solution for education, research and transportation. The American company, Ford, began setting up big plantations in the Amazon region in 1927. This project, Fordlandia, was ended due to uncontrolled problems with SALB (South American Leaf Blight) plague caused by the fungus Microcyclos ulei. More recently the Brazilian government introduced the PROBOR (Program for the Encouragement of Natural Rubber Production). This program was conducted in three phases and was based on very low interest rates. Approximately 200,000 hectares were contracted, but only about 120,000 succeeded. Basically, it failed for the same reason, i.e., the control of SALB was not achieved. Recently, however, private companies were quite successful in establishing 85,000 hectares of plantations far from the Amazon (IBAMA 1991-1993).

Table 2: Production of Natural Rubber in Brazil

<table>
<thead>
<tr>
<th>YEAR</th>
<th>PRODUCTION (1,000 kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PLANTATION</td>
</tr>
<tr>
<td>1985</td>
<td>5,811</td>
</tr>
<tr>
<td>1987</td>
<td>8,078</td>
</tr>
<tr>
<td>1989</td>
<td>13,757</td>
</tr>
<tr>
<td>1991</td>
<td>16,863</td>
</tr>
<tr>
<td>1993</td>
<td>34,526</td>
</tr>
<tr>
<td>1994</td>
<td>39,726</td>
</tr>
</tbody>
</table>

Table 2 shows the catastrophic breakdown of the native production. On the other hand, the tremendous increase in plantation production compensates completely for the losses in extraction.
Potential for Wild Rubber Extraction

The proximity of the end of native extraction is shown dramatically in Table 2. It is called the "bankruptcy" of the wild rubber extraction activities. However, it is important to notice that this was not a consequence of the destruction of the jungle, but just lack of economic motivation. As a result, those settlers are coming to the big cities, causing a series of social problems.

In spite of that, the extraction activity is important for the protection of the jungle. The *seringueiros* (wild rubber workers) have to take care of many hectares to get their rubber, they spend all day walking in the jungle. Sometimes they are called the soldiers of the jungle. According to the Brazilian Association of Natural Rubber Producers (Soares 1994), the only possibilities for the partial recovery of wild rubber extraction is a conjugation of efforts or strategy with the goals:

- assure the permanency of the population and even relocate the one that left for the cities;
- increase the productivity and production of raw materials from the forest (wild rubber, Brazilian nuts, fibers, specific fruits and drugs) to enhance the life standard of the producers;
- promote the sustainable uses of natural resources from the forest and halt the increase in jungle deforestation;
- promote a new Regional Land Distribution policy to avoid large internal migration;
- do not allow any potentially dangerous project without deep discussions with the organized associations.

Regarding NR, the main objective of a future program would be the density increase of the native rubber trees, aiming at the improvement in productivity and production. Table 3 shows the projection done by Soares for the potential of native extraction, assuming the success of the proposed strategy. Of course, this is a very optimistic projection, but could be feasible if the government acknowledges the value of the native extraction, considering the strategic and environmental sides.

<table>
<thead>
<tr>
<th>hypothesis</th>
<th>estimated population of hevea brasiliensis</th>
<th>possible production/tree</th>
<th>resulting production (1,000 kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. actual density</td>
<td>200 millions</td>
<td>2 kg/year</td>
<td>400,000</td>
</tr>
<tr>
<td>2. 100% increase</td>
<td>400 millions</td>
<td>2 kg/year</td>
<td>800,000</td>
</tr>
<tr>
<td>1. 200% increase</td>
<td>600 million</td>
<td>2 kg/year</td>
<td>1,200,000</td>
</tr>
</tbody>
</table>

Potential for the Plantations

The efforts for the establishment of NR plantations were done in traditional areas of native tree. They are very humid and hot, with a quite constant distribution of rain all over the year. However, the development of SALB is prevalent in humid areas. More than 120,000 hectares were funded by the government in these areas, however only 25% of the trees reached the maturity and with low production level (Pinheiro 1996).

In order to escape from the SALB, private landowner start to cultivate in subtropical areas with very promising results. Actually, the production of NR in Brazil is located mostly in Sao Paulo state and Mato Grosso state. There are millions of hectares in this condition ready to be used for NR plantations (Ortolani 1982). Others started to search in marginal areas of the jungle (escape areas) where there is a dry season of 4 to 5 months, to avoid the growth of the fungus in the epidemic form.
The most important escape areas are the marginal areas of the Amazonian jungle. These areas were already devastated or are still under destruction. Data from LANDSAT satellites point out that from 1978-1988 the deforestation rate was 20,400 km²/year and decrease to 11,100 km²/year in 1991. The reduction was mainly due to the economical recession. Nevertheless, the deforestation is still as high as 3,000 ha/day or more than 2 ha/min. Small farmers (less than 100 ha) were responsible for the destruction of about 30% of the forest, the rest was destroyed by medium to big farmers (Fearnside 1995). The successful establishment of rubber plantations in the area is already proved by the establishment of very large NR plantations. In such way, NR plantation could help to stop the destruction and recover degraded areas used for livestock (Pinheiro 1995).

Solid Rubber Industry

Since the establishment of the Brazilian automobile industry in the 50's, the country started to import NR. Many attempts were made, as already seen, to cope at least with the internal consumption. Figure 1 shows the trends of the NR consumption and its production based on the new plantations. Both are increasing, however the consumption is increasing even faster as a result of the automobile industry boom in Brazil. The production is expected to at least double in the next 5 years from the current 1.5 million to 3 or 4 million. The growing consumption is a trend all over the world, contributing even more to the present increase in interest for the rubber tree in Brazil.

![Figure 1. Production and Consumption of NR from 1985 to 1994](image)

Dipping Industry

Brazil is producing about 4000 t of concentrated latex on a dry basis, however the installed capacity is at least 5 times higher (Maia 1996). The NRL producers are shifting to solid rubber as the dipping industry is undergoing a very deep crisis. The crisis is a result of the change in the market policy, from total protection to open market.

The protection occurred on both sides. On the raw material side, the industry had to buy a percentage of Brazilian NR in order to be allowed to buy imported NR with better price and quality. This was a protection for NR producers but, of course, is prejudicial to the industry of goods. On the other hand, the market protection was very effective, as the tax for importing foreign products was sometimes higher than 100% when similar ones were produced in Brazil. Not only the market protection was weakening all the industries in Brazil, but also the extremely high inflation and interest rates during the last 30 years. It was not worth investing in production and the factories became obsolete.
The dipping industry in all South America is composed mostly of small and medium size industries and they could not compete with foreign products. Most of them went bankrupt or stopped the production of gloves, condoms and balloons and started to sell imported products using their trade name. However, some medium size industries are still producing in all South America, but, as the market is increasing faster than their investment capacity, they are also importing and selling using their trade name.

R&D Capabilities in RVNRL

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<td>1. Brazil</td>
<td>3 gamma 1.5 MeV</td>
<td>0.5 to 1.10⁹ Ci</td>
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<td></td>
<td>EB 6 low energy</td>
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<td>research</td>
<td></td>
</tr>
<tr>
<td>2. Argentina</td>
<td>2 gamma 2 low</td>
<td>200k and 500 kCi</td>
<td>government</td>
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<td></td>
<td>1 gamma</td>
<td>40k to 200 kCi</td>
<td>Institute</td>
<td></td>
</tr>
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</tr>
<tr>
<td>7. Mexico</td>
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FUTURE OF NR INDUSTRY AND CONCLUSIONS

The previous items reviewed the NR industry from extraction to dipping. It was shown that:

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- the NR industry of solid rubber is healthy as a result of the fast growing automobile industry;
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All these conditions constitute themselves a fertile ground for RVNRL. The dipping industry although not comparable to the solid rubber industry, is becoming more important every day, as gloves and condoms play an important role in sanitation and human welfare. Moreover, the dipping industry can play a key role in the Brazilian environmental dilemma, i.e., the forest should be maintained healthy and protected from devastating projects and at the same time needs of the inhabitants should be considered. The NR industry can help to solve the dilemma if certain conditions are met:

1. The rubber plantation in the escape areas is proved to be resistant to SALB and economically feasible without any government help. The plantations are very demanding in labor and this work force is not seasonable.

2. Presently, the wild rubber extraction is not economically feasible by itself in most places. However, the government can organize the production system and in some way reward for the environmental service.

3. Close to the end of the 20th, century the raw material production without any kind of industrialization process is not conceivable. The dipping industry has flexible scale and can be regional, so it can be established near wild rubber extraction centers or rubber plantations. Moreover, the consumption of the dipping products is increasing exponentially all over the world.

However, the only route to reverse the shrinking process of the Brazilian dipping industry and even to become competitive in international markets is to invest in new technologies that will cope with the future requirements for the goods, i.e., safe for the environment and human health. RVNRL has such qualities, products can be made very pure, in a clean environment (Makuuchi and Markovic 1991).

The RVNRL can clearly contribute to the success of the dipping industry in the Amazon and it can produce a chain reaction effect for the environment protection, first by promoting the wild rubber extraction with government support; second by stimulating the investments in plantations in degraded areas of the jungle, third by offering a better option than extraction of wood for exportation.

ACKNOWLEDGMENT

The authors wish to thanks the organizing committee of The 2nd International Symposium on RVNRL for the invitation. The authors are grateful to Dr. K. Makuuchi for his invaluable advice and IAEA for funding the researches on RVNRL inside the TC BRA 8/023.

They also wish to express their gratitude to Dr. Percy Putz and to Dr. Ademar A Queiroz do Valle for their informations and useful contributions to this paper. Many other Latin American experts have contributed to this paper, I would like to name just a few: Leonidas Calvi, Fabio Maia, Gunther Lottmann, Eurico Pinheiro and Edinaldo J. S. Cunha. Finally, a special thanks to my friend Richard Siemens for the review of the manuscript.

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Nadler (1976), Proceedings from the II National Seminar of Rubber Tree, Rio Branco, Acre, June 16-20, pp. 503-533.

Ortolani et al (1982); carta preliminar, Campinas, IAC/SUDHEVEA.


Maia F. (1996); private communication.

QUESTIONS & ANSWERS, and COMMENTS

Session I Part I:

Q1 Ong Eng Long  What are the ageing properties of RVNRL prepared using tBHP as a co-sensitiser?

A1 Chyagrit Siri-Upathum  The ageing properties were not tested.

Q2 Ong Eng Long  How does the irradiation dose used for the preparation of RVNRL affect the thermal degradation of RVNRL films?

A2 Alumanda Dela Rosa  The rate of thermal degradation of films prepared from latex irradiated at doses greater than 15 kGy tended to be higher than films prepared from latex irradiated at doses of less than 15 kGy.
**QUESTIONS & ANSWERS, and COMMENTS**

**Session I Part 2:**

<table>
<thead>
<tr>
<th>Q1</th>
<th>Willfried Bez</th>
<th>What are the types and levels of preservatives used in the NR latex?</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>Wan Manshol</td>
<td>The latex does not contain TMTD-ZnO as preservatives.</td>
</tr>
<tr>
<td>Q2</td>
<td>Marga Utama</td>
<td>What is the type of sensitiser and the level used in the preparation of RVNRL, and how long is the standing time before irradiation?</td>
</tr>
<tr>
<td>A2</td>
<td>Wan Manshol</td>
<td>The sensitiser used is n-butyl acrylate at 5 pphr, and the latex is left to stand for 6 hours prior to irradiation.</td>
</tr>
<tr>
<td>Q3</td>
<td>Feroza Akhtar</td>
<td>What stage of latex processing is used to mark the age of the latex?</td>
</tr>
<tr>
<td>A3</td>
<td>Wan Manshol</td>
<td>The age of the latex is taken from the time when the field latex is collected.</td>
</tr>
<tr>
<td>Q4</td>
<td>Makuuchi</td>
<td>What are the changes taking place during the six-month storage of NR latex concentrate?</td>
</tr>
<tr>
<td>A4</td>
<td>Wan Manshol</td>
<td>There is an increase in the mechanical stability time of the latex.</td>
</tr>
<tr>
<td></td>
<td>Thomas</td>
<td>During storage of latex, the phospholipids break down to form fatty acids.</td>
</tr>
<tr>
<td></td>
<td>Makuuchi</td>
<td>The tensile strength of RVNRL films prepared and tested at TRCRE Japan tended to be greater than 30 Mpa while those in the latex producing countries tended to be less than 30 Mpa. This observation may well be related to the effects of latex maturity.</td>
</tr>
<tr>
<td></td>
<td>Wan Manshol</td>
<td>The optimum maturation period of latex is about 3 weeks, and if it is longer than this, it will require a relatively higher irradiation dose for maximum tensile strength.</td>
</tr>
</tbody>
</table>
BIOLOGICAL EVALUATION OF RVNRL

Robert E. Geertsma, Tom J.H. Orzechowski, Mark Jonker, Jan - Willem Dorpema and
Jack A.A.M. van Asten
Laboratory for Medicines and Medical Devices
National Institute of Public Health and the Environment (RIVM)
P.O.Box 1, 3720 BA BILTHOVEN, THE NETHERLANDS

Abstract

Cytotoxicity testing (cell growth inhibition, LDH-assay) has shown that RVNRL materials are considerably less
cytotoxic than sulphur-vulcanised materials. Also the effect of applying different leaching times during the
production process was investigated and gave interesting results. Protein testing (BCA - comparable to a
Lowry assay ) has shown that some, but not all proteins are destroyed during irradiation. For the total protein
content of the materials as determined in this way, the effect of leaching proved to be very important. This was
also checked by; SDS-PAGE assays: After irradiation a smear is observed with SDS-PAGE; when the
irradiated material has been leached, most of the smear has disappeared. An important protein (14 kD) is still
present and seems hardly to be affected. The materials have also been evaluated clinically, using well
characterised patient sera (Western blotting) in order to determine whether the remaining proteins are
allergenic.

INTRODUCTION

In the mid eighties the use of medical gloves and condoms increased explosively to avoid the risk of being
infected by AIDS. Because of the fantastic mechanical properties of natural rubber latex (NRL) this unique
material was used to manufacture these products. After several years, however, a disadvantages of this way of
protection became obvious. An increasing number of people began to develop adverse reactions to latex
products. These reactions ranged from a simple rash or itchy feeling to more severe asthmatic and allergic
reactions.

The problems associated to use of NRL are caused mainly by three factors. The first one, which is currently
regarded as the most important one is a consequence of the fact that it is harvested from the rubber tree
Hevea Brasiliensis. Besides the rubber particles the raw latex also contains the tree’s natural proteins. A lot of these
proteins are destroyed or removed during processing, but often a considerable amount is still present in the final
product. During the use of for example the latex medical glove the proteins, which tend to migrate to the
surface, can come into contact with human tissues both of the user and the patient and cause allergic reactions
(Levy et al.. 1992; Slater 1994).

The type of reaction caused by these protein is classified as a Type I or immediate-type, IgE-mediated allergic
reaction. The clinical symptoms related to this reaction are seen as local or generalised urticaria (hives) with
edema, hayfever-like symptoms, and/or difficulty in breathing. In extreme cases anaphylactic reactions can
occur which may even, although rarely, result in death.

The second problem is mainly caused by the chemicals that are added to the latex in order to start the
vulcanisation process (accelerators, mostly dithiocarbamates, thiurams and mercaptobenzothiazoles) and to
provide the final product with its unique properties. These chemicals may act as specific contact sensitizers,
which cause a Type IV or delayed-type, T-cell mediated allergic reaction which is sometimes referred to as
allergic contact dermatitis. Clinical symptoms like redness, vesicles scratching, itching and a rough skin can
occur (Heese et al. 1991; Heese et al. 1991).

A third major problem, which is starting to be acknowledged more and more in the last few years, is connected
with the use of donning powder in the gloves (Thuscott 1995; Proceedings Symposium London 1996). Several
adverse effects are associated to glove powder. Adhesions after surgery in the abdominal area can sometimes
be attributed to glove powder particles. Also misdiagnosis of cancer and severe foreign body complications
can be caused by the powder. Furthermore, most important, glove powder can enhance the risk of allergic reactions.

Proteins and chemicals can be adsorbed and/or absorbed by the powder particles, which during the use of the gloves can become airborne. Subsequently they can cause allergic reactions after inhalation or deposition on human tissues (including inside a surgical wound).

National and international authorities and standardisation bodies like ISO (International Standardization Organization) and CEN (European Committee for Standardisation) have recognised the problem. Under the European legislation the Medical Device Directive (Council of the European Communities 1993) has been issued in which essential requirements have been formulated to which medical devices have to comply. Horizontal (for all products) and vertical (product-specific) standards have been developed to help manufacturers of medical devices: if they comply with the standards, they also comply to the European legislation. For latex gloves two series of standards are important. The first one is "Biological evaluation of medical devices" (EN 30993 1996) is a horizontal standard including recommendations and protocols for specific tests and other safety-related specifications. The second one is "Medical gloves for single use" (EN 455-1,2,3 1994), covering requirements for freedom from holes, physical properties and biocompatibility aspects.

Also manufacturers are becoming more and more aware of the problems that may result from the use of NRL. A lot of research has been done to identify possibilities of improving their products. This has resulted in the development of different processing regimes, especially interdicting additional leaching stages in order to remove as much of the extractable proteins and chemicals as possible.

Regarding the above mentioned problems associated to NRL, radiation vulcanized natural rubber latex (RVNRL) seems to be a very interesting alternative material (Makuuchi and Yochii). Two major advantages arise from the different way of processing NRL. At first, the accelerators necessary for sulphur vulcanization need not to be added to the material. The absence of these chemicals will probably cause a major reduction of Type IV allergic reactions. Secondly, gamma radiation can cause protein disintegration, which might cause a reduction of Type I allergic reactions.

To investigate the extent of these possible advantages, several tests series were carried out on RVNRL samples. These include cytotoxicity assays, which are very sensitive to a lot of chemicals (sulphur-vulcanised NRL is a known highly cytotoxicity assays, which are very sensitive to a lot of chemicals (sulphur-vulcanised NRL is a known highly cytotoxic material) and protein assays. The latter include a total protein assay and gel electrophoresis (SDS-PAGE), with the help of which proteins of different molecular weight can be separated. Finally immunoblotting with patient sera was performed in order to determine whether residual proteins that are found on the material have allergenic properties.

**PROCEEDURE**

**General**

A biological evaluation was made of RVNRL materials. It was considered very important to identify the influence of different processing steps. Therefore samples of all stages in the production process were investigated regarding several biocompatibility aspects of the material in comparison to conventionally produced (making use of sulphur containing accelerators for vulcanisation) latex products. The applied methods were performed in conformity with the international standards for biological evaluation of medical devices (EN 30993, 1996). A description of the investigated samples is put down in Table I.

**Materials and Methods**

**Extraction procedure**

For cytotoxicity testing the materials were sterilised using ethylene oxide or steam. From the sterile flat materials, 120 cm$^2$ was aseptically cut. The samples were extracted in sterile vial for 24 hours at 37°C. The extraction fluid was 20 ml Dulbecco's medium, supplemented with antibiotics penicillin (100U/ml) and streptomycin (100 mg/ml). The extracts were filtered through a 0.22 µm filter to remove debris and glove power.
Extraction of latex gloves or film for protein testing was performed with a slightly different protocol. 120 cm$^2$ was extracted for 18 hours at 37°C in 20ml PBS supplemented with 0.01% w/v sodium azide to prevent microbial growth, and concentrated with a Microcon 10 (Amicon, USA) microconcentrator by centrifugation for 40 min at 10,000g.

**Protein content**

Protein determinations were performed with the BCA (Bi Cinchoninic Acid) protein assay reagent (Pierce, USA) according to the manufacturer’s instructions. Principle of the test is the reduction of an alkaline Cu(II) solution by proteins, yielding Cu(I) ions which form a coloured complex with BCA (Smith et al. 1985). Concentration can then be determined spectrophotometrically at 562 nm. Calibration was done using several known concentrations of Bovine Serum Albumine (BSA). The method is comparable to the widespread Lowry method (Lowry et al. 1951), using a slightly simpler procedure.

**SDS-PAGE analysis**

Liquid latex samples were diluted 1:2 in distilled water and then added 1:1 to sample buffer Tris-HCl, 0.125mM; pH 6.8, 4% (w/v) SDS, 0.2% (w/v) bromophenol blue. Dithiotreitol (DTT) 0.1M, was added (1:10) when reduction of the samples was needed. The samples were heated at 100°C for 2 min. The amount of sample used was 3 ml. For fresh latex supernatant the protein concentration per lane was 2 mg. SDS-PAGE analysis of extracts was performed on a 8-18% precasted polyacrylamide gel (Excelgel, Pharmacia, Sweden). High and low molecular weight markers (Biorad, California, USA) were included. Electrophoresis was performed at 450V till the marker dye reached the bottom of the gel. The gel was used for silverstaining or for immunoblotting.

**Immunoblotting**

After electrophoresis the gel was removed from its support by a filmremover (Pharmacia, Sweden). The proteins were transferred by electroblotting (Multiphor, Pharmacia, Sweden) to a nitrocellulose membrane (Pharmacia, Sweden.). After transfer, the membrane was saturated for two hours in blocking solution containing 10nM Tris-HCl pH 7.4, 65mM, NaCl and 0.05% non-fat dried milk powder (Protifar, Nutricia, The Netherlands). Patient sera from latex allergic patients were used. IgE antibodies were detected by a monoclonal mouse antihuman IgE (CLB, The Netherlands) and next visualised by a peroxides-labelled rat antimouse antibody (CLB, The Netherlands).

**Cell growth inhibition test (CGI)**

This assay was basically performed according to the assay described by Pelletier (Pelletier 1988), with some small modifications. 10µl containing approximately 4,000 L929 fibroblast cells grown in Basal Medium Eagle (BME) were seeded in a 96 wells round bottom microtiter plate (Corning). The cells were incubated for 24 hours. Subsequently, 100µ1 Dulbecco’s medium (without fenolred) was added to the wells. The cells were incubated for another 24 hours and then fixed with 100µ1 10% (v/v) formalin in PBS for 10 min. The wells were washed twice with 100µ1 10 mM borate, pH 8.4 A 1% (w/v) methylene blue solution (100µ1) was added and incubated for 10 minutes. Following the incubation the wells were again washed twice with the borate solution. 100µ1 0.15M HCl was added to the cells and incubated with agitation for 10 minutes. The extinction of the solution was measured at 650 nm with a photospectrometer (Bio-Tek Instruments). Cell growth inhibition was determined by calculating the change in extinction of cells incubated with extract ($E_a$), both compared to the extinction at $t=0$($E_0$). In the form of an equation this is: \[ \text{%CGI} = 1 - \frac{(E_a - E_0)}{(E_b - E_0)} \] Of all samples 12 separate measurements were performed. The average and mean deviation (SD) were calculated. Positive and negative reference materials were included to assess the validity of the test.

**Lactate dehydrogenase leakage assay (LDH)**

This method was adapted from a test originally described in 1983 (Korzeniowski and Callewaert 1983). The assay is used measure leakage of the cytoplasmatic enzyme lactate dehydrogenase (LDH). Leakage is a function of membrane permeabilisation caused by chemical present in extracts of medical devices. The ratio of leakage of LDH in the presence of extracts and the total amount of LDH in the cells corrected for spontaneous leakage gives the cytotoxicity percentage. A cell suspension of $2 \times 10^5$ cells/ml in complete Dulbecco’s medium (without fenolred, supplemented with 10% FBS and antibiotics) was used to seed a 96 wells microtiter plate.
Following incubation for 24 hours, the medium was refreshed (FBS was omitted) and the extracts were added 1:1. The plate were incubated for 24 hours, subsequently the plate were centrifuged (5min. 1500rpm, 302K Sigma) at room temperature. Control cells were lysed with 20μl 1% (v/v) Triton X-100. From all wells 80μl was transferred to a new microtiter plate and 80 μl of a substrate solution containing lactate, NAD and complex [(INT) was added. LDH activity could then be determined because it initiated a two step reaction resulting in a colour change of the complex which could be measured during 15 minutes at 490 nm in an a Biokinetics reader. Eight samples per extract were tested. The average and the mean deviation were calculated. Positive and negative reference materials were included to assess the validity of the test.

RESULTS

Cytotoxicity testing

Cytotoxicity tests were performed only on the final product (latex gloves and films), because it was practically not feasible to perform the tests on the liquid samples. Furthermore, the cytotoxic properties of the materials are likely to change most dramatically in the final processing step in which vulcanisation takes place.

The results of both the cell growth inhibition assay (%CGI) and the LDH leakage (%LDH) are summarised in the Table 2. It was found that all the RVNRL films (both gamma and beta irradiated) and gloves score low to very low values of cytotoxicity, whereas the SVNRL films can be considered highly cytotoxic. Materials that are not cytotoxic induce less than 10% CGI and slightly negative values in the LDH assay. Unleached gamma-vulcanised RVNRL (sample 5a) was moderately cytotoxic. The leached samples (1, 5b-5f) showed low cytotoxicity. Of the Beta-vulcanised films (samples 17-19) also the unleached sample had a low cytotoxicity. Both samples with and without antioxidant (11 and 12) resulted in low levels of cytotoxicity.

Protein testing

BCA assay (total protein content)

The results of BCA testing on liquid samples and on films or gloves be compared directly, because of the liquid samples a total protein content is determined, while of the films and gloves total amount of extractable protein is measured. the results for both series if samples are summarised in Tables 3 and 4.

In Table 3, it shows that different batches of raw latex can differ markedly in the concentration of protein. (see also Figure 5). Compared to the internallaboratory reference material and concentration in the latexes obtained from MINT and JAERI seem rather high.

In samples 7-9 a very strange phenomenon is observed after formulation the protein concentration dropped significantly, while after irradiation a high protein content could be determined again.

The results in table 4 (see also figure 4) show that unleachedRVNRL film contain high amounts of extractable protein (samples5a and 17). After leaching for one hour the amount of extractable protein is greatly reduced (sample 5b and 18). Prolonged leaching times up to 24 hours reduce the extractable protein content only slightly more (samples 4, 5c-5f and 19). SVNRL films show the same relative pattern and also the absolute values are comparable to those found for the RVNRL films (samples 6a-6f). Both the commercial gloves that were tested contained high amounts of extractable proteins (sampled 21 and 22).

SDS-PAGE and immuno-assay (western blotting) of liquid samples

An SDS-PAGE assay was made of all the liquid. The result are shown in Figure 5. The numbers printed in bold refer to the sample nrs. as listed in Table 1. The marker used was a board range marker (Biorad; bottom to top: 6.5-14.4-21.5-31-45-66-97-116-200 kD).

Lanes 2-4 are the Malaysian samples. The raw latex yielded a smear in which only proteins in the 14 kD range may be identified. Strangely enough, formulating the latex seems to have an effect on proteins, it was not possible to explain this in a satisfactory way. There was no distinctive effect of irradiation.
Lanes 6-8 and 10 are the Japanese samples from the gamma-irradiated series. Again, the raw latex yielded a smear. This time the formulated latex shows considerably less smearing. The reason for this change is not clear. After irradiation substantially more smearing is observed. This can be explained by the destructive effect irradiation has on proteins (smearing is caused by denatured proteins). Addition of antioxidant does not change the protein pattern.

Lanes 11,12 and 14 are the Japanese samples from the E-Beam-irradiated series. The same effects as in the gamma-irradiated series are observed: a lot of smear in the latex, considerably less in the formulated latex and again a lot of smear after irradiation.

The Laboratory reference material in lane 15 shows a distinct pattern of discrete bands. If the raw materials that were used in the irradiation experiments would have shown similar patterns instead of the smear, it would have been possible to identify the proteins that were destroyed by irradiation.

Immunoblotting of the liquid samples was performed with seventeen patient sera. However, probably eight of these sera were too weak. Only nine of the sera reacted with the laboratory reference raw latex (sample 20) and therefore only these nine were included in the evaluation. The combined sera results showed reaction to over twenty proteins in the range from 12 to 97 kD.

The raw latex used from the production of RVNRL (samples 1 and 7) produced reactions only with three of the sera. All three showed a distinct smear over the entire lane. Discrete bands were visible only at 12-14 kD, 20-22 kD and 26-28 kD. Formulated latex (sample 2) produced considerably less smearing and discrete bands at 12-14 kD, 20-22 kD, 26-28 kD and 66 kD with the same three sera. Iradiated latex from sample 9 showed no detectable reaction, but also the control reacted relatively weakly. Preliminary tests performed earlier with an older serum did show some smearing also in this sample.

SDS-PAGE and immuno-assay (Western Blotting) of latex film extracts

The SDS-PAGE results were consistent with the BCA total protein determinations. Unfortunately the results were not duplicated, yet. Electrophoresis of extracts from the unleached RVNRL and SVNRL samples (5a and 6a) showed a smear over the lane, with several more discrete bands at 6.5, 14, 42, 60 and 66 kD visible. Especially the 14 kD protein band was very prominent. Extracts of the leached samples showed practically no more smearing. Only slightly visible bands at 14, 42, 60 and 66 kD could be determined in samples 1 (24 hours leached RVNRL glove), 5b (1 hour leached RVNRL film), 6b and 6f (1, resp. 24 hours leached SVNRL films). Sample 5f (24 hours leached RVNRL films) showed no proteins at all.

Only preliminary immunoblotting assays were performed with an older serum. This showed a clearly positive response to unleached samples and no reaction with any of the leached samples.
Table 1: Sample description

<table>
<thead>
<tr>
<th>Sample Nr.</th>
<th>Supplier - Rad. Type</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>MINT - γ</td>
<td>raw latex, HA (0.7%), DRC 60.34%</td>
</tr>
<tr>
<td>2.</td>
<td>MINT - γ</td>
<td>formulated latex: 1 + 5 phr nBA + 0.02 phr potassium lauric acid + DRC 50%</td>
</tr>
<tr>
<td>3.</td>
<td>MINT - γ</td>
<td>irradiated latex: 2, γ-irradiated with ±13 kGy, DRC 53.0%</td>
</tr>
<tr>
<td>4.</td>
<td>MINT - γ</td>
<td>gloves: from manual dipping with 3, leached 24 h in dist. water 25° C, dried in air 70° C until transparent</td>
</tr>
<tr>
<td>5.</td>
<td>MINT - γ</td>
<td>films: from dipping with 3, a) unleached - b) leached in dist. water - c) 1h, d) 3h, e) 5h, f) 7h, g) 24h - dried in air</td>
</tr>
<tr>
<td>6.</td>
<td>MINT - γ</td>
<td>films: from dipping with sulphur-vulcan. latex (using S, ZnO, TMTD), prep. + treatment identical to 5</td>
</tr>
<tr>
<td>7.</td>
<td>JAERI - γ</td>
<td>raw latex, HA, diluted with 1% ammonia to TSC 50%</td>
</tr>
<tr>
<td>8.</td>
<td>JAERI - γ</td>
<td>formulated latex: 7, + 0.2 phr KOH + 5 phr nBA</td>
</tr>
<tr>
<td>9.</td>
<td>JAERI - γ</td>
<td>irradiated latex: 8, γ-irradiated with ±22 kGy, dose rate 11 kGy/h</td>
</tr>
<tr>
<td>10.</td>
<td>JAERI - γ</td>
<td>irradiated latex + antioxidant: 9, + 1 phr 16 (TNPP)</td>
</tr>
<tr>
<td>11.</td>
<td>JAERI - γ</td>
<td>films: from dipping with 9, dried in air-25° C, leached 24h with 1% ammonia, washed with deionized water, treated with 30 mg/l CaCO$_3$-sol.-20° C-20 min, air dried-25° C, air dried-80° C-1h.</td>
</tr>
<tr>
<td>12.</td>
<td>JAERI - γ</td>
<td>films: from dipping with 10, dried in air-25° C, leached 24h with 1% ammonia, washed with deionized water, treated with 30 mg/l CaCO$_3$-sol.-20° C-20 min, air dried-25° C, air dried-80° C-1h.</td>
</tr>
<tr>
<td>13.</td>
<td>JAERI - β</td>
<td>raw latex, DRC 60%</td>
</tr>
<tr>
<td>14.</td>
<td>JAERI - β</td>
<td>formulated latex: 13, diluted with 1% ammonia to DRC 50% + 0.25 phr BYK-022</td>
</tr>
<tr>
<td>15.</td>
<td>JAERI - β</td>
<td>irradiated latex: 14, irrd. with low energy E-beam-300 kV-40 mA-15 min.</td>
</tr>
<tr>
<td>16.</td>
<td>JAERI - β</td>
<td>TNPP: 50% emulsion by mixing sodium dodecyl sulphate polyvinylpyrrolidone with Tris (Nonylated Phenyl) Phosphite (antioxidant)</td>
</tr>
<tr>
<td>17.</td>
<td>JAERI - β</td>
<td>films: 15, mixed with TNPP, air dried-25° C until transparent, air dried-80° C-1h</td>
</tr>
<tr>
<td>18.</td>
<td>JAERI - β</td>
<td>films: 15, mixed with TNPP, dried in air-25° C until transparent, leached 1h with 1% ammonia, air dried treated with 30 mg/l CaCO$_3$-sol.-50° C-20min, air dried-25° C, air dried-80° C-1h</td>
</tr>
<tr>
<td>19.</td>
<td>JAERI - β</td>
<td>films: 15, Mixed with TNPP, dried in air-25° C until transparent leached 24h with 1% ammonia, air dried treated with 30 mg/l CaCO$_3$-sol.-50° C-20min, air dried-25° C, air dried-80° C-1h</td>
</tr>
<tr>
<td>20.</td>
<td>reference</td>
<td>Raw latex supernatant (Internal laboratory ref. 17793b)</td>
</tr>
<tr>
<td>21.</td>
<td>reference</td>
<td>Triflex Baxter (commercial glove)</td>
</tr>
<tr>
<td>22.</td>
<td>reference</td>
<td>Ansell Gammex (commercial glove)</td>
</tr>
</tbody>
</table>
Table 2: BCA assay of latex film extracts

<table>
<thead>
<tr>
<th>nr.</th>
<th>description</th>
<th>% CGI. ± md</th>
<th>5LDH. ± md</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>RVNRL glove</td>
<td>20.1 ± 16.0</td>
<td>-</td>
</tr>
<tr>
<td>5a</td>
<td>RVNRL film γ - unleached</td>
<td>40.5 ± 12.8</td>
<td>3.5 ± 2.6</td>
</tr>
<tr>
<td>5b</td>
<td>RVNRL film γ - leached 1h</td>
<td>21.7 ± 7.7</td>
<td>-0.9 ± 0.7</td>
</tr>
<tr>
<td>5c</td>
<td>RVNRL film γ - leached 3h</td>
<td>23.3 ± 9.3</td>
<td>-0.6 ± 1.2</td>
</tr>
<tr>
<td>5d</td>
<td>RVNRL film γ - leached 5h</td>
<td>23.1 ± 9.5</td>
<td>-1.8 ± 0.8</td>
</tr>
<tr>
<td>5e</td>
<td>RVNRL film γ - leached 7h</td>
<td>24.9 ± 7.0</td>
<td>-1.6 ± 0.8</td>
</tr>
<tr>
<td>5f</td>
<td>RVNRL film γ - leached 24h</td>
<td>23.1 ± 11.3</td>
<td>-2.1 ± 2.4</td>
</tr>
<tr>
<td>6a</td>
<td>SVNRL film - unleached</td>
<td>163.7 ± 19.1</td>
<td>11.1 ± 28.0</td>
</tr>
<tr>
<td>6b</td>
<td>SVNRL film - leached 1h</td>
<td>169.2 ± 17.8</td>
<td>26.6 ± 30.4</td>
</tr>
<tr>
<td>6c</td>
<td>SVNRL film - leached 3h</td>
<td>170.2 ± 8.0</td>
<td>25.8 ± 29.8</td>
</tr>
<tr>
<td>6d</td>
<td>SVNRL film - leached 5h</td>
<td>170.4 ± 19.8</td>
<td>31.6 ± 31.6</td>
</tr>
<tr>
<td>6e</td>
<td>SVNRL film - leached 24h</td>
<td>166.7 ± 17.7</td>
<td>35.1 ± 30.6</td>
</tr>
<tr>
<td>6f</td>
<td>SVNRL film - leached 24h</td>
<td>151.5 ± 22.0</td>
<td>42.8 ± 32.7</td>
</tr>
<tr>
<td>11</td>
<td>RVNRL film γ - no antioxidant</td>
<td>12.5 ± 4.6</td>
<td>-0.3 ± 1.1</td>
</tr>
<tr>
<td>12</td>
<td>RVNRL film γ - with antioxidant</td>
<td>24.8 ± 5.5</td>
<td>-0.5 ± 0.9</td>
</tr>
<tr>
<td>17</td>
<td>RVNRL film β - unleached</td>
<td>19.1 ± 3.6</td>
<td>-2.6 ± 2.4</td>
</tr>
<tr>
<td>18</td>
<td>RVNRL film β - leached 1h</td>
<td>22.6 ± 7.9</td>
<td>-1.2 ± 0.9</td>
</tr>
<tr>
<td>19</td>
<td>RVNRL film β - leached 24h</td>
<td>13.7 ± 5.1</td>
<td>-0.6 ± 1.0</td>
</tr>
<tr>
<td>21</td>
<td>SVNRL glove (commercial)</td>
<td>170.0 ± 3.6</td>
<td>85.1 ± 34.4</td>
</tr>
</tbody>
</table>

A graphical representation is made in Figure 1 and 2

Table 3: BCA assay of liquid samples

<table>
<thead>
<tr>
<th>nr.</th>
<th>description</th>
<th>mg/ml ± sd</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>raw latex MINT</td>
<td>11.9 ± 1.3</td>
</tr>
<tr>
<td>2</td>
<td>formulated latex MINT</td>
<td>13.0 ± 1.6</td>
</tr>
<tr>
<td>3</td>
<td>γ - irradiated latex MINT</td>
<td>12.5 ± 1.1</td>
</tr>
<tr>
<td>7</td>
<td>raw latex JAERI</td>
<td>8.0 ± 0.5</td>
</tr>
<tr>
<td>8</td>
<td>formulated latex JAERI</td>
<td>2.8 ± 0.8</td>
</tr>
<tr>
<td>9</td>
<td>γ - irradiated latex JAERI</td>
<td>10.6 ± 2.9</td>
</tr>
<tr>
<td>10</td>
<td>γ - irradiated latex JAERI + antiox.</td>
<td>8.5 ± 1.1</td>
</tr>
<tr>
<td>13</td>
<td>raw latex JAERI</td>
<td>10.2 ± 0.7</td>
</tr>
<tr>
<td>14</td>
<td>formulated latex JAERI</td>
<td>8.5 ± 2.1</td>
</tr>
<tr>
<td>15</td>
<td>β - irradiated JAERI</td>
<td>9.4 ± 1.4</td>
</tr>
<tr>
<td>20</td>
<td>raw latex lab. reference</td>
<td>3.0 ± 0.7</td>
</tr>
</tbody>
</table>
Table 4: BCA assay of latex film extracts

<table>
<thead>
<tr>
<th>nr.</th>
<th>description</th>
<th>μg/g latex ± sd</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>RVNRL glove</td>
<td>8.9 ± 0.9</td>
</tr>
<tr>
<td>5a</td>
<td>RVNRL film γ - unleached</td>
<td>109.0 ± 6.3</td>
</tr>
<tr>
<td>5b</td>
<td>RVNRL film γ - leached 1h</td>
<td>9.3 ± 0.7</td>
</tr>
<tr>
<td>5c</td>
<td>RVNRL film γ - leached 3h</td>
<td>9.6 ± 0.7</td>
</tr>
<tr>
<td>5d</td>
<td>RVNRL film γ - leached 5h</td>
<td>6.3 ± 0.4</td>
</tr>
<tr>
<td>5e</td>
<td>RVNRL film γ - leached 7h</td>
<td>6.5 ± 0.6</td>
</tr>
<tr>
<td>5f</td>
<td>RVNRL film γ - leached 24h</td>
<td>4.4 ± 0.4</td>
</tr>
<tr>
<td>6a</td>
<td>SVNRL film - unleached</td>
<td>117.7 ± 7.4</td>
</tr>
<tr>
<td>6b</td>
<td>SVNRL film - leached 1h</td>
<td>12.5 ± 0.6</td>
</tr>
<tr>
<td>6c</td>
<td>SVNRL film - leached 3h</td>
<td>9.2 ± 0.5</td>
</tr>
<tr>
<td>6d</td>
<td>SVNRL film - leached 5h</td>
<td>7.3 ± 0.2</td>
</tr>
<tr>
<td>6e</td>
<td>SVNRL film - leached 7h</td>
<td>5.8 ± 0.1</td>
</tr>
<tr>
<td>6f</td>
<td>SVNRL film - leached 24h</td>
<td>7.4 ± 0.1</td>
</tr>
<tr>
<td>11</td>
<td>RVNRL film γ - no antioxidant</td>
<td>8.6 ± 0.4</td>
</tr>
<tr>
<td>12</td>
<td>RVNRL film γ - with antioxidant</td>
<td>5.9 ± 1.3</td>
</tr>
<tr>
<td>17</td>
<td>RVNRL film β - unleached</td>
<td>40.2 ± 3.5</td>
</tr>
<tr>
<td>18</td>
<td>RVNRL film β - leached 1h</td>
<td>5.6 ± 0.2</td>
</tr>
<tr>
<td>19</td>
<td>RVNRL film β - leached 24h</td>
<td>5.9 ± 0.1</td>
</tr>
<tr>
<td>21</td>
<td>SVNRL glove (commercial)</td>
<td>60.4 ± 18.4</td>
</tr>
<tr>
<td>22</td>
<td>SVNRL glove (commercial)</td>
<td>140.3 ± 11.0</td>
</tr>
</tbody>
</table>

DISCUSSION

From the cytotoxicity tests it is obvious that the absence of the chemicals in the products is of great influence. Although the clinical relevance of cytotoxicity testing is not clearly established, the low values found in the two tests for the RVNRL materials in contrast to the high values for SVNRL materials provide a good indication that also clinically problems caused by chemicals, like Type IV allergies, will be greatly reduced in RVNRL materials in comparison to SVNRL materials.

The great difference in cytotoxic potency of the two types of vulcanised NRL was visible in both tests, although it was more distinct in the CGI assay. This can be explained by the fact, that in the LDH assay the cytotoxic effect is measured only by the parameter membrane damage. With the CGI assay a total effect is determined, which means also influences on the cell metabolism are measured.

The kind of radiation that was used to vulcanise the RVNRL materials (γ or B) does not seem to have a considerable influence with regard to the cytotoxicity characteristics of the materials, except for the fact that the latter were already low cytotoxic before leaching. The same values of cytotoxicity were found with both types of radiation.

From the series of gamma-vulcanised films with different leaching times (samples 5a-5f) it becomes clear that leaching is very important, but the effect is already completely reached after a 1 hour leaching time.

With regard to the protein testing the two types of vulcanised materials scored similar results. Both total protein determinations and SDS-PAGE assays show very distinctly that in order to obtain lower levels of protein content the most important factor is the leaching of the final products. Both the RVNRL and the SVNRL materials contained a considerable amount of extractable proteins before leaching, while after leaching only a low level of extractable proteins was left. The levels had the same order of magnitude for both types of material.
As was found for the cytotoxic potency, the biggest part of the leaching effect on extractable protein contents was also reached in the first hour of leaching. However, results from the SDS-PAGE assays indicate that the leaching process is not always equally effective. Even in 24 hours leached gloves, as well as in one hour leached films, protein bands could be determined.

The two commercial gloves that were included in the protein assays, which both had high amounts of extractable proteins, cannot be considered representative for the commercial SVNRL gloves that are currently available. Manufacturers have adjusted the processing of their gloves considerably over the last few years, which has resulted in reports of many glove types that contain low levels of extractable proteins. Recent testing at the RIVM showed that gloves of the same brand and type are now much better in this respect than three years ago (unpublished results).

The results of the immunoassays on the liquid samples are very interesting since after radiation no allergenic reaction was measured. However, given the fact that in this (unduplicated) test series the controls reacted relatively weakly, and the fact that, although only in preliminary testing with one older serum, allergenic reactions were found in extracts from products made from this irradiated latex, as well as in the irradiated latex itself, this result should not be overestimated.

**CONCLUSION**

The absence of the accelerators that are necessary for sulphur vulcanisation RVNRL products results in a great reduction of the cytotoxicity if the products are compared with SVNRL products that were processed in the same way. This is an indication that RVNRL products will also cause less Type IV allergy. It is, however, important that the products are leached after the final processing stage.

Irradiation does have a destructive effect on NRL proteins. However, not all proteins are destroyed and the remaining ones are probably still able to provoke Type I allergic reactions. When compared with the SVNRL products, no significant difference in extractable protein contents could be established. It was clearly shown that, to an even greater extent than with regard to cytotoxicity, effective leaching of the producers is essential.
ACKNOWLEDGEMENTS

Dr. Makuuchi of the Japan Atomic Research Institute, and Dr. Wan Manshol of the Malaysian Institute for Nuclear Technology are kindly thanked for the provision of RVNRL samples. Dr. Stevens of the University Hospital in Leuven is kindly thanked for the provision of serum from latex allergic patients.

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Proceeding Regent International Symposium “Glove Powder” - The hazards which demand a ban” London, 18 May 1996. To be published


Figure 1: Cell Growth Inhibition
Figure 3: BCA assay of liquid samples
Figure 4: BCA assay of latex film extracts
Figure 5: SDS-PAGE analysis - 1. marker; 2. raw latex; 3. formulated latex; 4. gamma-irradiated latex; 5. marker; 6. raw latex; 7. formulated latex; 8. gamma-irradiated latex; 9. marker; 10. gamma-irradiated latex with antioxidant; 11. raw latex; 12. formulated latex; 13. marker; 14. E-beam-irradiated latex; 15. laboratory reference. raw latex 20.
STUDYING THE ALLERGICABILITY OF PROTEINS IN DRIED LATEX FILMS VULCANIZED BY RADIATION

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The Nuclear Research Institute, Dalat
13 Dinh Tien Hoang, DALAT, VIETNAM

ABSTRACT

The nitrogen content in dried latex films after leaching in various media has been determined. The amount of protein in leached rubber films was evaluated in the 0.9% saline solution. Electrophoretic analysis of proteins from the saline extracts of dried latex films, which were vulcanized by gamma-rays of Co-60 at the 25 kGy absorption dose using n-butyl acrylate as a sensitizer, was also carried out. The pyrogenic tests on rabbit were examined. From the experimental results, it was concluded that the applications of RVNRL films are safe for end-users, and it was indicated that either surfactant or diluted alkaline solution was one of the best media to treat soluble proteins from rubber films due to their skin allergicabilities.

INTRODUCTION

Latex specific protein can cause immediate-type cutaneous, nasal, brochial, and systematic reactions. The latex allergen appears to be a mixture of proteins in a molecular weight-range from 10 - 67 kd (Jaeger et al. 1992). Protein has been reported to have some undesirable effects on natural rubber properties, rubber containing protein gave no significant effect on cured characteristics. Protein and some amino-acids tended to some improvements in properties such as modulus, heat build-up and stress-relaxation compared to purified natural rubber. The non-rubber substances accounted for 3% - 5%, of which 3% was made up of proteins. Some of the soluble serum protein would be washed away during coagulation and processing of latex, but a large proportion of them would be retained in the rubber (Othman et al. 1988). The protein content of field latex was around 1% of the weight of field latex. About 20% of the protein was absorbed on the rubber particles, the remainder was in the serum phase (Nadarajah 1991).

PROCEDURE

Material and methods

Natural rubber latex (NRL) was irradiated at an absorbed dose of 25 kGy with 2.5 parts of hundred rubber (phr) of n-butyl acrylate (n-BA) sensitizer using Co-60 Gamma Source at BATAN, Indonesia. Films from the irradiated NRL called RVNRL were leached overnight in the following media: sodium lauryl sulphate (LSNa), ammonia (NH₄OH), chloric acid (HCl), acetic acid (CH₃COOH), sodium hydroxide (NaOH), distilled water (H₂O), ethylic alcohol (EtOH), detergent, polyethylene glycol (PE-6000), quartamin, sodium chloride (NaCl), sulphuric acid (H₂SO₄). And chemicals used were tricine buffer, agar, albumin, Na₂CO₃, CuSO₄, potassium tartrate, Folin reagent, etc.
**Determination of nitrogen content**

Around 1 g of leached rubber films was used for this test. Nitrogen content of the RVNRL films after leaching in different media was determined according to method of testing rubber nitrogen content (D 3533-82) on specifications (E-147) for apparatus for micro-determination of nitrogen by Kjeldahl method, ASTM standards.

**Protein assay**

About 5 g of leached rubber films was immersed in 50 mL of 0.9% saline solution for 48 hrs. The protein concentration of the 0.9% saline extract of the RVNRL films after leaching in various media was detected according to the Lowry method with albumin as a standard reagent and using spectrophotometer (KOK-2-T 4.2, USSR).

**Electrophoretic analysis**

Approximately 10 g sample was extracted with slight shake in 2% saline solution for 24 hrs. Electrophoresis was performed with the 2% saline protein extract of leached and unleached RVNRL films using a gradient of 2% agar and tricine buffer (Bio-Rad Laboratory) at a 15 mA current intensity for using Bio-Rad electrophoretic apparatus. This test was carried out with low, average, high protein contained extracts from the leached RVNRL films.

**Pyrogenic tests on rabbit**

About 1 mL of 0.9% saline extract from protein contained RVNRL films leached in some media with low, average, high residual soluble protein content in saline solution was diluted into 5 mL by distilled water, pasteurized at 125°C, 1 atm, for 30 min. and then directly injected into intravenousness of 2 kg weighed rabbit. The tested rabbits were controlled by change of temperature in time.

**RESULTS AND DISCUSSION**

Figure 1 shows relations between 0.9% saline extracted protein contents and concentration of various leaching media. It was noted that protein extracted in 0.9% saline solution was the least when RVNRL films was first leached in 1% ammonia or 1% NaOH solution. It meant that alkaline media such as NaOH, NH₄OH were either the best ones to remove proteins from the rubber films or the media, which effected on deformation of the protein structure. So the media had made proteins insoluble in 0.9% saline solution. Subsequently surfactant reagent like quartamin, LSNa, detergent, etc. were at an average level, and eventually acetic acid, EtOH, PE-6000 and HCl were at a higher. In fact, at any HCl concentrations, there was no change in extracted protein content.
Figure 1. Relationship between soluble protein content in saline and concentration of various leaching media.

Figure 2 shows relations between insolubly residual nitrogen content including proteins, amino-acids, and nitrogen-containing components after leaching in different media and concentration of washing media. At a 1.0% lower concentration of the leaching media, detergent or HCl solution were considered as there be insoluble nitrogen content remained at a low level.

Figure 2. Relationship between residual nitrogen content after leaching and concentration of washing media.
On the contrary, diluted EtOH or acetic acid existed a high-level retained nitrogen content. At any concentrations of the alkaline solutions, remain nitrogen content seemed to be unchangeable. In addition, the other surfactant solution had an average-level unleached nitrogen content. It was explained that diluted HCl or detergent solution could be used to release effectively nitrogen contained components from RVNRL films in comparison with distilled water and some other solutions due to these medium compatibilities that did not cause the deformation of structure of the nitrogen-containing components. In fact, in this test, it is recognized that the deformation of protein structure has occurred when RVNRL films were leached in alkaline media.

Figure 3 shows effect of temperature on solubly residual protein and unleached nitrogen content in distilled water. It was clear that 0.9% saline protein extract increased with increasing temperature of leached distillation water for 2 hrs, but the higher 60°C extracted protein content dropped. It was due to modification and shrinkage of specific protein molecules when the temperature of the leaching media was over 60°C. It was also shown in Figure 3 that at 60°C residual nitrogen content obtained a relatively low value. That temperature could be suitable one to get nitrogen substances off RVNRL films.

Figure 4 shows effect of the leaching time in distilled water on 0.9% saline soluble protein content and residual nitrogen content. It could be said that the leaching time of about 15 hrs at room temperature was appropriate one to remove protein contained comoponents from RVNRL films. Insolubly residual nitrogen
content in this experiment was very low in comparison with to unleaching sample. And 0.9% saline protein extract minimized for 15 hour leaching time at ambient temperature.

![Graph showing the effect of leaching time on soluble protein content in saline solution and residual nitrogen content.](image)

Figure 4. Effect of the leaching time on soluble protein content in saline solution and residual nitrogen content.

Figure 5 shows tris-agar gel electrophoresis of soluble protein extract in 0.9% saline solution from primarily leaching RVNRL films with 2% agar. It was found that all soluble extract did not resolve into distinct bands. Especially no trace appeared using the 0.9% saline protein extract from RVNRL films leached in ammonia solution.

![Image of tris-agar gel electrophoresis](image)

Figure 5. Tris-agar gel electrophoresis of soluble protein extract in 0.9% saline after leaching in various media.

**Note:**

- a. Acetic acid precipitated NRL extract.
- b. Acetic acid precipitated 2.5 Mrad RVNRL extract.
- c. LSNa leached 2.5 Mrad RVNRL film extract.
- d. Unleached NRL film extract.
e. 2.5 Mrad RVNRL film extract after leaching in distilled water.  
f. 2.5 Mrad RVNRL film extract after leaching in ammonia.

Table 1. Pyrogenic test results in rabbits

<table>
<thead>
<tr>
<th>Time, hr</th>
<th>Rabbit 0</th>
<th>Rabbit 1</th>
<th>Rabbit 2</th>
<th>Rabbit 3</th>
<th>Rabbit 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>38.85</td>
<td>38.80</td>
<td>38.70</td>
<td>39.00</td>
<td>38.90</td>
</tr>
<tr>
<td>1</td>
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<td>39.00</td>
<td>39.50</td>
<td>39.30</td>
<td>39.95</td>
</tr>
<tr>
<td>2</td>
<td>39.10</td>
<td>39.20</td>
<td>39.40</td>
<td>39.70</td>
<td>40.50</td>
</tr>
<tr>
<td>3</td>
<td>38.90</td>
<td>39.40</td>
<td>39.60</td>
<td>39.60</td>
<td>40.60</td>
</tr>
<tr>
<td>5</td>
<td>39.20</td>
<td>39.50</td>
<td>39.40</td>
<td>39.80</td>
<td>39.80</td>
</tr>
<tr>
<td>7</td>
<td>39.00</td>
<td>39.30</td>
<td>39.20</td>
<td>39.70</td>
<td>39.50</td>
</tr>
<tr>
<td>9</td>
<td>39.10</td>
<td>39.20</td>
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<td>39.60</td>
</tr>
<tr>
<td>22</td>
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<td>39.20</td>
<td>39.30</td>
<td>39.20</td>
<td>39.40</td>
</tr>
<tr>
<td>24</td>
<td>39.20</td>
<td>39.10</td>
<td>39.00</td>
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<tr>
<td>27</td>
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<td>39.00</td>
<td>39.05</td>
<td>39.20</td>
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</tr>
<tr>
<td>31</td>
<td>39.10</td>
<td>39.00</td>
<td>39.10</td>
<td>39.50</td>
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<tr>
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</tr>
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<td>48</td>
<td>38.90</td>
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<td>39.10</td>
<td>39.20</td>
<td>39.50</td>
</tr>
<tr>
<td>53</td>
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<td>39.10</td>
<td>39.20</td>
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<td>39.50</td>
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<td>60</td>
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<td>73</td>
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<td>38.90</td>
<td>39.05</td>
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<tr>
<td>96</td>
<td>39.00</td>
<td>39.00</td>
<td>39.00</td>
<td>39.10</td>
<td>39.00</td>
</tr>
</tbody>
</table>

Average temperature

<table>
<thead>
<tr>
<th>Rabbit 0</th>
<th>Rabbit 1</th>
<th>Rabbit 2</th>
<th>Rabbit 3</th>
<th>Rabbit 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>39.03</td>
<td>39.13</td>
<td>39.19</td>
<td>39.33</td>
<td>39.53</td>
</tr>
</tbody>
</table>

Note:
- Rabbit 0 for reference rabbit
- Rabbit 1 for rabbit injected by the extract of the RVNRL film leached in 1% ammonia
- Rabbit 2 for that leached in 0.1% detergent
- Rabbit 3 for that leached in 0.5% PE.6000
- Rabbit 4 for that leached in 1% HCl

Table 1 shows pyrogenic test results in rabbits. Rabbit body temperature observed from 0-96 hrs revealed that the rabbit should be pyrogenic due to unleached RVNRL films with 0.5°C difference if compared to reference rabbit. However, distilled 0.9% saline protein extract with changeably selected protein content from 0.007 mg/g to 0.3 mg/g after rubber samples leached or unleached in some washing media to be considered as solubly or insolubly deformed protein within a low average distribution range, especially in ammonia solution, the rabbit body temperature seems to be normal. Rabbit 4 shows that rabbit body temperature increased from 38.9°C to 40.5°C due to injection of 0.9% saline soluble protein extract from RVNRL films leached in 1% HCl solution after the injection conducted 2-3 hrs. It could be said that after completion of leaching in HCl solution, the soluble protein which was higher than that of other media, could be extracted in 0.9% saline. But no pyrogenic symptom should be attributed to soluble remained protein in RVNRL films. The tested rabbits look like to have a good physical strength.
CONCLUSION

From experimental results, it was concluded that the best treatment media for RVNRL films are either diluted alkaline solution, because the media could make deformation of the protein structure to limit an remarkable amount of soluble protein released and leach a part of soluble protein from RVNRL films, or neutral surfactant solution which could dissolve and reduce soluble protein existence before use of the product from RVNRL. It was anticipated that specific latex protein should cause allergy for the users, if the RVNRL films or their dipping products were not reasonably, fully treated.

ACKNOWLEDGEMENT

We would like to thank Dr Tran Tich Canh, Chief of the Radiation Processing Department, Dr Le Van Khoi, Director of the Centre for Nuclear Techniques, Hochiminh City, Vietnam, for permitting to present this paper.

REFERENCES


DETERMINATION OF SOLUBLE PROTEIN CONTENTS FROM RVNRL

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ABSTRACT

This project was carried out to determine the soluble protein contents on RVNRL film vulcanisates, with respect to the RVNRL storage time, gamma irradiation dose absorbed by the latex and the effect of different leaching time and leaching conditions. These three factors are important in the hope to determine the best possible mean of minimizing the soluble protein contents in products made from RVNRL. Within the nine months storage period employed in the study, the results show that, the longer the storage period the less the soluble protein extracted from the film samples. Gamma irradiation dose absorbed by the samples, between 5.3 kGy to 25.2 kGy seems to influence the soluble protein contents of the RVNRL films vulcanisates. The higher the dose the more was the soluble protein extracted from the film samples. At an absorbed dose of 5.3 kGy and 25.2 kGy, the soluble contents were 0.198 mg/ml and 0.247 mg/ml respectively. At a fixed leaching temperature, the soluble proteins increases with leaching time and at a fixed leaching time, the soluble proteins increases with leaching temperature. The highest extractable protein contents was determined at a leaching time of 10 minutes and leaching temperature of 90°C. The protein analysis were done by using Modified Lowry Method.

INTRODUCTION

Over the last eight years or so, a number of papers have reported cases of contact urticaria (Kopman, A., Hannuksela, M., 1983), anaphylactic shock and related responses on exposure to dipped latex products (Turjanmaa, K. Reunala, T. Tuimala and Karkkainen, 1984). These reported cases were known as Type I response for allergic reaction to latex products due to the presence of soluble protein.

Several methods were used to reduce the extractable protein contents of dipped latex products were reported (Faridah Yusof and Yeang, H.Y., 1992). These include the introduction of low protein, deproteinised latex to the latex based dipped product industries.

In this study, the potential of RVNRL (Radiation Vulcanised Natural Rubber Latex) is being exploited. This paper described the results of the determination of soluble protein contents from RVNRL film vulcanised with respect to the effect of different storage periods on RVNRL, the γ-irradiation dose absorbed by the latex and the effect of different leaching treatments, leaching time and leaching temperature.

MATERIALS AND METHODS

Materials

Latex used in these studies was of a high ammonia type. Proteins analysis were determined according to Modified Lowry Method. The standard used was Lowry Micro D.C. Protein Assay supplied by Bio-Rad Laboratories USA. The concentration of protein were determined at 570 nm by using UV-Spectrophotometer. The latter was calibrated using Didymium and Holmium Filter Type II supplied by Pye Unicam Ltd. Cambridge, England.
Methods

The studies were carried out on RVNRL film vulcanisates prepared by coagulant dipping method. The first set of studies were to see the effects of the storage periods of between 0 to 9 months on the soluble protein contents of RVNRL film vulcanisates and unirradiated latex films.

The second set of studies were to determine the effect of irradiation dose of between about 5 kGy to 25 kGy on the extractable proteins from their film vulcanisates. In this study, a set of film vulcanisates were initially leached in distilled water at 60°C for a period of 5 minutes, and another set of sample were leached under the similar conditions for 10 minutes. Leached samples were dried in an air convection oven at 70°C until transparent, before they were subjected to protein extraction by using phosphate buffer saline as the solvent. The amount of soluble proteins were determine from the solvent and the results are presented in Table 2. Their graphical representations are given in Figure 2. The studies were repeated by changing the leaching times to 5, 10, 15 and 30 minutes, but using RVNRL prepared at an irradiation dose of 12 kGy. The results are given in Table 3.

The third set of studies were to determine the effect of leaching temperature, 30°C, 60°C and 90°C on the soluble protein contents of RVNRL film vulcanisates. The leaching time used was 5 and 10 minutes. The results are given in Table 4 and their graphical representation are given in Figure 3.

In the three sets of studies, the samples which were initially leached by the conditions described above were dried in an air convection oven before they were finally leached in phosphate buffer saline for 3 hours. The final protein contents of the samples were analysed from the phosphate buffer solvent.

RESULTS AND DISCUSSIONS

Table 1: Effects of The Storage Periods Within 9 Months on The Soluble Proteins

<table>
<thead>
<tr>
<th>Time (Months)</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Latex</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L1</td>
<td>0.38</td>
<td>0.31</td>
<td>0.30</td>
<td>0.29</td>
<td>0.25</td>
<td>0.24</td>
<td>0.10</td>
<td>0.07</td>
<td>0.05</td>
<td>0.03</td>
</tr>
<tr>
<td>L2</td>
<td>0.04</td>
<td>0.07</td>
<td>0.08</td>
<td>0.09</td>
<td>0.11</td>
<td>0.16</td>
<td>0.15</td>
<td>0.13</td>
<td>0.11</td>
<td>0.10</td>
</tr>
<tr>
<td><strong>RVNRL</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L1</td>
<td>0.30</td>
<td>0.38</td>
<td>0.40</td>
<td>0.30</td>
<td>0.22</td>
<td>0.18</td>
<td>0.13</td>
<td>0.08</td>
<td>0.08</td>
<td>0.05</td>
</tr>
<tr>
<td>L2</td>
<td>0.03</td>
<td>0.04</td>
<td>0.04</td>
<td>0.05</td>
<td>0.04</td>
<td>0.03</td>
<td>0.02</td>
<td>0.01</td>
<td>0.009</td>
<td>0.007</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSIONS

From Table 1, in general the soluble protein from RVNRL film vulcanisates and unirradiated latex films were found to increase with storage times. The reason was not known for certain. However, there is a possibility that the long polypeptides chain which were initially broken down during the latex irradiation stage finally reform with storage times.

The soluble protein obtained from the samples leached in distilled water at 60°C for 3 minutes shown that the soluble protein contents from unirradiated latex decreases with storage periods. Under similar treatment, the soluble protein contents determined on RVNRL film vulcanisates were found to increase with storage time of up to 3 months before started to decrease again. See the results given in Table 1 as L1. Further extractions of proteins from the samples using phosphate buffer saline as solvent, it was found that the soluble proteins from unirradiated latex increases with storage periods of up to 5 months before started to decrease again, and RVNRL has shown the increased in soluble protein contents up to 3 months storage periods before started to decrease again. These results are given in Table 1 as L2.

Table 2 : The Effects of Irradiating The Latex To Different Doses on The Amount of Soluble Protein Contents

<table>
<thead>
<tr>
<th>Dose, kGy</th>
<th>Soluble protein contents (mg/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5 minutes leached</td>
</tr>
<tr>
<td>5.3</td>
<td>0.022</td>
</tr>
<tr>
<td>6.0</td>
<td>0.029</td>
</tr>
<tr>
<td>9.3</td>
<td>0.043</td>
</tr>
<tr>
<td>12.0</td>
<td>0.053</td>
</tr>
<tr>
<td>13.0</td>
<td>0.058</td>
</tr>
<tr>
<td>15.0</td>
<td>0.064</td>
</tr>
<tr>
<td>19.0</td>
<td>0.075</td>
</tr>
<tr>
<td>25.2</td>
<td>0.078</td>
</tr>
</tbody>
</table>
Table 3: Effects of Leaching Times on The Soluble Protein Contents of a Latex Irradiated at 12.0 kGy

<table>
<thead>
<tr>
<th>Leaching time, (mins)</th>
<th>Soluble protein contents (mg/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.053</td>
</tr>
<tr>
<td>10</td>
<td>0.047</td>
</tr>
<tr>
<td>15</td>
<td>0.035</td>
</tr>
<tr>
<td>30</td>
<td>0.025</td>
</tr>
</tbody>
</table>

From Table 2 and Figure 2, the results show that within the irradiation dose employed in the studies, the soluble protein contents increased as the irradiation dose increased. Similar trend of results were shown by both sets of samples leached for 5 and 10 minutes. However, the set of sample initially leached for 10 minutes have the lower extractable proteins.

As shown in Table 3, the extractable protein from a sample reduced as the initial leaching time increased. At a fixed leaching time, the soluble protein contents increased with irradiation dose. The increase in irradiation dose probably increase the breaking of polypeptides chain making it more soluble and easy to leach. Therefore, increased in soluble protein contents were observed.

Table 4: Effect of Leaching Temperature and Time on The Amount of Soluble Protein Contents

<table>
<thead>
<tr>
<th>Leaching time (min.)</th>
<th>Leaching temp. (°C)</th>
<th>Soluble protein contents (mg/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>30</td>
<td>0.061</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.048</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>0.028</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>0.051</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.037</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>0.021</td>
</tr>
</tbody>
</table>
As shown in Table 4 and Figure 3, at a fixed leaching time, 5 minutes the amount of soluble proteins extracted from the samples were influenced by the leaching temperature. The higher the leaching temperature, the lower was the remaining protein contents in the samples. These were exhibited by the decrease in the soluble protein determined on the phosphate buffer saline used.

Similar results were observed for the sample leached for 10 minutes. From these results, leaching temperature is an important parameter in reducing soluble protein level from products made from RVNRL. The function of the temperature is to activate the molecule chain of the polyisoprene molecules and hence open up the opportunity for the remaining protein to be leached out from the samples.

CONCLUSIONS

From the results of this studies carried out so far, the following conclusions are made:

1. Soluble protein contents of RVNRL film vulcanisates are influenced by many factors including the storage periods of the RVNRL, dose employed in the latex irradiation stage as well as the leaching parameters.

2. RVNRL seems to exhibit high value of soluble protein contents. Proper leaching will help to reduce the proteins in any products made from it.

3. RVNRL is a potential material for latex based industry at this point in time.
ACKNOWLEDGEMENT

The authors are grateful to their co-workers in Rubber Processing Group in MINT for their excellent effort in making this project a success. The authors are also grateful to the Malaysian Government for providing generous fund for this project under the IRPA programme.

REFERENCES


STATUS OF RVNRL IN GERMAN LATEX INDUSTRY AND ITS INTRODUCTION TO THE EUROPEAN MARKET

Willfried Bez
Kautschuch - Gesellschaft mbH
Frankfurt, Germany.

ABSTRACT

Reasons to look for an alternative crosslinking system avoiding sulphur curing was the restrictive policy of the German Health Authorities concerning nitrosamines. It was concluded that radiation curing offers further advantages. By avoiding the accelerators, type IV allergy is excluded, cytotoxicity is minimised to a very low level, films have better clarity and when thoroughly leached higher electrical resistance. Treatment of waste gives no SO\textsubscript{2} emissions by burning, no Zn in the ashes and possibly better microbial degradation. A development was carried out to irradiate natural latex by electron beam with a Dynamitron equipment. It was found trimethylolpropanetrimethacrylate to be a suitable sensitizer. Because of high prices this development was interrupted.

For future application trials and efforts to introduce RVNRL in the market gamma ray radiated natural latex either from Batan, Indonesia or MINT, Malaysia are used. Mainly dipped goods were produce, but radiated natural latex has shown good results in other processes.

During discussions with customers it has proved necessary to establish specifications for RVNRL. A serious problem using natural latex for the production of medical devices is the type I allergy. Attempts are made to dip surgical gloves, leach them thoroughly and control extractable proteins were reduced to the very low level of 6.5 \mu g/g. Out of 18 patients sensitive to natural latex protein wearing gloves made from RVNRL only six have shown a positive response. That means RVNRL could help to solve the protein allergy problem. Further developments on this line are scheduled.

INTRODUCTION

One reason to look for an alternative crosslinking system avoiding sulfur curing was the restrictive policy of the German Health Authorities concerning nitrosamines in latex dipped teats (Bundesgesetzblatt, 1981).

As generally known dithiocarbamates used as accelerators in curing processes cause the formation of nitrosamines. Other possibilities to cure rubber in latex is a carbon-carbon crosslinking either by peroxides or by radiation. We started developments to radiate natural rubber latex by electron beam (W. Bez, 1995).

The last stage of these experiments was conducted with an equipment to radiate the latex continuously in 300 kg batches. We found trimethylolpropanetrimethacrylate to be an effective sensitizer, low in odour and low in skin irritation. Other findings were lower crosslinking dose by increasing the amount of non-rubbers. So we got higher tensile strength using evaporated latex concentrates, having higher non-rubbers, especially higher protein content.

Further advantages of RVNRL-films are the avoidance of type IV allergy, caused mainly by the accelerators, no problems with MBT, which is under attack by the Health Authorities, less toxicity, better clarity of films, no SO\textsubscript{2} emissions burning waste, probably better microbial degradation of waste and leached films having higher electrical resistance.
Because of these advantages the German latex using industry was very interested in this development, and we made trials with this electron beam crosslinked natural rubber latex in a number of different applications.

Best results we obtained in the dipping industry. That means production of teats, toys, balloons, condoms, household-gloves but as well medical devices like surgical gloves, examination gloves, catheders and medical tubes.

Advantages were also seen in the productions of cork soles because of a better appearance. We could convince one customer producing urinal condoms to use RVNRL. This company was the only one employing radiated natural rubber latex over a period of more than one year.

Because of the too high investment costs we stopped the development of radiation process by electron beam.

Following up we obtained gamma ray radiated latex from Batan, Indonesia. But we run into problems concerning constant quality and clean packing.

In a discussion the following parameters as specifications for RVNRL were agreed upon from Batan and our customer, see table 1.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total solids, %</td>
<td>&gt; 59.0</td>
</tr>
<tr>
<td>Dry rubber content, %</td>
<td>&gt; 58.0</td>
</tr>
<tr>
<td>Total alkalinity, %</td>
<td>&gt; 0.6</td>
</tr>
<tr>
<td>KOH number</td>
<td>&lt; 0.8</td>
</tr>
<tr>
<td>Coagulum content, %</td>
<td>&lt; 0.08</td>
</tr>
<tr>
<td>Mechanical stability, sec.</td>
<td>&gt; 650</td>
</tr>
<tr>
<td>VFA number</td>
<td>&lt; 0.2</td>
</tr>
<tr>
<td>Tensile strength, MPa</td>
<td>20.0</td>
</tr>
<tr>
<td>Elongation at break, %</td>
<td>&gt; 750</td>
</tr>
<tr>
<td>Modulus 500 %, MPa</td>
<td>2 - 3</td>
</tr>
<tr>
<td>Modulus 700 %, MPa</td>
<td>8 - 13</td>
</tr>
</tbody>
</table>

Since three years we coordinated further market activities with MINT, mainly because of their decision to construct production equipment for higher amounts of RVNRL.

The situation now in Europe concerning the natural latex consuming industry are intensified regulations, MBT as an accelerator attacked and the level of nitrosatables reduced to 100 ppb.

A further serious problem, especially in the medical field, is the type I allergy. This allergy is caused by the proteins of the natural rubber latex injuring the immune system which brings about a condition of hypersensitivity known as anaphylaxis. On subsequent exposure, the interaction of the allergen with the antibody formed in the sensitizing phase, culminates through a complex mechanism in a systemic release of histamine and other amines. The main effect of histamine in the circulation is to dilate the peripheral vessels, with a consequent severe fall in blood pressure and anaphylactic shock. Consequences are speeding of the heart rate and breathing difficulty (S.J. Dalrymple and B.G. Audley, 1992).
Because approximately 3% of hospital employees and 5 - 10% of physicians and nurses working in operation units are allergic to natural rubber latex, a solution of this problem has a very high priority.

Films prepared from irradiated natural rubber latex give a very high level of extractable protein. We suppose that the proteins during the radiation process are changed and therefore are more soluble. To follow up this idea surgical gloves were produced from RVNRL, thoroughly leached and tested for allergy response.

EXPERIMENTAL

Production of gloves
To produce gloves, porcelain formers were heated for 15 minutes to 120° C, then immersed in a 15% aqueous Ca(NO₃)₂ solution, dried at room temperature and after that dipped in the RVNRL. Beading was done before a wet gel leaching for 5 minutes and then drying 15 minutes at 120° C. After stripping the gloves were leached for 24 hours in flowing tap water. The last treatment before final drying was a washing process for 15 minutes at 40° C with a 0,2% Savinase 16.0 LNR solution.

Clinical tests
Clinical tests were carried out in the Dermatologische Klinik at the University of Erlangen. 18 patients who are diagnosed to have immediate type allergy to natural rubber latex proteins were tested by prick test and observation after 20 and 40 minutes and by wearing the gloves during several hours. For the prick test aqueous extracts as well as films of gloves were used. The latex itself was high speed centrifuged and the obtained serum controlled. Prick tests were classified correspond to severity of response from 1 to 4.

Extractable proteins
Extractable proteins were determined by a modified Lowry method - EN 455.

RESULTS AND DISCUSSION

As can be seen from table 2, extractable proteins in RVNRL gloves were reduced after leaching to the very low level of 16 µg/g and after a final enzyme treatment to a very minimum of 6.5 µg/g.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Extractable proteins</th>
</tr>
</thead>
<tbody>
<tr>
<td>After dipping</td>
<td>1000 µg/g</td>
</tr>
<tr>
<td>After wet gel leaching</td>
<td>850 µg/g</td>
</tr>
<tr>
<td>After 24 h leaching</td>
<td>16 µg/g</td>
</tr>
<tr>
<td>After enzyme treatment</td>
<td>6.5 µg/g</td>
</tr>
</tbody>
</table>
From the 18 sensitive patients wearing the RVNRL gloves during a period of several hours only six showed a positive response, see table 3.

### Table 3: Glove Wearing Trials

<table>
<thead>
<tr>
<th>Sample</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>positive</td>
</tr>
<tr>
<td>2</td>
<td>negative</td>
</tr>
<tr>
<td>3</td>
<td>negative</td>
</tr>
<tr>
<td>4</td>
<td>negative</td>
</tr>
<tr>
<td>5</td>
<td>negative</td>
</tr>
<tr>
<td>6</td>
<td>negative</td>
</tr>
<tr>
<td>7</td>
<td>positive</td>
</tr>
<tr>
<td>8</td>
<td>negative</td>
</tr>
<tr>
<td>9</td>
<td>positive</td>
</tr>
<tr>
<td>10</td>
<td>positive</td>
</tr>
<tr>
<td>11</td>
<td>negative</td>
</tr>
<tr>
<td>12</td>
<td>positive</td>
</tr>
<tr>
<td>13</td>
<td>negative</td>
</tr>
<tr>
<td>14</td>
<td>negative</td>
</tr>
<tr>
<td>15</td>
<td>negative</td>
</tr>
<tr>
<td>16</td>
<td>negative</td>
</tr>
<tr>
<td>17</td>
<td>positive</td>
</tr>
<tr>
<td>18</td>
<td>negative</td>
</tr>
<tr>
<td>19</td>
<td>negative</td>
</tr>
</tbody>
</table>

Obviously the proteins in natural latex concentrates are changed during the radiation process and are after that more soluble. A thorough leaching reduces extractable proteins and with this response to type I allergy. An enzyme treatment diminishes proteins further to an extremely low level, but it must be considered that enzymes can also be the reason for allergy.

In the prick tests of latex serum compared to normal centrifuged latex, RVNRL showed only a slight reduced response. But extracts and films of RVNRL gloves reduced the response significantly compared to sulfur cured products. A reduction of response is also obtained by powder free gloves, that means chlorinated articles, see table 4 and table 5.

### Table 4: Summary of Prick-Tests from 18 Patients after 20 Minutes

<table>
<thead>
<tr>
<th></th>
<th>Frequency of prick-tests</th>
<th>Average value</th>
<th>Response value %</th>
<th>Protein concentrate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 1 2 3 4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Natural latex serum</td>
<td>0 0 0 4 14</td>
<td>3.78</td>
<td>100</td>
<td>1100 µg/g</td>
</tr>
<tr>
<td>RVNRL serum</td>
<td>1 0 1 3 13</td>
<td>3.50</td>
<td>94.4</td>
<td>N.D</td>
</tr>
<tr>
<td>Extract of RVNRL gloves</td>
<td>10 3 4 1 0</td>
<td>0.78</td>
<td>44.4</td>
<td>6.8 µg/g</td>
</tr>
<tr>
<td>Extract of sulfur cured gloves</td>
<td>3 3 2 8 2</td>
<td>2.14</td>
<td>83.3</td>
<td>129 µg/g</td>
</tr>
<tr>
<td>Extract of s.c.g. low powder</td>
<td>1 1 2 5 9</td>
<td>3.11</td>
<td>94.4</td>
<td>259 µg/g</td>
</tr>
<tr>
<td>Extract of s.c.g. powder free</td>
<td>3 9 5 1 0</td>
<td>1.22</td>
<td>83.3</td>
<td>24.1 µg/g</td>
</tr>
<tr>
<td>Film of RVNRL glove</td>
<td>9 7 2 0 0</td>
<td>0.61</td>
<td>50.0</td>
<td>6.2 µg/g</td>
</tr>
<tr>
<td>Film of s.c.g. low powder</td>
<td>3 6 4 4 1</td>
<td>1.67</td>
<td>83.3</td>
<td>966 µg/g</td>
</tr>
<tr>
<td>Film of s.c.g. powder free</td>
<td>9 7 0 2 0</td>
<td>0.72</td>
<td>50.0</td>
<td>35.5 µg/g</td>
</tr>
</tbody>
</table>
Table 5: Summary of Prick-Tests from 18 Patients after 40 Minutes

<table>
<thead>
<tr>
<th></th>
<th>Frequency of prick-tests</th>
<th>Average value</th>
<th>Response value %</th>
<th>Protein concentrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural latex serum</td>
<td>0 1 1 2 3 4</td>
<td>3.78</td>
<td>100</td>
<td>10200 µg/g</td>
</tr>
<tr>
<td>RVNRL serum</td>
<td>1 0 1 2 14</td>
<td>3.56</td>
<td>94.4</td>
<td>N.D.</td>
</tr>
<tr>
<td>Extract of RVNRL gloves</td>
<td>11 2 4 1 0</td>
<td>0.72</td>
<td>38.9</td>
<td>6.8 µg/g</td>
</tr>
<tr>
<td>Extract of sulfur cured gloves</td>
<td>4 2 1 8 3</td>
<td>2.22</td>
<td>77.8</td>
<td>129 µg/g</td>
</tr>
<tr>
<td>Extract of s.c.g. low powder</td>
<td>2 0 1 2 13</td>
<td>3.33</td>
<td>88.9</td>
<td>259 µg/g</td>
</tr>
<tr>
<td>Extract of s.c.g. powder free</td>
<td>5 3 7 3 1</td>
<td>1.44</td>
<td>72.2</td>
<td>24.1 µg/g</td>
</tr>
<tr>
<td>Film of RVNRL glove</td>
<td>9 3 3 2 1</td>
<td>1.06</td>
<td>50.0</td>
<td>6.2 µg/g</td>
</tr>
<tr>
<td>Film of s.c.g. low powder</td>
<td>5 4 5 3 1</td>
<td>1.50</td>
<td>72.2</td>
<td>965 µg/g</td>
</tr>
<tr>
<td>Film of s.c.g. powder free</td>
<td>11 4 1 0 2</td>
<td>0.78</td>
<td>38.9</td>
<td>35.5 µg/g</td>
</tr>
</tbody>
</table>

CONCLUSION

The radiation process does not inhibit the allergy effect of proteins. However, after leaching natural rubber latex gloves made from RVNRL, extractable proteins are reduced to a very low level and the response of sensitized patients are reduced dramatically.

This is a further and very important advantage of radiated natural rubber latex. Because of the promising effects of powder free gloves further development should be done by after treatment of RVNRL gloves with chlorination.

REFERENCES

Bundesgesetzblatt, Jahrgang 1981; Teil I, Seite 1406


S. J. Dalrymple and B. G. Audley Allergenic Proteins in Dipped Products: Factors Influencing Extractable Protein Levels Rubber Developments Vo. 45 No. 2/3 1992, Seite 51
EXTRACTABLE PROTEIN CONTENT OF RADIATION VULCANIZED NATURAL RUBBER LATEX FILMS

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Abstract

The effects of processing conditions on extractable protein content of coagulant dipped radiation vulcanized natural rubber latex films have been investigated. Drying of wet-gel of radiation vulcanized latex films even at a relatively low temperature of 70°C resulted in increases of extractable protein content of the films. The extractable protein content is dependent upon both the temperature and time of drying of wet-gel deposit. Wet-gel leaching of film alone is not adequate to reduce the extractable protein content of films to low levels. Combination of wet-gel leaching, post-leaching, a dip in corn starch slurry, followed by drying at a low temperature of 70°C reduces the extractable protein content of films to very low levels.

INTRODUCTION

Type 1 or immediate hypersensitivity reactions to natural rubber (NR) latex was first reported in Germany in 1927. The next published case appeared in 1979. Between 1989 - 1992, the US Food and Drug Administration reported a number of cases of immediate hypersensitivity reactions associated with latex allergy. These immediate hypersensitive reactions have been attributed to proteinous allergens present in NR latex. These incidents have led to strenuous efforts in the rubber industry to reduce the levels of proteins in NR latex products.

Great amount of work has been carried out by the Rubber Research Institute of Malaysia (RRIM) on reduction of protein content of sulphur vulcanized NR latex products. The work by Esah et. al. showed that natural rubber latex films containing extractable protein content of less than 0.1 mg/g as determined by the RRIM Modified Lowry Microassay gave low degree of allergenic reactions in persons showing latex hypersensitivity. So far, there is no report published on extractable protein content of films or products made from radiation vulcanized NR latex (RVNRL). This paper discusses the effects of processing conditions on extractable protein content of RVNRL films.

EXPERIMENTAL

Two batches of HA latices, designated as A and B, were used to prepare RVNRL. The RVNRL was prepared by using n-butyl acrylate (5 p.h.r.) as a sensitizer and irradiating the latex mixture with 12 kGy of gamma rays. Irganox 1520 (1 p.h.r.) antioxidant was added into the RVNRLs. The total solids of the latex compounds were adjusted to 45% by adding appropriate amount of distilled water.

Coagulant dipped films were prepared using 10% calcium nitrate in industrial methylated spirits (IMS) and 30% cyclohexylamine acetate in IMS. The cyclohexylamine acetate was prepared by mixing cyclohexylamine, acetic acid and IMS. The following formulation was used to prepare a 30% cyclohexylamine acetate solution:
Cyclohexylamine & 18.6 
Acetic acid & 11.4 
IMS & 70.0 

A glass plate was used as a former. The former was immersed in the coagulant and then placed in an oven at 70°C to partially dry the coagulant. It was then immersed in the latex compound for 10 seconds. The wet-gel was allowed to consolidate at room temperature for a few minutes, then leached in distilled water at 50°C. The water contained in 2.5 liter beaker was changed after dipping three sets of 2-3 samples. The latex film was dried at 70 - 100°C. Some of the dried samples were given post-leaching treatment at 50°C in distilled water and slurry dip before final drying at 70°C for 40 minutes. The slurry was prepared by mixing corn starch, Vulcastab LW (cetyl oleyl alcohol-ethylene oxide condensate) as a wetting agent and water. The following formulation was used to prepare a 10% corn starch slurry:

<table>
<thead>
<tr>
<th>parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corn starch</td>
</tr>
<tr>
<td>Vulcastab LW</td>
</tr>
<tr>
<td>Water</td>
</tr>
</tbody>
</table>

A sulphur prevulcanized latex was also prepared using HA latex (B). Comparison of extractable protein content of RVNRL (B) films and those of sulphur prevulcanized latex (B) films will be made. The following formulation was used to prepare a sulphur prevulcanized natural rubber latex:

<table>
<thead>
<tr>
<th>parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA latex (B)</td>
</tr>
<tr>
<td>Potassium laurate</td>
</tr>
<tr>
<td>Potassium hydroxide</td>
</tr>
<tr>
<td>Sulphur</td>
</tr>
<tr>
<td>Zinc diethyldithiocarbamate</td>
</tr>
<tr>
<td>Zinc oxide</td>
</tr>
</tbody>
</table>

The compound was heated at 60°C for 6 hours. Irganox 1520 (1 p.h.r.) was added in the prevulcanized latex. Coagulant dipped films were prepared using the procedure as described in the preceding paragraph.

The soluble protein content of film samples was analyzed using the RRIM Modified Lowry Microassay with pre-precipitation of protein using trichloroacetic and phosphotungstic acids and the results calibrated against bovine serum albumin.

RESULTS AND DISCUSSION

All the data shown in the table of results are those for dipped films using calcium nitrate as the coagulant or otherwise stated. The thickness of films prepared using RVNRL and sulphur prevulcanized NR latex is in the range 0.2 - 0.3 mm.

EFFECT OF LEACHING CONDITIONS AND DRYING TEMPERATURES UPON EXTRACTABLE PROTEIN CONTENT OF RVNRL (A) FILMS

RVNRL films, cast or coagulant dipped, that were dried at room temperature showed very low soluble protein content of 0.06 - 0.12 mg/g despite that the films were unleached (Table 1). Data on extractable protein content of unleached sulphur prevulcanized HA latex (A) films that are dried at room temperature are not available. For comparison, it was shown earlier that an unleached sulphur prevulcanized latex cast film that was dried at room temperature also showed a low extractable protein content of 0.30 mg/g. In this case, the prevulcanized latex was prepared using 1.0 p.h.r. sulphur, 1.0 p.h.r. zinc diethyldithiocarbamate and 0.25 p.h.r. zinc oxide and the latex compound was prevulcanized at 70°C for 2 hours.
Table 1: Extractable protein content of unleached radiation vulcanized NR latex (A) films dried at room temperature

<table>
<thead>
<tr>
<th>Type of film</th>
<th>Protein content (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cast</td>
<td>0.059</td>
</tr>
<tr>
<td>Coagulant dipped, calcium nitrate</td>
<td>0.118</td>
</tr>
<tr>
<td>Coagulant dipped, cyclohexylamine acetate</td>
<td>0.061</td>
</tr>
</tbody>
</table>

The extractable protein content of leached RVNRL films that were dried at 70°C - 100°C (Table 2) was found to be significantly higher in comparison to those of unleached RVNRL films that were dried at room temperature (Table 1). In the present investigation, it took about 90 minutes, 60 minutes and 30 minutes to dry wet-gel of RVNRL at 70°C, 80°C and 100°C respectively. The extractable protein content appeared to be affected by a combination of both the drying temperature and drying time. Drying of leached wet-gel of RVNRL at 70°C for 90 minutes tended to produce higher extractable protein content than drying the leached wet-gel at 100°C for 30 minutes. However, the effect of drying temperature and drying time of leached wet-gel of RVNRL became less pronounced with increasing wet-gel leaching time.

Table 2: Effect of leaching and drying conditions on extractable protein content of radiation vulcanized NR latex (A) films

<table>
<thead>
<tr>
<th>Wet-gel leaching at 50°C (min.)</th>
<th>Drying at 70°C (min.)</th>
<th>Drying at 80°C (min.)</th>
<th>Drying at 100°C (min.)</th>
<th>Post-leaching at 50°C (min.)</th>
<th>Slurry dip (s)</th>
<th>Post-drying at 70°C (min.)</th>
<th>Protein content (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>90</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.200</td>
</tr>
<tr>
<td>3</td>
<td>90</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.957</td>
</tr>
<tr>
<td>5</td>
<td>90</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.490</td>
</tr>
<tr>
<td>1</td>
<td>-</td>
<td>60</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.852</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>60</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.719</td>
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<tr>
<td>5</td>
<td>-</td>
<td>60</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>1.526</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>30</td>
<td>-</td>
<td>-</td>
<td>40</td>
<td>1.326</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>30</td>
<td>2</td>
<td>-</td>
<td>40</td>
<td>1.137</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>30</td>
<td>0.8</td>
<td>10</td>
<td>40</td>
<td>1.319</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>30</td>
<td>1.8</td>
<td>10</td>
<td>40</td>
<td>1.080</td>
</tr>
<tr>
<td>1</td>
<td>-</td>
<td>-</td>
<td>30</td>
<td>0.8</td>
<td>10</td>
<td>40</td>
<td>0.870</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>-</td>
<td>30</td>
<td>0.8</td>
<td>10</td>
<td>40</td>
<td>0.495</td>
</tr>
<tr>
<td>1</td>
<td>-</td>
<td>-</td>
<td>30</td>
<td>1.8</td>
<td>10</td>
<td>40</td>
<td>0.547</td>
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<tr>
<td>2</td>
<td>-</td>
<td>-</td>
<td>30</td>
<td>1.8</td>
<td>10</td>
<td>40</td>
<td>0.413</td>
</tr>
</tbody>
</table>
Wet-gel leaching alone appeared to be not so effective in bringing down extractable protein content of films to low values. Thus for instance, the sample that had been wet-gel leached for 5 minutes at 50°C and dried at 100°C showed a relatively high extractable protein content of about 1.4 mg/g. A lower extractable protein content of about 1.1 mg/g was obtained when sample dried at 100°C underwent post-leaching alone for 2 minutes at 50°C followed by drying at 70°C. The importance of post-leaching of latex films in the reduction of extractable protein content of latex vulcanizates, in particular prevulcanized latex films has been demonstrated earlier\(^6\)\(^9\). The effect of corn starch slurry dip in the reduction of extractable protein content for samples that did not undergo wet-gel leaching process appeared to be insignificant.

Combination of wet-gel leaching, post-leaching, slurry dip and then followed by drying at a relatively mild temperature of 70°C produced a much more significant reduction of extractable proteins compared to the other leaching procedures described in the preceding paragraph. For instance, the sample that had been wet-gel leached for 2 minutes at 50°C, then dried at 100°C, post-leached for 1.8 minutes at 50°C, dipped into corn starch slurry for 10 seconds and then dried at 70°C showed extractable protein content of about 0.4 mg/g.

**FURTHER INVESTIGATION ON FACTORS AFFECTING EXTRACTABLE PROTEIN CONTENT OF FILMS PREPARED FROM RVNRL (B) AND DRIED AT 100°C**

The results in Table 2 show that drying of wet-gels of RVNRL at 100°C for 30 minutes tended to produce lower extractable protein content of films than drying the wet-gels at 80°C for 60 minutes or at 70°C for 90 minutes. Furthermore drying of film at a high temperature of say 100°C would increase productivity. A more detailed study on extractable protein content of films dried at 100°C using RVNRL (B) was carried out.

**Effect of leaching conditions on extractable protein content of RVNRL (B) films**

Table 3 shows that prolonged wet-gel leaching of film for 10 minutes at 50°C reduced the extractable protein content of RVNRL (B) film from a value of more than 2.5 mg/g to a value of 0.85 mg/g. Combination of wet-gel leaching and post-leaching reduce further the extractable protein content. However when the wet-gel leaching time was kept constant at 2 minutes, increasing the post-leaching time from 1.5 minutes to 3 minutes did not bring about further significant reduction of extractable proteins.

**Table 3: Effect of leaching and drying conditions on extractable protein content of radiation vulcanized NR latex (B) films**

<table>
<thead>
<tr>
<th>Leaching and drying conditions</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th>Protein content (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet-gel leaching at 50°C (min.)</td>
<td>Drying at 100°C (min.)</td>
<td>Post-leaching at 50°C (min.)</td>
<td>Slurry dip (s)</td>
<td>Post-drying at 70°C (min.)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.457</td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.980</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.854</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>1</td>
<td>-</td>
<td>40</td>
<td>0.870</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>1.5</td>
<td>-</td>
<td>40</td>
<td>0.475</td>
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<td>30</td>
<td>2</td>
<td>-</td>
<td>40</td>
<td>0.446</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>3</td>
<td>-</td>
<td>40</td>
<td>0.401</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>0.75</td>
<td>10</td>
<td>40</td>
<td>0.113</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>0.75</td>
<td>10</td>
<td>40</td>
<td>0.100</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>0.75</td>
<td>10</td>
<td>40</td>
<td>0.103</td>
</tr>
<tr>
<td>4</td>
<td>30</td>
<td>0.75</td>
<td>10</td>
<td>40</td>
<td>0.071</td>
</tr>
</tbody>
</table>
Combination of wet-gel leaching, post-leaching and slurry dip resulted in reduction of extractable protein content to very low values of about 0.1 mg/g. However when the post-leaching time was kept constant at 0.75 minutes, increasing the wet-gel leaching time from 1 minute to 4 minutes did not bring about further significant reduction of extractable proteins.

Comparison of extractable protein content of RVNRL (A) films and RVNRL (B) films

Comparison of results in Table 2 and Table 3 for films that underwent wet-gel leaching alone and dried at 100°C seem to suggest that RVNRL (B) has a higher extractable proteins than RVNRL (A). The RVNRL (B) films that underwent wet-gel leaching for 3 minutes at 50°C and then dried for 30 minutes at 100°C showed extractable protein content of about 2.5 mg/g. The corresponding RVNRL (A) film showed extractable protein content of about 1.5 mg/g.

Although RVNRL (B) seemed to have higher extractable proteins than RVNRL (A), however the proteins in RVNRL (B) films tended to be more easily removed than the proteins in RVNRL (A) films. This observation applies for both type of leaching procedures used i.e. wet-gel leaching or wet-gel leaching plus post-leaching of films.

Effect of cyclohexylamine acetate on extractable protein content of RVNRL (B) films

Comparison of the results shown in Table 3 and Table 4 indicate that the type of coagulant used to make dipped products also affect extractable protein content. The results clearly show that dipped films prepared using cyclohexylamine acetate produced substantially higher extractable protein content than those prepared using calcium nitrate. For instance, RVNRL (B) film that was prepared using cyclohexylamine acetate, wet-gel leached for 2 minutes at 50°C, post-leached for 1.5 minutes at 50°C and then dried for 40 minutes at 70°C showed extractable protein content of about 1.7 mg/g. The corresponding film prepared using calcium nitrate showed extractable protein content of about 0.5 mg/g.

Table 4: Effect of using cyclohexylamine acetate as a coagulant on extractable protein content of radiation vulcanized NR latex (B) films

<table>
<thead>
<tr>
<th>Leaching and drying conditions</th>
<th>Protein content (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet-gel leaching at 50°C (min.)</td>
<td>Drying at 100°C (min.)</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
</tr>
</tbody>
</table>

Comparison between extractable protein content of RVNRL (B) and sulphur prevulcanized latex (B) films

RVNRL (B) films that were wet-gel leached for 3 - 5 minutes and then dried at 100°C for 30 minutes showed higher extractable protein content (Table 4) than the corresponding sulphur prevulcanized latex (B) films (Table 5). However when the wet-gel leaching time was increased to 10 minutes or the films were given wet-gel leaching as well as post-leaching, the difference in the extractable protein content of RVNRL (B) films and sulphur prevulcanized latex (B) films became insignificant.
Table 5: Effect of leaching and drying conditions on extractable protein content of sulphur prevulcanized latex (B) films

<table>
<thead>
<tr>
<th>Wet-gel leaching at 50°C (min.)</th>
<th>Drying at 100°C (min.)</th>
<th>Post-leaching at 50°C (min.)</th>
<th>Slurry dip (s)</th>
<th>Post-drying at 70°C (min.)</th>
<th>Protein content (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.403</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.251</td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.144</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.822</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>0.5</td>
<td>-</td>
<td>40</td>
<td>0.485</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>1</td>
<td>-</td>
<td>40</td>
<td>0.464</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>1.5</td>
<td>-</td>
<td>40</td>
<td>0.419</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>2</td>
<td>-</td>
<td>40</td>
<td>0.215</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>3</td>
<td>-</td>
<td>40</td>
<td>0.161</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>1</td>
<td>10</td>
<td>40</td>
<td>0.233</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>2</td>
<td>10</td>
<td>40</td>
<td>0.213</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>3</td>
<td>10</td>
<td>40</td>
<td>0.198</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>4</td>
<td>10</td>
<td>40</td>
<td>0.108</td>
</tr>
</tbody>
</table>

It is noteworthy that the extractable protein content of sulphur prevulcanized latex films is also dependent upon the type and the levels of compounding ingredients used.\cite{7,9}

**CONCLUSION**

Wet-gel leaching of RVNRL films alone could not reduce the extractable protein content of these films to a low value of say 0.1 mg/g if the films are dried at temperature range of 70°C - 100°C. When the films are dried at a relatively high temperature of 100°C, a leaching procedure comprising wet-gel leaching, post-leaching, a slurry dip followed by final drying at 70°C could produce films having low extractable protein content. The extractable protein content of RVNRL films tends to be also affected by the source of latex used. With adequate leaching of films, the extractable protein content of RVNRL films tends to be rather similar to that of sulphur prevulcanized latex films. The use of cyclohexylamine acetate as a coagulant for dipping resulted in significantly higher extractable protein content of RVNRL films compared to when using calcium nitrate as a coagulant.

**ACKNOWLEDGEMENT**

The authors wish to thank Puan Salmah Wasimon and the Latex Protein Group of RRIM for their technical assistance. The assistance of Sinagama staff of MINT is also appreciated.
REFERENCE


EXTRACTABLE PROTEINS FROM ELECTRON BEAM (EB) IRRADIATED NATURAL RUBBER (NR) LATEX

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Takasaki Radiation Chemistry Research Establishment
Japan Atomic Energy Research Institute, JAPAN.

ABSTRACT

The protein assay of natural rubber latex (NRL) vulcanized by low energy electron beam (EB, 300 keV, 30 mA) has been carried out using Bicinchoninic acid (BCA) reagent. Extractable protein in irradiated latex film was determined by measuring the absorption of colored solution at 562 nm using UV spectrometer. The effect of various radiation doses on the extractable protein content of NRL was investigated. It was found that the quantity of extractable protein increases with radiation dose. When compared with gamma-ray irradiated samples the same trend was observed. EB irradiated latex films are leached in 1% ammonia water for various lengths of time. From the results it was established that within 2 hours of leaching in ammonia water most of the extractable protein (96%) were removed from rubber film.

INTRODUCTION

Radiation vulcanization of natural rubber latex is an alternative to conventional sulfur vulcanization for the production of goods being in contact with the human body. Vulcanization by gamma radiation does not need chemicals such as dithiocarbamates, thiozoles, amines and thurems and therefore should be a suitable basic substance for nitrosamine free products. Recently low energy electron beam has been successfully tried to induce vulcanization of NRL (Makuuchi 1995; Makuuchi et al. 1995). The use of low energy electron beam is more economical compared to high energy electron beam or gamma rays as because bioshielding is not necessary. Moreover during vulcanization by gamma rays monomer n-butyl acrylate (n-BA) is used as a radiation sensitizer; but electron beam does not need n-butyl acrylate to initiate the reaction of radiation crosslinking.

Fresh natural rubber latex contains proteins. The composition of these proteins changes on processing the fresh latex to high ammoniated latex concentrate and also on vulcanization of high ammonia latex concentrate. Natural rubber products contain two kinds of proteins - strongly bound to the rubber particles in the latex and soluble serum derived protein. The latter generally gives rise to most of the extractable protein. Allergy to latex containing articles is becoming more important because it can result in unexpected life-threatening anaphylactic reactions in sensitized individuals. Serum of latex contains proteins, most of them are in the acidic zone of the pH gradient, display the ability to bind human IgE indicating their allergenic character (Pendle 1993; Palosuo 1993; Soili 1993).

The present study investigates the extractable protein content of latex films with various radiation doses. The effects of various leaching agents and extraction time on extractable protein content has been studied.
PROCEDURE

To vulcanize natural rubber latex by radiation 50% concentrated latex was prepared by diluting with 1% ammonia water. Potassium hydroxide at a quantity of 0.02% was added to stabilize the latex.

Electron beam irradiation of the latex was carried out at beam current 30 mA using self-shielded accelerator model 330-100-60 of Nissan High voltage company. During irradiation the latex was constantly stirred (150 r.p.m.) to ensure homogeneous irradiation of the latex. Defoamer BYK-022 at 0.24% was added to latex to destroy the ability of latex to foam on the surface of latex when it was stirred.

Natural rubber latex was irradiated by gamma radiation at doses 10, 15, 20, 30 kGy using 5 phr n-BA as a sensitizer. The irradiated latex was cast on glass plate and air dried till transparent and then heated at 80°C for 1 hour.

Extractable protein in natural rubber was determined using Bicinchoninic acid (BCA) assay method (Yagami et al. 1993). Two grams of latex specimen were extracted with 10 mL portions of phosphate buffered saline pH 7.4 (PBS) at room temperature for two hours and then the resulting solution was assayed by BCA method. The BCA method utilize the color change resulting from the strong complex formed between Cu²⁺ and BCA. PBS solution containing rubber protein was reacted with BCA working reagent using a standard protocol (Smith et al. 1985). The assay was conducted by adding 250 μL aliquot of the sample to 5mL of the BCA protein working reagent and incubating the resulting solution at 37°C for 1 hour. After the sample had been cooled to room temperature, its absorbence at 562 nm was determined using Shimadzu UV-visible spectrometer. A standard curve was obtained using concentrations of BSA (bovine serum albumin) from 0.2 to 1.0 mg/mL in aqueous solution against water blank.

RESULTS AND DISCUSSION

Electron beam irradiation of latex shows that the increase of irradiation time gives the increase in extractable protein content (Fig.1). An increase of 213% was observed when the length of radiation time was 35 min with beam current 30 mA. Proteins in natural rubber latex can be decomposed by radiation which gives rise to increase the amount of extractable protein in irradiated latex film.

Results of irradiated latex film prepared by gamma radiation are shown in Fig.2. The latex is irradiated at radiation doses 10, 15, 20 and 30 kGy and for the latex films extractable protein contents are 2.06, 2.10, 2.57 and 2.94 mg/g respectively. From the results it can be seen that with the increase of radiation dose extractable protein content also increases. This may also be due to degradation of proteins in natural rubber latex by gamma radiation to water soluble form.

For radiation vulcanized latex film leaching is an important step (Feroza et al. 1995; Shukri et al. 1990) which gives rise to increase tensile properties. It also improves the appearance of product. Natural rubber field latex contains less than 5% protein (Feroza et al, 1995). Washing removes mainly water soluble proteins. Fig. 3 shows the results of leaching of EB irradiated latex film in 1% ammonia solution at various lengths of leaching time. From the figure it is evident that most of the soluble protein (96%) is removed from latex film within 2 hours of leaching.

As the quantity of extractable protein and also the nature of soluble proteins is not unique, so to get reproducible result is very difficult. Latex films, irradiated by gamma rays are leached with water and 1% ammonia solution (Fig. 4 & 5). The variability of results of extractable protein content indicates that 1% ammonia solution can extracts more protein from the film than water.
Alcohol is used as leaching agent and it effects on tensile properties of latex (Feroza Akhtar, et al. 1995, Wahab S.B.H.A et al. 1990). As a leaching agent four concentrations of ethanol were tried and it was observed that extractable protein content was higher when alcohol concentration was low (Fig.6). Dilute alcohol solutions can remove more protein than concentrated alcohol solution. The results indicate that at an extraction period of 24 hours, 25% ethanol can remove as much protein as with 1% ammonia solution at extraction period of 1 hour. Extractable protein content of latex films after alcohol and ammonia treatments is shown in Table 1 where methanol, ethanol and i-propanol are used as leaching gents. The electron beam irradiated cast films are leached in each alcohol for 1 and 24 hours. Then immediately these films are subjected to ammonia leaching for 24 hours. Results in Table 2 shows that values of extractable protein are always higher (16%) when leached with alcohol for 24 hours.

Table 1: Extractable protein content of latex film after alcohol and ammonia treatment of radiation vulcanized natural rubber latex film.

<table>
<thead>
<tr>
<th>Sl.no.</th>
<th>Treatment condition</th>
<th>Protein content, (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Control (not treated)</td>
<td>2.104</td>
</tr>
<tr>
<td>2.</td>
<td>24 hrs in 1% ammonia water</td>
<td>0.0483</td>
</tr>
<tr>
<td>3.</td>
<td>1 hr. in methanol followed by 24 hrs in 1% ammonia water</td>
<td>0.0543</td>
</tr>
<tr>
<td>4.</td>
<td>24 hrs. in methanol followed by 24 hrs. in 1% ammonia water</td>
<td>0.0632</td>
</tr>
<tr>
<td>5.</td>
<td>1 hr in ethanol followed by 24 hrs. in ammonia water</td>
<td>0.050</td>
</tr>
<tr>
<td>6.</td>
<td>24 hours in ethanol followed by 24 hours in 1% ammonia water</td>
<td>0.0576</td>
</tr>
<tr>
<td>7.</td>
<td>1 hr in i-propanol followed by 24 hrs. in ammonia water</td>
<td>0.0497</td>
</tr>
<tr>
<td>8.</td>
<td>24 hours in i-propanol followed by 24 hours in 1% ammonia water</td>
<td>0.0588</td>
</tr>
</tbody>
</table>

Table 2: Extractable protein content of latex film before and after irradiation

<table>
<thead>
<tr>
<th></th>
<th>Before processing</th>
<th>Processed by</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Without n-BA</td>
<td>With n-BA</td>
<td>Electron beam</td>
<td>Gamma ray</td>
</tr>
<tr>
<td>Extractable protein (mg/g)</td>
<td>2.104</td>
<td>1.632</td>
<td>2.807</td>
<td>2.104</td>
</tr>
</tbody>
</table>

For irradiation of latex by gamma rays n-BA was added to latex as a sensitizer to reduce the optimum radiation dose of vulcanization. Electron beam vulcanization of natural rubber latex does not need sensitizer. Table 2 shows the results of cast films prepared from latexes before and after radiation by gamma rays, electron beam and conventional sulfur vulcanized latex film. Optimum radiation dose for gamma ray was taken 20 kGy and that of electron beam (EB) was 15 minutes of exposure time of 300 keV (low energy) accelerator with beam current 30 mA. From the results stated in Table 2 it can be seen that before irradiation cast latex films without and with n-butyl acrylate contain different quantities of extractable protein and they are 2.104 and 1.632 mg/g, respectively. The addition of n-BA suppresses the value of extractable protein content. After irradiation the electron beam irradiated cast latex film has higher protein content than gamma ray irradiated latex film and for sulfur vulcanized latex film the value is yet less.
ACKNOWLEDGMENT

One of the authors wishes to express sincere thanks to STA of Japan for inviting her to Japan to carry out this work.

REFERENCES


Fig. 1. Protein content of latex irradiated for various lengths of time.

(Electron energy = 300 keV, beam current = 30 mA)
Fig. 2. Extractable protein content in latex film at various gamma radiation doses.
Fig. 3. Extractable protein content of EB irradiated latex film leached in 1% aqueous ammonia for various lengths of time.
Fig. 4. Extractable protein content of latex films at various lengths of leaching time in water.
Fig. 5. Extractable protein content of latex films leached with 1% aqueous ammonia containing 50 ppm CaCO₃.
Fig. 6. Extractable protein content of electron beam irradiated latex film at various concentrations of ethanol.
QUESTIONS & ANSWERS, and COMMENTS

Session II

C1. Machi
   It would be useful to determine the effects of irradiation upon the molecular weight of latex proteins.

Geertsma
   Differences in the composition of latex proteins before and after irradiation of latex were not observed.

Q2 Geertsma
   Has Dr. Bez carried out similar studies using SPVL?

A2 Bez
   Not yet.

C3
   Protein issues seem to create more problems for RVNRL.

J. Anand
   The leaching process will determine the extractable proteins of RVNRL films.

Geertsma
   The advantage of RVNRL in Type IV allergy is more significant than the protein problem in RVNRL.

C4 Thomas
   The specification for tensile strength of RVNRL film should be at least 20 MPa.

Bez
   We reduced the specifications for RVNRL in order to avoid problems of selling the products.

Desai
   The ASTM specification for tensile strength of examination gloves has been lowered to 14 MPa now.
CURRENT TREND IN LATEX DIPPED PRODUCTS MANUFACTURING

Winston S.C. Wong

President
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Selangor Darul Ehsan, Malaysia.

INTRODUCTION

First of all, I would like to congratulate the National and the Technical Organising Committees for successfully organising this Symposium which will undoubtedly bring the latex industry into a new horizon. We are also particularly proud to be the host country for this Symposium and I would like to take this opportunity to welcome our foreign guests by saying “Selamat Datang” which means “Welcome” in the Malay language. I hope that you can take some time to see our beautiful country before returning home.

I am also very grateful that MARGMA has been invited as a Joint Organiser, thus enabling the Association to play a role in the National Organising Committee as well as the Technical Committee. We consider it a great honour and privilege both to the Association and to me, to be given the opportunity to share with you a brief Keynote Address on the Current Trend in Latex Dipped Products Manufacturing with particular reference to the Malaysian scenario.

First of all, I would like to give a small introduction of the Malaysian Rubber Glove Manufacturers’ Association (MARGMA), its activities as well as its aims and objectives.

MARGMA was established in 1989 and has been the voice and advocate for the industry in the Country; dealing with related trade associations and government agencies in shaping and monitoring new directions in the development of the industry.

In brief, the aims and objectives of MARGMA are as follows:

a. to bring about a common understanding amongst all manufacturers.

b. to work towards improving and standardising a “Malaysian Latex Glove”

c. to represent all its members on their interests and grievances and

d. to disseminate the latest information in technological advancements.

Presently, MARGMA has 69 members out of which 48 are ordinary members whilst 21 are associate members. We are also proud to say that MARGMA members represents about 85% of the total production capacity of latex gloves in Malaysia. Our membership covers from the Small and Medium Industries to the giant multi-national companies.

Current trends would not be current if we do not have a history. So let’s take a brief look at the historical developments of the latex dipped products and one will be able to visualise how the industry has developed or evolved over the years - especially the glove industry.

Latex dipped products became significant during the 1970’s and expanded thereafter with the participation of multi-national companies. By latex dipped products, we would be referring to gloves (in particular), condoms, catheters and other items that meets the similar manufacturing concept.
The industry continued to expand during the 1980's especially after the implementation of the Industrial Master Plan (IMP) by the Government in 1986 whereby more focus was on the manufacturing sector. The upsurge in growth beyond one's imagination was during 1986/7 - attributed to the global AIDS scare which propelled glove prices to phenomenal levels. Latex glove manufacturing plants mushroomed all over Malaysia by investors trying to capitalise in the booming market.

Obviously, the market boom was short-lived and by end of 1988 or in early 1989, the market collapsed due to the rapid oversupply situation resulting in the prices of examination gloves plunging to rock bottom. More than 300 licenses were approved by the government for the manufacturer of latex examination gloves out of which about 200 were in operation then. It was just too much for the market to absorb.

It is also interesting to note that despite the collapse of the market whereby glove prices plunged, the examination glove market increased by about 30% during the same period. Malaysia's export figure for latex gloves increased from about RM750,000.00 in 1988 to about RM900,000.00 in 1989.

The period of correction was painful and many manufacturers of latex glove succumbed to the market situation and only the fittest survived the storm which recovered only around late 1990 - when we saw some light at the end of the tunnel. Since then, the market continued to improve as the simple economic fundamental of supply/demand sets its equation into proper perspective.

Since then we never look back and today with a total of about 85 manufacturers of latex gloves in Malaysia, we have successfully made this into multi-Billion Ringgit industry with our exports totaling approximately RM2.5 billion (which is approx. USD1.0 billion).

As we have experienced the pain in 1988 we should now enjoy the sweetness of our success and we are proud to say that Malaysia is now the world's largest consumer of NR latex and is also a major producer of latex gloves (both medical and domestic or industrial), latex thread, condoms, catheters, etc. The success has been related mostly to our concept of Quality. Thanks to the support from the various government agencies especially the Malaysian Rubber Research Development Board and the Rubber Research Institute of Malaysia as well as SIRIM and MIDA, we are able to achieve a product of superior quality surpassing quality standards worldwide.

We are also fortunate to be host country for quite a number of multi-national companies who have relocated their operations to Malaysia and bringing with them a technology which meets world standards not only in manufacturing, but in Research and Development, product innovation, as well as other important aspects such as packaging and other related fields.

The latex goods sector has been experiencing double digit growths over the past few years and I am happy to append some of the export figures as follows:

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>Total Latex Goods, RM</td>
<td>2.00B</td>
<td>2.33B</td>
<td>2.64B</td>
<td>3.10B(est.)</td>
</tr>
<tr>
<td>Latex Gloves</td>
<td>1.03B</td>
<td>1.63B</td>
<td>1.89B</td>
<td>2.27B</td>
</tr>
<tr>
<td>(Glove Output-billion prs.)</td>
<td>3.47b.prs.</td>
<td>5.80b.prs.</td>
<td>6.54b.prs.</td>
<td>7.51b.prs.</td>
</tr>
</tbody>
</table>

As a matter of interest, the total export of the rubber industry consisting of rubber as a commodity as well as manufactured down stream products for Malaysia totalled approximately RM7.20 billion in 1995 out of which manufactured item consists of RM3.10 billion as mentioned earlier and latex gloves of all types in RM2.27 billion. We would expect total export of latex gloves for 1996 to exceed RM2.5 billion.
One would not deny the fact that the above are impressive figures with a very steady growth and we hope that the industry will continue to perform as expected and such growths will not happen without a continuous effort to resolve current issues and threats which are continuously being faced by the industry.

"Perceptions vs Reality"

Health related issues of protein allergy, nitrosamines and bio-compatibility of latex products continue to give us an unfavourable image. The protein allergy issue has led to the manufacture of latex products made from substituted synthetic materials, which are by themselves not totally free from chemicals either. However, we need to bear in mind that these issues may have been blown out of proportion although isolated and insignificant cases have occurred to highly sensitive persons. Therefore, the perception of the serious nature of these issues far outweighs the reality of the matter which is the result of the adverse effects of campaigns against the use of NR latex in medical products.

Anyhow, all these issues are currently being looked into by R&D agencies from both the public and private sectors and serious research efforts have resulted in containing and clarifying most of these issues. The RRIM has also developed a new low protein latex (LOPROL) for the local latex industry and the subject matter of RVNRL we are deliberating during this Symposium will definitely be able to bring us closer to achieving a chemical free product.

Threats from Synthetic Materials

The encroachment of synthetic materials in latex dipped products has posed a serious challenge to the use of NR latex. Further R&D is therefore urgently required and intensified in order to upgrade the quality as well as the characteristics of NR latex and eliminate its negative effects so as to ensure its position as the natural choice as a raw material in latex dipped products manufacturing. And again, I believe the RVNRL is a new technology towards this end.

Labour

The latex dipped products industry is known to be quite labour intensive and both the public and private sectors are putting in more efforts into providing a more automated process.

In Malaysia, about 45,000 workers (or about 75% in the rubber based industry) are employed in latex dipped goods manufacturing, which generates an export value of RM3.10 billion (1995 Estimate). Based on the above figure, we have a contribution per workforce of about RM75,000 - which is quite high as compared to other developing countries. Again I would like to emphasise that even though our labour force is getting a little more expensive as compared to our neighbouring countries, our productivity is still relatively on a high and comfortable figure.

A point worth noting is the current heavy dependance on foreign labour by the industry, and in a recent survey conducted by MARGMA, we found that most (if not all) its members employs at least 20% of foreign labour - mostly from Bangladesh and Indonesia.

Dependance on manual operation is not our long term strategy and therefore, automation will be the answer to a more efficient and stable operation and it requires an all round support including R&D and local machine supply and engineering support services.

Pricing

Looking at a more macro point of view, the factor of pricing has always been an important criteria in determining the market position of the product and therefore, the industry must evolve itself to be as cost effective as possible to ensure it can maintain its economics favourably. The threat from synthetic materials also hovers over our price structures and we must not price ourselves too high so as to attract substitutes into the market. Therefore, in the development of any new product or new technology, we
must not let the realities of market forces surpass us and we must ensure that the end product has an economically acceptable price.

**Environmental Issue**

Waste management in the production of latex products is also a cause of concern. Manufacturers today are expected to be responsible corporate citizens and gone were the days where we can simply discharge our wastes any way we like. In heading to be a developed nation, we begin to realise there is always a price to pay to ensure we continue to have a healthy environment and to ensure our habitat is not being endangered.

In Malaysia, the problem of waste treatment has always been a major concern and both the private and public sectors must work hand in hand to ensure the common interests of achieving a commercially viable waste disposal and treatment facility can be met.

More R&D should be provided to increase the down stream usage of sludge for other possible end products and we hope the RRIM will be able to contribute further towards this end.

**Product Certification**

Another area of interest and to a certain degree of confusion is the numerous product certification by the various bodies (and the changes in requirements) which latex products manufacturers have to keep track on - this is especially so on latex dipped products for medical purposes.

Today, we have our local SIRIM product markings, then we have the FDA compliance or the ASTM standard, the CE Mark, the ISO Standards with the ISO 14000 as the latest (correct me if I am wrong) and the various other existing standards which manufacturers have to deal with. Obviously all these standards have its good intention i.e. to ensure quality standards are consistently met with proper tracability, etc., etc. but one will realise most of the requirements are repeated and manufacturers spend time and money in trying to ensure they are properly accredited by the various agencies which may not really enhance their product specification.

Towards this end, MARGMA is working towards introducing a Standard Malaysian Glove which will not only meet all the most stringent standards in the world, but will try to surpass them if possible. We hope to achieve this in the very near and foreseeable future.

In summing up, a strategic plan for a broader product range is important for the future development of the industry and the latex dipped products sector must consolidate and diversify to have innovative value added products to meet changing consumer preferences and/or requirements. Value-added latex goods include low-protein/hypoallergenic/powder-free/sterilised medical gloves, industrial gloves, high value balloons, flexi-toys, theatrical masks and various medical devises besides catheters - all in all we need a significant product differentiation in terms of quality as well as technological characteristics in order to sustain the challenges ahead.

The challenges for a chemical-free and environment friendly latex dipped product is real and the stage is set for this new challenge and we hope to achieve this in the near future.

The increasing need for automation in production and packaging should require more focus and coupled with more product innovation, the industry will be set for a bright future.

Last but not least, we are certain that NR Latex is here to stay but I do not discount the possibility of more developments of working and blending with synthetics in a win-win situation in the near future and lets keep our eyes and ears open.
A TEST TRIAL IRRADIATION OF NATURAL RUBBER LATEX ON LARGE SCALE FOR THE PRODUCTION OF EXAMINATION GLOVES IN A PRODUCTION SCALE

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Sudath Wellage  
Hanwella Rubber Products ltd., Colombo,  
SRI LANKA

ABSTRACT

Radiation Vulcanization of natural rubber latex has been developed extensively through various research and development programmes. During these investigations many data was collected and from these data it was proved that radiation vulcanized natural rubber latex (RVNRL) can be used as a new material for industry. (RVNRL symposium 1989; Makuuchi IAEA report) This material has been extensively tested in making of dipped goods and extruded products. However, these investigations were confined only to laboratory experiments and these experiments mainly reflected material properties of RVNRL and only a little was observed about its behaviour in actual production scale operation.

The present exercise was carried out mainly to study the behavior of the material in production scale by irradiating latex on a large scale and producing gloves in a production scale plant.

It was found that RVNRL can be used in conventional glove plants without making major alteration to the plant. Quality of the gloves that were produced using RVNRL is acceptable. It was also found that the small deviation of vulcanization dose will affect the crosslinking density of films. This will drastically reduce the tensile strength of the film. Crosslinking density or pre-vulcanized relax modulus (PRM) at 100% is a reliable property to control the pre vulcanization of latex by radiation.

INTRODUCTION

Radiation Vulcanization of Natural Rubber Latex (RVNRL) has several advantages over the conventional vulcanization with sulfur such as less or absence of toxicity free from nitrosoamines and accelerator induced allergies, low in cytotoxicity, and cleaner process. Research and development work on RVNRL has been carrying out since 1980's. Most of the work was confined to the laboratory tests while a little was examined in production scale operation.
In this exercise the behavior of natural rubber (NR) latex in production scale was studied. It is known that with increasing radiation dose the tensile strength of irradiate NR latex film passes through a maximum. Therefore the optimum radiation dose should be determined very accurately to obtain the maximum tensile strength of the latex films. Hence the vulcanizing dose was found by carrying out small scale irradiation before the pilot scale production. Two tons of specially prepared centrifuged natural rubber latex (Patent no. 10134) was prepared at Messrs. Latexam (pvt) Ltd. The irradiation of latex was carried out in two batches using the irradiator in Jakarta, Indonesia. Preparation of gloves with irradiated latex was done in a production scale plant at Hanwella Rubber Products (Pvt.) Ltd. in Sri Lanka. Then the two batches were tested in production in two separate stages. The properties of centrifuged latex used in this exercise is given in Table 1.

Table 1: Properties of NR Latex.

<table>
<thead>
<tr>
<th>Property</th>
<th>Observed Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry rubber content %</td>
<td>60.00</td>
</tr>
<tr>
<td>Total solid content %</td>
<td>61.5</td>
</tr>
<tr>
<td>MST sec.</td>
<td>1800</td>
</tr>
<tr>
<td>VFA</td>
<td>0.017</td>
</tr>
<tr>
<td>pH</td>
<td>10.00</td>
</tr>
<tr>
<td>Total alkalinity</td>
<td>0.35</td>
</tr>
</tbody>
</table>

EXPERIMENTAL

Materials

Centrifuged latex was supplied by latexam (Pvt.) Ltd. in Sri Lanka. Industrial grade normal butyl acrylate (n-BA), Ammonia were used. Antioxidants namely, Tris (nonylated phenyl) phosphite (TNP), 2,5-Di-tert-amylydroquinone (DAH) were supplied from Japan. All other raw materials required for the exercise were collected from established suppliers in the country.

The Co-60 irradiator at the Centre for the Application of Isotope and Radiation (CAIR) - BATAN, Jakarta was used in this study for irradiation. The activity of Co-60 was 104 kci and dose rate was 1.0 kgy/hr.

Determination of optimum dose

Preparation of latex for irradiation:

Latex was prepared for irradiation according to the following formulation.

\[
g \begin{align*}
60\% \text{ natural rubber latex} & = 167 \\
0.6\% \text{ ammonia water} & = 19.1 \\
n-\text{BA} & = 5.00
\end{align*}
\]

Firstly natural rubber latex was diluted with ammonia water followed with the addition of n-BA. Normal butyl acrylate was added in small proportions directly to latex while latex was being stirred efficiently. The prepared latex was kept for 24 hr before irradiation.
Irradiation of latex:

Latex was irradiated to appropriate dose in 2.5 lt screw cap glass bottle. The Co-60 panoramic irradiator was used for irradiation of latex.

Preparation of cast films:

Films were cast using 10cm x 15cm glass molds. Cast films were leached in deionized water for 24 hours and dried in air. Dry films were heated at 70°C for one hour and left in a desicator.

Preparation of films by dipping:

Coagulant dipping films were made by using a 7% solution of Ca(NO₃)₂ in water. Leaching of films were carried out in wet gel stage at 80°C for 5 minutes. Thereafter it was dried at 90°C in an air circulating oven.

Testing:

Prepared RVNR latex and film were tested for tensile strength, crosslinking density, pre-vulcanized relaxed modulus (PRM), and viscosity of the latex.

Pilot Scale Irradiation (1)

Latex was irradiated in pilot scale. Batch 1 was prepared to the following formulation.

<table>
<thead>
<tr>
<th></th>
<th>kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Latex</td>
<td>925.0</td>
</tr>
<tr>
<td>n-BA</td>
<td>106.3</td>
</tr>
<tr>
<td>0.6% Ammonia water</td>
<td>27.7</td>
</tr>
</tbody>
</table>

First latex (185 x 5 kg) was charged into the mixing vessel followed by the addition of ammonia water. Then n-BA was added slowly into the mixing vessel while stirring. Initially the stirrer speed was set at 35 r.p.m. It was found that this speed was not sufficient for adequate dispersion of n-BA. Therefore stirrer speed was increased to 70 r.p.m. and addition was high mixing was sufficient. The mix was left for 16-24 hours and irradiated to 12 kgy using the latex irradiator. Irradiation time was 12 hours.

Pilot scale irradiation (2)

The batch(2) was formulated similar to the first batch as follows:

<table>
<thead>
<tr>
<th></th>
<th>kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Latex</td>
<td>925</td>
</tr>
<tr>
<td>n-BA</td>
<td>27.7</td>
</tr>
<tr>
<td>0.6% ammonia water</td>
<td>106.3</td>
</tr>
<tr>
<td>Ammonium laurate</td>
<td>0.270</td>
</tr>
</tbody>
</table>

Normal butyl acrylate was emulsified with 30 kg of ammonia water and 270g of ammonium laurate using the emulsifier. The emulsion was stable to carry out further addition. The stirrer speed of the mixing tank was increased to 70 r.p.m. followed with the addition of the rest of the ammonia water. Then n-BA emulsion was added directly to the mixing tank during a period of 15 - 20 minutes. The stirring was continued for a period of one hour.
The batch was left for 24 hours and transferred to the irradiation vessel. The stirrer speed of the irradiation vessel was set to 25 r.p.m. The latex was irradiated with radiation from Co-60. PRM was measured at different intervals during irradiation. The irradiation was stopped after PRM reached the required value. Nitrogen gas was bubble through the irradiation vessel during irradiation.

Preparation of examination gloves

Latex was diluted to 45% TSC using 0.6% ammonia water. 1.6 phr of antioxidant was added to irradiated latex as a dispersion Antioxidant was a combination of TNP and DAH at a ratio of 3:1 (Makuuchi et al. 1993; Yoshi et al 1993; Chandralal internal report to IAEA). Coagulant was 7% Ca(NO₃)₂ & 3% CaCO₃ in water with 0.3% non ionic surfactant. The production rate was set for 56 formers per minute. Cycle time was about 30 minutes.

Testing of gloves

Gloves were tested for physical properties and aging. Aging was carried out at 70°C for 7 days.

RESULTS AND DISCUSSION

In preparation of latex for irradiation, n-BA was added directly into the latex. There should be sufficient mixing for the monomer to get dispersed in the latex for neat addition of sensitiser.

![Figure 1: Tensile Strength films at different dose prepared with 5 phr n-BA](image-url)

Figure 1 shows the tensile strength of films prepared by casting and by dipping at different radiation doses. It was observed that in both cases the maximum tensile strength of 26 Mpa was reached around 12 kgy radiation dose. Deviation from this value drastically reduces the tensile strength.
Figure 2: Crosslinking Density of cast films at different dose prepared with 5 phr n-BA

Figure 2 shows the crosslinking density of cast films prepared from irradiated latex at different doses. The crosslinking density was calculated using Flowry Rheiner Equation. It is found that maximum tensile strength is reached when crosslinking density is around $1.07 \times 10^{-4}$ moles of crosslink/cm$^3$. Crosslinking density was measured from dipped films showed similar values.

Figure 3: Modulus of films at different doses with n-BA

Figure 3 shows the 100% and 300% pre vulcanized relaxed modulus carried out for latex irradiated to different doses. It can be seen that both properties have similar trends. However from our investigations it was seen that the reproducibility of 100% is better than that of 300%. In our work modulus was recorded as an index.
Table 2 shows the linear swelling ratio of latex films made from irradiated latex. It can be seen that the difference in linear swelling of films over the proposed dose range is not significant.

<table>
<thead>
<tr>
<th>Dose (Mrad)</th>
<th>Swelling ratio %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
</tr>
<tr>
<td>1.2</td>
<td>93</td>
</tr>
<tr>
<td>1.5</td>
<td>91</td>
</tr>
<tr>
<td>1.8</td>
<td>90</td>
</tr>
<tr>
<td>2.0</td>
<td>88</td>
</tr>
</tbody>
</table>

Table 3 shows the viscosity of latex samples measured after two weeks. It can be seen that the viscosity of samples are below unirradiated sample which contains n-BA. The unirradiated latex shows slight increase in viscosity after 2 weeks which indicates that the special latex is stable against increase in viscosity due to n-BA addition.

<table>
<thead>
<tr>
<th>Dose (kgy)</th>
<th>Viscosity (mpas).</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 after 2 weeks</td>
<td>23.7</td>
</tr>
<tr>
<td>12 after 2 weeks</td>
<td>21.2</td>
</tr>
<tr>
<td>15 after 2 weeks</td>
<td>21.9</td>
</tr>
<tr>
<td>18 after 2 weeks</td>
<td>22.5</td>
</tr>
<tr>
<td>20 after 2 weeks</td>
<td>22.5</td>
</tr>
<tr>
<td>0 after 1 day</td>
<td>30.3</td>
</tr>
<tr>
<td>0 after 1 week</td>
<td>35.6</td>
</tr>
</tbody>
</table>

Pilot scale irradiation (1)

The latex mixing tank wall consisted of coagulated latex and irradiated latex contained a small percentage of coagulum. The reason for this was that the neat addition of monomer to latex was not correct. This was mainly due to insufficient stirring which would have prevented the monomer from getting mixed with the latex. If the monomer was found floating without getting mixed with latex then there could be a possibility of lump formation.

Table 4: Physical properties of latex films made from pilot scale batch (1).

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coagulant dipped film</td>
<td></td>
</tr>
<tr>
<td>Tensile strength Mpa</td>
<td>20</td>
</tr>
<tr>
<td>Elongation at break %</td>
<td>950</td>
</tr>
<tr>
<td>Cast film</td>
<td></td>
</tr>
<tr>
<td>Tensile Strength Mpa</td>
<td>19.4</td>
</tr>
<tr>
<td>Elongation at break %</td>
<td>918</td>
</tr>
<tr>
<td>Crosslinking density mols/cm3</td>
<td>$1.3 \times 10^{-4}$</td>
</tr>
<tr>
<td>100% PRM (index)</td>
<td>8.8</td>
</tr>
</tbody>
</table>
Examination gloves were made by coagulant dipping method. It was found that gloves could be very easily removed from the glove former without becoming tacky. Table 4 shows the tensile strength and elongation at break of films made by casting and dipping. Results reveal that tensile strength of these films are lower than what was expected. However the crosslinking density shows that the latex is over irradiated.

Pilot scale irradiation (2)

Table 5 shows the PRM value at different irradiation time. It can be seen that the sample after 8 hours of irradiation, reached the PRM value close to the value of the sample that received a radiation dose of 12 kgy from our laboratory experiment.

<table>
<thead>
<tr>
<th>Time (hours)</th>
<th>PRM (index)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>5.9</td>
</tr>
<tr>
<td>6</td>
<td>6.6</td>
</tr>
<tr>
<td>8</td>
<td>7.8</td>
</tr>
</tbody>
</table>

The irradiated latex sample did not have any coagulum as in the previous batch. This indicates that the addition of monomer after emulsifying to latex is a better method compared to the earlier method.

Table 6: Physical properties of latex films made from pilot scale batch (2).

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coagulant dipped film</td>
<td></td>
</tr>
<tr>
<td>Tensile strength Mpa</td>
<td>25</td>
</tr>
<tr>
<td>Elongation at break %</td>
<td>1050</td>
</tr>
<tr>
<td>Cast film</td>
<td></td>
</tr>
<tr>
<td>Tensile strength Mpa</td>
<td>25.1</td>
</tr>
<tr>
<td>Elongation at break %</td>
<td>1047</td>
</tr>
<tr>
<td>Crosslinking density mols/Cm$^3$</td>
<td>$1.09 \times 10^4$</td>
</tr>
<tr>
<td>100% PRM (index)</td>
<td>7.8</td>
</tr>
</tbody>
</table>

Table 6 shows the tensile strength value of films prepared with coagulant dipped and cast films. It also shows the crosslinking density of cast films. From these data it can be said that the crosslinking density of the present irradiated latex is slightly higher than what was required. However the batch was within specification for the production of examination gloves.

Glove Production in the Line

The gloves that were made were free of most of the common defects that are observed in conventional systems. The stripping of the glove from the former had no drastic difference compared to conventional system. However the gloves that were produce in this test trial had a thickness between 0.1 - 0.15 mm which is less than the thickness of a normal conventional examination glove. Due to low thickness sometime glove got torn in removing from the former. This could be over come by increasing the thickness.
Table 7: Temperature at different stages.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Washing of formers</td>
<td>93</td>
</tr>
<tr>
<td>Drying oven 1</td>
<td>50</td>
</tr>
<tr>
<td>Coagulant</td>
<td>54</td>
</tr>
<tr>
<td>Drying oven 2</td>
<td>00</td>
</tr>
<tr>
<td>Dipping tank</td>
<td>30</td>
</tr>
<tr>
<td>Drying oven 3</td>
<td>45</td>
</tr>
<tr>
<td>Leaching tank</td>
<td>45</td>
</tr>
<tr>
<td>Oven entrance</td>
<td>110</td>
</tr>
<tr>
<td>Oven exit</td>
<td>45</td>
</tr>
</tbody>
</table>

Table 8: Aging properties of coagulant dipped latex films from Batch (1) and Batch (2)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile Strength (Mpa)</th>
<th>Elongation at Break %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch (1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Before aging</td>
<td>25.7</td>
<td>875</td>
</tr>
<tr>
<td>After aging</td>
<td>27.2</td>
<td>956</td>
</tr>
<tr>
<td>Batch (2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Before aging</td>
<td>27.2</td>
<td>945</td>
</tr>
<tr>
<td>After aging</td>
<td>28.0</td>
<td>878</td>
</tr>
</tbody>
</table>

* Aging at 70°C 7 days.

Physical properties of the glove before and after aging is shown in Table 8. Results reveal that they are similar to value that was obtained in Indonesia. Aging properties are acceptable. The increase in tensile strength after aging may be due to better fusion of latex particles in the film.

CONCLUSION

RVNRL as a new material to produce gloves can be used in conventional plants without making major alteration. The gloves that were produced showed similarities in performance or better compared to gloves that were produced using conventional sulfur pre vulcanized systems. However to carry out detail analysis to optimum accepted quality level (AQL) a full scale trial has to be carried out in a production plant with more material.

Pre vulcanization relax modulus is a sensitive test for controlling the vulcanization during irradiation and it could give a greater control to the batch to complete at optimum vulcanization.
ACKNOWLEDGMENT

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REFERENCE

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Progress in radiation vulcanization of Natural Rubber Latex, K. Makuuchi, report to IAEA.


Internal Report JAERI - C. Chandralal and K. Makuuchi.
RUBBER THREAD MADE FROM A MIXTURE OF RVNRL AND NR-g-PMMA.

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Cibitung, Bekasi, Indonesia

ABSTRACT

Natural rubber grafted with methyl methacrylate (NR-g-PMMA) latex has been mixed with radiation vulcanized natural rubber latex (RVNRL) (1:1 by weight) to be the material for rubber thread. The NR-g-PMMA is produced by radiation of methyl methacrylate (MMA) onto natural rubber latex with various concentration of monomer 50, 75, and 100 phr (part per hundred ratio of rubber) at the irradiation dose of 5 kGy. The physical and mechanical properties of latex, film and thread from the mixed latex are evaluated. The results show that by increasing the concentration of NR-g-PMMA in RVNRL the modulus of thread increases, while for obtaining the modulus of thread meets to the ISO standard, the RVNRL should be mixed with 100 phr of NR-g-PMMA latex.

INTRODUCTION

The production of natural rubber latex thread has been introduced since 1922 (Weiss 1979). Then it has been developed continuously, and to day the production of good quality rubber thread is a complex technical operation.

One of the typical sulfur compound formulation for rubber thread based on centrifuged latex is shown in Table 1. By using this formulation, the 300% modulus is about 2-3 MPa (Pendle and Gorton 1979, Colling and Gorton 1984).

Table 1: Typical sulfur compound formulation for rubber thread

<table>
<thead>
<tr>
<th>Material</th>
<th>part by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>60% Natural rubber latex</td>
<td>166.7</td>
</tr>
<tr>
<td>20% Potassium laurate solution</td>
<td>2.5</td>
</tr>
<tr>
<td>10% Potassium hidroxide solution</td>
<td>4.0</td>
</tr>
<tr>
<td>50% Sulfur dispersion</td>
<td>3.5</td>
</tr>
<tr>
<td>50% Zinc 2-mercaptobenzthiazol dispersion</td>
<td>3.0</td>
</tr>
<tr>
<td>50% Zinc dibutyl dithiocarbamate dispersion</td>
<td>0.5</td>
</tr>
<tr>
<td>40% Antioxidant dispersion</td>
<td>5.0</td>
</tr>
<tr>
<td>50% Titanium dioxide dispersion</td>
<td>10-20</td>
</tr>
<tr>
<td>50% Zinc oxide dispersion</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Drying and cure 10 to 15 minutes, at 130°C
One of the drawbacks of this sulfur vulcanizate is the liberation of nitrosamine originated from the accelerators and their residues which are harmful to the human bodies. Radiation vulcanized natural rubber latex (RVNRL) sensitized by n-butyl acrylate (nBA) monomer (2 phr) has been suggested a suitable raw material for deeped products such as baby teats, surgical gloves, and catheters as well as rubber threads. Since this vulcanization process is chemical free, nitrosamine will not be liberated in the system. The irradiation has also destroyed the protein in this latex, and thereby RVNRL may also meet the requirement of free protein allergic products (Makuuchi 1994).

In spite of the above advantages of RVNRL, it does not meet the requirement for rubber thread due to its low modulus (1.1 MPa). Three alternatives to improve the modulus of the rubber thread (Colling and Gorton 1979):
- Increasing the sulfur content in vulcanization system.
- Increasing the time and temperature of the vulcanization process.
- Addition of filler which increases the modulus induces decreasing of the elongation at break.

In the previous paper, it has been reported that the addition of sulfur vulcanized latex into RVNRL (1:1 by weight) has improved the 300% modulus of RVNRL from 1.1 to 2.5 MPa (Utama 1986). Although the modulus has been improved, this addition may induce nitrosamine into the whole system and protein allergic to the consumers.

Poly(methyl methacrylate) (PMMA) is a strength and rigid polymer. Its clarity and transparency make PMMA to be applied for lenses, windows, fiber optics, and some construction materials. The modulus of elasticity is reported to be about 33000 MPa content (Higgins 1994, Brandrut and Immergut 1989). Moreover, PMMA appears to be non toxic. Based on these facts, PMMA has been selected to be a substitute of sulfur vulcanize to improve the modulus of RVNRL.

Since it is impossible to blend PMMA with the liquid RVNRL, the monomer itself (MMA) must be grafted on the rubber particles (NR-g-PMMA). Radiation grafting of MMA onto NRL produces high strength modulus (2-3 MPa) depends on the monomer content (Sundardi and Kadarijah 1984, Utama 1993). Blending of RVNRL with NR-g-MMA is supposed to improve the modulus to meet the requirement of rubber thread, and it will avoid the addition of sulfur vulcanize.

This study is trying to get information on the possibility of blending of RVNRL with NR-g-PMMA for producing rubber thread that is free from nitrosamine and has low cytotoxicity.

**EXPERIMENTALS**

**Materials**

The natural rubber latex was high amoniated (60% DRC) from Prabu Mulih Plantation, South Sumatra. n-Butylacrylate (nBA), methyl methacrylate (MMA) were technical grade monomers and other chemicals such as, cetic acid, talcum powder etc.

**Equipment**

A Panorama Irradiator, loaded with 80 kCi (1991) of cobalt-60 was used for preparation of the RVNRL located at CAIR-BATAN Pasar Jumat, Jakarta. The automatic rubber thread factory was located at Cibirung, Bekasi, out side the centre. The equipments for testing latex and rubber thread such as klaxon stirrer for measuring the mechanical stability time of latex, tensile tester for measuring the tensile properties of the rubber film and the thread, etc.
Preparation of the RVNRL

A mixture of 2 phr of n-BA was added in the emulsion from into the natural rubber latex (NRL) stirred for one hour and irradiated with gamma rays from Cobalt-60 source. Irradiation dose was 25 kGy at dose rate of 1.2 kGy. After irradiation the properties of their latex and its films: pH, viscosity, total solid content, 300% modulus, tensile strength, elongation at break were measured. The spectra of infra-red (IR) was measured by FTIR.

Preparation of NR-g-PMMA

Methyl methacrylate emulsion (50%) was added into diluted natural rubber latex (50% DRC). The concentrations of MMA in NRL were 50, 75, or 100 phr. The mixture was stirred for one hour then irradiated at 5 kGy, with a dose rate of 1.2 kGy. Degree of conversion and copolymerization were determined after irradiation. Also the spectra of infra red was observed.

Figure 1: Flow diagram for producing rubber thread.

Preparation of the rubber thread (Figure 1)

The flow diagram for producing rubber thread is shown on Figure 1. The latex from the tank (A) was flowed through a capillary into an coagulant bath containing acid, and coagulated. The thread was removed from the coagulating bath, and washed before being dried and heated in continous oven. The processing condition was shown on Table 2.

Table 2: The processing condition for production thread from the mixture of RVNRL and NR-g-PMMA.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Processing condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure of vessel, atm</td>
<td>1</td>
</tr>
<tr>
<td>Diameter of capillary, mm</td>
<td>0.5</td>
</tr>
<tr>
<td>Concentration of acetic acid,%</td>
<td>30, 45, 60</td>
</tr>
<tr>
<td>Temperature of washing batch °C</td>
<td>50</td>
</tr>
<tr>
<td>Temperature of drying oven, °C</td>
<td>90-130</td>
</tr>
</tbody>
</table>

Testing of the rubber thred. The physical and mechanical properties of rubber thread were measured according to the standard methode (ASTM 1984).
RESULT AND DISCUSSION

The latex and its film properties

Table 3 shows that the pH, VFA, and viscosity of the irradiated (RVNRL) are higher than the unirradiated (NR) ones. The ammonia content was lower, while MST, TSC, and DRC were quite the same. The increase of VFA and decrease of the ammonia content due to the formation of fatty acids by irradiation on the protein molecules, and the radiolysis of nBA that has been used as the sensitizer. WANG CHUNLEI et al. have reported that the hydrolysis of n-BA in the latex produces acrylic acid. Homopolimerization of n-BA induced stickness and has been supposed to increase the viscosity of the latex. However, the degradation of the protein molecules on the rubber particles by irradiation may also have contribute to the increase of the viscosity.

Table 3: Properties of natural rubber latex (NRL) before and after irradiation (RVNRL).

<table>
<thead>
<tr>
<th>Properties</th>
<th>NRL</th>
<th>RVNRL</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A. Latex</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>10.65</td>
<td>10.70</td>
</tr>
<tr>
<td>Total solid content</td>
<td>59.59</td>
<td>59.60</td>
</tr>
<tr>
<td>Dry rubber content</td>
<td>58.12</td>
<td>58.11</td>
</tr>
<tr>
<td>NH₄ content</td>
<td>1.55</td>
<td>1.25</td>
</tr>
<tr>
<td>VFA number</td>
<td>0.020</td>
<td>0.023</td>
</tr>
<tr>
<td>MST, sec</td>
<td>1800</td>
<td>1800</td>
</tr>
<tr>
<td>Viscosity, Cps</td>
<td>23</td>
<td>27</td>
</tr>
<tr>
<td><strong>B. Film</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300% Modulus, MPa</td>
<td>0.1</td>
<td>1.1</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>2.1</td>
<td>25.1</td>
</tr>
<tr>
<td>Elongation at break, %</td>
<td>1000</td>
<td>990</td>
</tr>
<tr>
<td>Permanent set, %</td>
<td>64</td>
<td>10</td>
</tr>
</tbody>
</table>

Figure 2 shows the IR spectra of NR latex in the presence of MMA after extraction with aceton for 24 hours. The excess monomer as well as its homopolymer are dissolved by the aceton. The specific fingerprint of NR is shown in Fig.2a, the absorption at 830 cm⁻¹ is due to cis 1,4- polyisoprene. After grafting occurs, changes of the specific fingerprint have been observed: The absorption at 830 cm⁻¹ decreases and accompanied by the appearance of absorption at 1155 and 1735 cm⁻¹. Those peaks impart the existence of isopropyl and carbonyl both peaks increase where as the intensity of the polyisoprene (830 cm⁻¹) decrease with the increase of monomer concentration (Fig.2b). This indicates the occurrence of grafting onto the NR particles.
Wavenumbers, cm$^{-1}$.

**Figure 2**: Infra-red spectra of the mixture of NR and MMA before (A) and after (B) irradiation.

**Table 4**: Monomer conversion and degree of grafting of NR-g-PMMA.

<table>
<thead>
<tr>
<th>Monomer content in the latex (phr)</th>
<th>Monomer conversion (%)</th>
<th>Degree of grafting (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>96</td>
<td>48 (L)</td>
</tr>
<tr>
<td>75</td>
<td>96</td>
<td>72 (M)</td>
</tr>
<tr>
<td>100</td>
<td>95</td>
<td>95 (H)</td>
</tr>
</tbody>
</table>

Table 4 shows that most of the monomer has been converted into both homopolymer and grafted onto rubber particles, and the degree of grafting increases with the increase of monomer content.

Each of the grafted latex was blended with RVNRL as a filler to improve its modulus and tensile at break. The low (L), medium (M) and high (H) degree of grafted NR were blended with the composition shown in Table 5.
Table 5. Composition of RVNRL/NR-g-PMMA blends.

<table>
<thead>
<tr>
<th>Composition blends</th>
<th>Ratio of weight</th>
<th>Type</th>
<th>NR-g-PMMA content (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RVNRL/L*</td>
<td>2/1</td>
<td>I</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>1/1</td>
<td>II</td>
<td>48</td>
</tr>
<tr>
<td>RVNRL/M*</td>
<td>2/1</td>
<td>III</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>1/1</td>
<td>IV</td>
<td>72</td>
</tr>
<tr>
<td>RVNRL/H*</td>
<td>2/1</td>
<td>V</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>1/1</td>
<td>VI</td>
<td>95</td>
</tr>
</tbody>
</table>

* L,M,H : NR-g-PMMA latex with low, medium, and high degree of grafting.

Table 6. Mechanical properties of the film obtained from the latex blends.

<table>
<thead>
<tr>
<th>Type</th>
<th>300% Modulus (MPa)</th>
<th>Tensile at break (MPa)</th>
<th>Elongation at break (%)</th>
<th>Permanet set (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RVNRL</td>
<td>1.1</td>
<td>25.2</td>
<td>1000</td>
<td>8</td>
</tr>
<tr>
<td>I</td>
<td>1.7</td>
<td>29.5</td>
<td>900</td>
<td>7</td>
</tr>
<tr>
<td>II</td>
<td>2.5</td>
<td>31.0</td>
<td>890</td>
<td>5</td>
</tr>
<tr>
<td>III</td>
<td>2.0</td>
<td>28.9</td>
<td>900</td>
<td>7</td>
</tr>
<tr>
<td>IV</td>
<td>2.8</td>
<td>25.4</td>
<td>800</td>
<td>4</td>
</tr>
<tr>
<td>V</td>
<td>2.3</td>
<td>29.0</td>
<td>890</td>
<td>6</td>
</tr>
<tr>
<td>VI</td>
<td>3.0</td>
<td>24.0</td>
<td>700</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 6 shows the mechanical properties of the films obtained from the latex blends. Blending with NR-g-PMMA has significantly improved the modulus of RVNRL. For any composition, the presence of NR-g-PMMA in the ratio of 1/1 induced highest modulus, but decrease of elongation at break and the permanent set. Although the tensile at break also improved by blending, but it tend to decrease with increasing the NR-g-PMMA content. The reduction of elongation at break is attributed to the discontinuity of the amorphous part due to the present of the grafted PMMA. The PMMA character appears at high degree of grafting such as 72 and 95%, therefore the films become tough (low permanent set, elongation at break and tensile strength).

The rubber thread properties

In order to produce the rubber thread, composition of type II (RVNRL/L=1/1) has been selected to be the raw a material. The concentration of acetic acid as the coagulant and temperature of heating are important factors in producing rubber threads.
Table 7 shows the properties of the rubber thread obtained from type II blend at different concentration of acetic acid. The mechanical properties were independent of the acid concentration, but browning became dominant at high concentration such as 60%.

Table 7. Physical and mechanical properties of rubber thread from the mixture of RVNRL and NR-g-PMMA composition type II with different acetic acid concentration.

<table>
<thead>
<tr>
<th>Properties</th>
<th>30% Modulus, MPa.</th>
<th>Tensile at break, MPa.</th>
<th>Elongation at break, %</th>
<th>Permanent set, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour</td>
<td>b</td>
<td>2.5</td>
<td>29</td>
<td>930</td>
</tr>
<tr>
<td>300% Modulus, MPa.</td>
<td>2.5</td>
<td>2.5</td>
<td>900</td>
<td>4</td>
</tr>
<tr>
<td>Tensile at break, MPa.</td>
<td>29</td>
<td>29</td>
<td>900</td>
<td>4</td>
</tr>
<tr>
<td>Elongation at break, %</td>
<td>930</td>
<td>900</td>
<td>900</td>
<td>4</td>
</tr>
<tr>
<td>Concentration of acetic acid, %</td>
<td>db</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

h=brown. db=dark brown.

![Figure 3. Effect of heating temperature on the physical and mechanical properties of rubber thread from the mixture of RVNRL and NR-g-PMMA.](image)

There is a tendency that by increasing the acetic acid concentration, the colour of rubber thread changes from brown to dark brown, while modulus, tensile at break, elongation at break, and permanent set are quite the same. The change of colour is caused by the oxidation of the tread by residual of acetic acid.

**Effect of heating temperature**

Unlike in the sulfur vulcanisate, the purpose of heating in RVNRL is mainly to reduce the water content rather than vulcanization. Figure 3 shows the effect of heating temperature on the water content and physical as well as mechanical properties of the rubber thread. It can be seen that the optimum heating temperature is 110 °C. At the optimum temperature the tensile at break is maximum, while the modulus is quite constant and the water content of thread less than 1%.
Table 8: Physical and mechanical properties of rubber thread from the mixture of RVNRL and 50 phr NR-g-PMMA with composition 1:1 by weight.

<table>
<thead>
<tr>
<th>Properties</th>
<th>RVNRL</th>
<th>CRT</th>
<th>ISO#</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter, mm.</td>
<td>0.48</td>
<td>0.46</td>
<td>-</td>
</tr>
<tr>
<td>Density, g/cm.</td>
<td>0.98</td>
<td>0.99</td>
<td>-</td>
</tr>
<tr>
<td>Weigh, g/m.</td>
<td>0.1648</td>
<td>0.1657</td>
<td>-</td>
</tr>
<tr>
<td>Length m/g.</td>
<td>6.0046</td>
<td>6.0350</td>
<td>-</td>
</tr>
<tr>
<td>300 Modulus, MPa.</td>
<td>2.3</td>
<td>2.4</td>
<td>2.4</td>
</tr>
<tr>
<td>Tensile at break, MPa.</td>
<td>31</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Elongation at break, %.</td>
<td>900</td>
<td>700*</td>
<td>500*</td>
</tr>
<tr>
<td>Permanent set, %.</td>
<td>4</td>
<td>3**</td>
<td>-</td>
</tr>
<tr>
<td>Moisture content, %.</td>
<td>0.9</td>
<td>1**</td>
<td>-</td>
</tr>
</tbody>
</table>

# ISO 123-75. * minimum, ** maximum

By using the optimum condition processing e.g.: diameter of capillary 0.5 mm, concentration of acetic acid 30%, temperature of washing batch 50°C, and temperature of drying oven 100-110°C, the physical and mechanical properties is shown on Table 8. From this table indicates that the mixture of RVNRL and NR-g-PMMA is possible for producing rubber thread with the physical and mechanical properties satisfy with the ISO standard.

**CONCLUSION**

It is indicated that the mixture of irradiated RVNRL and 50-100 phr NR-g-PMMA with composition 1:1 can be used as a raw material for producing rubber thread.

**ACKNOLEDMENTS**

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PRODUCTION OF RVNRL AND MANUFACTURE OF PRODUCTS FROM IT

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RVNRL Plant, Rubber Board
Kottayam - 686 009, India

ABSTRACT

The procedure of the trial irradiation of latex at the pilot plant are discussed. Factors influencing the quality of RVNRL during trial production are identified. Procedure for processing of radiation prevulcanised latex into end products has been standardised. Household gloves, industrial gloves, toy baloons, blood transfusion tubes and nipples are manufactured commercially from RVNRL produced at Rubber Board.

INTRODUCTION

The pilot plant for producing prevulcanised latex using gamma radiation was loaded with 0.37 PBq. of Cobalt-60 during April 1992. Trials started immediately following the source installation. 33 batches of latex have been irradiated under different conditions for standardising the parameters of radiation vulcanisation of latex. In association with Bhabha Atomic Research Centre, Mumbai frequent dosimetry studies were also carried out in the plant for estimating the correct dose required for obtaining the optimum properties to the processed latex. The RVNRL thus processed was supplied to different small scale product manufacturers in various fields and their feedback was collected.

Materials and Method

a) Latex: Highly stabilised low ammonia latex processed and supplied by PLPC, Rubber Board. The field latex is preserved with 0.3% ammonia and 0.025% TMTD/ZnO (1:1). 0.15% ammonium laurate is then added. Required amount of DAHP is added, stirred and allowed to stand for 3 days and centrifuged. The ammonia content of the centrifuged latex was adjusted to 0.3% and TMTD/ZnO (1:1) was adjusted to 0.025% on the latex. The latex thus processed has the following properties.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>DRC</td>
<td>60%</td>
</tr>
<tr>
<td>Coagulum content</td>
<td>Trace</td>
</tr>
<tr>
<td>TSC</td>
<td>61.5%</td>
</tr>
<tr>
<td>Sludge content</td>
<td>Trace</td>
</tr>
<tr>
<td>MST</td>
<td>&gt; 1600 Secs</td>
</tr>
<tr>
<td>Manganese</td>
<td>Trace</td>
</tr>
<tr>
<td>KOH No.</td>
<td>0.4 to 0.5</td>
</tr>
<tr>
<td>VFA</td>
<td>&lt; 0.02</td>
</tr>
<tr>
<td>Copper</td>
<td>Below 1 ppm</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Below 10 ppm</td>
</tr>
<tr>
<td>NH₃%</td>
<td>0.35</td>
</tr>
</tbody>
</table>

b) Butyl Acrylate: IPCL, Baroda.

c) Carbon Tetra Chloride, Potassium Hydroxide, Ammonia: Merck (India) Ltd., Qualigens fine chemicals.

Stabilised low ammonia latex is transferred to the product vessel (1000 litres capacity) after one week maturation. The latex is compounded as per the formulation given below.

<table>
<thead>
<tr>
<th>Component</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>60% H.S.LA latex</td>
<td>167</td>
</tr>
<tr>
<td>10% KOH</td>
<td>2</td>
</tr>
<tr>
<td>n-BA</td>
<td>1</td>
</tr>
<tr>
<td>CCl₄</td>
<td>1</td>
</tr>
<tr>
<td>0.2% ammonia water</td>
<td>2</td>
</tr>
</tbody>
</table>
During compounding latex is stirred at 30 to 40 rpm. The product vessel with compounded latex is taken to the radiation chamber and aligned in position. There the latex is placed for maturation for 12 hours. The matured latex under slow stirring is exposed to gamma radiation by operating the plant. Irradiation is continued till 25 KGy is received by the latex. After completion of irradiation, ZDC is added to the irradiated latex at 0.75 phr and the product vessel is taken out to the material handling area for transferring RVNRL to drums for subsequent product development/testing operations.

As a reference method the gamma-chamber 900 is made use to correlate the results obtained. For that a sample of the compounded latex is taken from the product vessel and irradiated in the gamma chamber to the level of 25 KGy for complete vulcanisation. After adding the required antioxidant, films are casted using both gamma-chamber irradiated and pilot plant processed RVNRL. The partially dried films are then leached in cold water for four hours and dried at room temperature. The final drying is done at 80°C for five hours. Dumbell samples are cut from these sheets and tested for tensile properties.

### Standardised Process Parameters

33 batches of RVNRL were processed in the pilot plant with a view to standardise process parameters. Trials were carried out by varying the following conditions:

1. Quality of latex taken for irradiation.
2. Quantity of latex per batch.
3. Sensitisers and compounding.
4. Dose rate.
5. Irradiation atmosphere.

#### 1. Quality of Latex

The physical properties of the RVNRL produced mainly depend on the quality of the latex irradiated. Studies revealed that a latex having very low VFA and high stability is best suited to produce good quality RVNRL. Moreover fresh latex is more suitable than aged latex.

#### 2. Quantity of Latex per Batch

According to the observations made during trials of irradiation the quantity of latex taken in the product vessel has a profound effect in the radiation dose absorbed by the latex. In the exposed condition, the Cobalt-60 source unit occupies the centre of the product vessel and maximum dose absorption is noted when latex is taken to the full capacity (1000 Litres). Wastage of energy at various levels of loading the product vessel has been measured using gamma area monitor. Results are given in Table 1.

<table>
<thead>
<tr>
<th>Quantity of latex in the product vessel</th>
<th>Wasted energy in terms of dose rate (microSievert per hour)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Empty product vessel</td>
<td>65-70</td>
</tr>
<tr>
<td>2. 600 litres of latex filled</td>
<td>20-25</td>
</tr>
<tr>
<td>3. 800 litres of latex filled</td>
<td>15-20</td>
</tr>
<tr>
<td>4. 1000 litres of latex filled</td>
<td>5-10</td>
</tr>
</tbody>
</table>

Hence the varying quantity of latex in the vessel, the final product will give different properties for the same period of irradiation. Therefore for maximum efficiency, the product vessel has to be charged with the full capacity.
3. Sensitisers and Final Compounding

The effect of various sensitisers at different doses were studied. On the basis of this, the most suitable sensitisier for RVNRL processing at the pilot plant was found to be 5 phr dose of n-butyl acrylate (n-BA) or a 2 phr dose of n-BA and carbon tetra chloride in the ratio 1:1. But the product manufacturers are reluctant to buy RVNRL processed using 5 phr n-BA due to the smell of n-BA. So a 2 phr dose of n-BA and CCl₄ in the ratio 1:1 is adopted for RVNRL processing at the pilot plant. The final compounding was tried at 55 drc and 58 drc and got comparable results in both cases. As most of the products are made by dipping and since the present consumers are preferring a higher drc material, at pilot plant the final compounding is practiced at 58 drc.

4. Dose Rate Effect

At present the dose rate of RVNRL plant facility as on June 1996 is only 0.108 KGy per hour. So, for delivering 25 KGy, it requires nearly 232 hours of exposure. For processing one batch, nearly 15 days are needed when two shifts are planned per day. The results obtained for the processed latex are not fully satisfactory. This may be due to the low dose rate that ultimately results in long irradiation time required for processing RVNRL. For processing good quality RVNRL, definitely the processing time has to be reduced to such an extent that the processing will be completed within one or two days by continuous irradiation. This can be achieved only by increasing the dose rate by using a high activity Cobalt-60 source.

5. Irradiation Atmosphere

This factor has influence on determining the quality of RVNRL produced. The existing product vessel do not have much flexibility for irradiation under different conditions. The oxygen entrapped in the latex and in the empty space of the vessel is converted to ozone during irradiation. This ozone formed is likely to react with the latex which is under constant stirring during irradiation.

In the preliminary trials, the tensile properties were very poor since the vessel was frequently opened for collecting samples. Later some methods were adopted to prevent entry of air in the product vessel. The RVNRL thus processed has got superior properties. Moreover, when the processing is made continuous, it is seen that the physical properties are further improved. Hence it is expected that by complete replacement of air from the vessel by an inert gas like nitrogen, the tensile properties of the processed latex can be further improved.

Dose Estimation Procedure

1. Alanine Dosimetry and  
2. Fricke Dosimetry.

Since alanine dosimetry measurement system is costly, fricke dosimetry is being used for the regular dosimetry studies.

Water was taken in the product vessel and the vessel was aligned in position. The dosimetric solution was filled in the irradiation vials (4 X 10⁻⁶m³ glass tube with stopper) and are kept inside the product vessel at different positions and irradiated for 60 minutes. Optical density with respect to unirradiated fricke solution was measured using the spectrophotometer and the absorbed dose was calculated. The values are given in Table 2.
Table 2: Optical density with respect to unirradiated fricke solution

<table>
<thead>
<tr>
<th>SI. No.</th>
<th>Distance from top of the product vessel</th>
<th>Measurement positions</th>
<th>Absorbed dose rate (KGY/hour)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.315 m</td>
<td>Top</td>
<td>0.050</td>
</tr>
<tr>
<td>2.</td>
<td>0.473 m</td>
<td>Middle</td>
<td>0.057</td>
</tr>
<tr>
<td>3.</td>
<td>0.630 m</td>
<td>Bottom</td>
<td>0.160</td>
</tr>
<tr>
<td>4.</td>
<td>0.788 m</td>
<td></td>
<td>0.205</td>
</tr>
<tr>
<td>5.</td>
<td>0.945 m</td>
<td></td>
<td>0.089</td>
</tr>
<tr>
<td>6.</td>
<td>1.200 m</td>
<td></td>
<td>0.111</td>
</tr>
</tbody>
</table>

Note: Date of measurement - 14/3/1996
Product vessel - 1.2m dia X 1.2m height
Average dose rate = 0.112 KGY/hour.

So the calculated average dose rate inside the product vessel is found to be 0.112 KGY/hour as on 14/3/96. Using this value the irradiation time required to deliver 25 KGY to rubber latex is 223 hours.

Fields of Application of RVNRL Produced

From 1992 to 1995, 33 batches of RVNRL were produced. Since the source strength of the facility is low and medium of irradiation is not free from air, the RVNRL produced was not having properties comparable to that of conventionally pre-vulcanised latex. Yet the RVNRL processed in all the batches was accepted by the product manufacturers for producing following types of dipped goods.

Table 3: The production of RVNRL and its consumption in different product manufacturing applications from 1992 to 1995.

<table>
<thead>
<tr>
<th>SI No.</th>
<th>Year</th>
<th>Quantity produced in litres</th>
<th>Consumption in %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Gloves (household &amp; industrial)</td>
</tr>
<tr>
<td>1.</td>
<td>1992</td>
<td>7000</td>
<td>60</td>
</tr>
<tr>
<td>2.</td>
<td>1993</td>
<td>13000</td>
<td>46</td>
</tr>
<tr>
<td>3.</td>
<td>1994</td>
<td>4000</td>
<td>92</td>
</tr>
<tr>
<td>4.</td>
<td>1995</td>
<td>6000</td>
<td>60</td>
</tr>
</tbody>
</table>

Discussions with the RVNRL consumers showed that the products manufactured with it have the following merits and demerits.

Merits

1. Better product acceptability by the consumers.
2. Better clarity of the products.
3. Lower modulus.
4. Simple process.
5. Less man power during production
6. Lower ash content
7. Lower latex viscosity.

Demerits

1. Inferior ageing property.
2. Low tensile strength.
3. High set.
CONCLUSION

RVNRL can find applications in the field of surgical and examination gloves, catheters, balloons, pharmaceutical tubings etc. The RVNRL pilot plant at Rubber Board, India can be effectively utilized by modifying the existing product vessel and enhancing the source strength.

ACKNOWLEDGEMENT

The authors express their gratitude to Shri K.J. Mathew, Chairman, Rubber Board for granting permission to present this paper at the Second International Symposium at Kuala Lumpur, Malaysia. The authors also express their thanks to Dr. E.V. Thomas, Director, Department of Processing and Product Development for his support and guidance at various stages of preparation of this paper.

REFERENCES


APPLICATION OF RADIATION VULCANIZED NATURAL RUBBER LATEX IN INDONESIA

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ABSTRACT

The center has carried out R&D of Radiation Vulcanization Natural Rubber Latex (RVNRL) technology and introduced it to the industries since the inauguration and operation of the latex pilot plant in 1983. After years of experiences and the environmental consideration, n-butylacrylate (n-BA) has replaced CCl₄ as the sensitizer. Until now the introduction program shows that radiation vulcanized latex is more suitable for home industries than large industries. The obstacle of the program is the marketing of the dipped products. In spite of these problems, the introduction of this technology to the people in some undeveloped area of Java has supported the national program to improve their living standard. The problems of nitrosamine and protein allergic have turn up RVNRL to be the substitute of sulfur vulcanized latex in the future. The cooperation with a national condom manufacturer (PT. Mitra Banjaran) has applied RVNRL for condom production in the large scale. Soft condoms with less probability of pinhole are obtained, but the technical problem is stickiness after pilling. Supplies to a baby teat and a rubber thread manufacturer offers great advantages by not using any chemicals. In spite of the advantages, the problem of latex viscosity for dipping and the low modulus of elasticity of the threads arise. Through those input CAIR-BATAN is conducting the research and development in improving the crosslinking among the rubber particles that are supposed to be the reason of the stickiness and low modulus of elasticity. This effort is expected to be able to broaden the application of RVNRL, and it will be achieved only by the involvement of rubber chemist, rubber technologist, and radiation chemist.

INTRODUCTION

Indonesia has started the study on Radiation Vulcanization of Natural Rubber Latex (RVNRL) as early as 1970. The operation of the 215 kCi latex irradiator in 1983 has made CAIR-BATAN the pioneer of RVNRL among the RCA member countries. Since its operation, this facility has become a training center for the member countries attended by national and international research institutes as well as the private sectors. However, the research and development of the technology were carried out by each member country (Makuuchi 1990).

Along with the improvement of the radiation technique, introduction of RVNRL technology to the related industries has been carried out. Development of new sensitizer and the stringent environmental regulation have shifted CCl₄ as the main sensitizer. Since 1993, n-butylacrylate (n-BA) is the only sensitizer in RVNRL technology in Indonesia. In spite of the promising technique, the introduction to the industries faces many problems, especially in the large scale industries. Those problems are not just the economic consideration, but also the technical problems arise due to the changing of process.

This paper describes the experiences and the recent R&D program carried out at CAIR-BATAN to improve the transfer to the industries.
DEVELOPMENT OF SENSITIZER

Chlorinated hydrocarbon, specially CCl₄ was the first common sensitizer in developing RVNRL (Minoura and Asao 1961). In spite of its efficiency, this compound is not accepted under the health aspects. New sensitizers have been developed in effort to reduce or totally replace this sensitizer. Acrylic compounds were the candidates therefore. The development of acrylic sensitizers as single compounds or combination with other compounds has been reported at the first symposium in Tokyo (1990).

In order to reduce the concentration of CCl₄ in the pilot plant operation, a combination of n-BA with CCl₄ (1 phr/1 phr) was used (Yanti and Sundardi 1988). Irradiation dose of 20 to 30 kGy gave the maximum tensile at break (Tb) and good aging properties of the rubber film. For several years this sensitizer was applied in the RVRNL that were supplied to the industries at that time.

Considering our intention to promote more intensively RVNRL as well as the health consideration, n-BA was the only sensitizer in the RVNRL technology since 1993. This monomer is available in the local market, and the stabilization of several local concentrate latex against this monomer has been evaluated.

The standard concentration of n-BA until now is 2 phr (part per hundred rubber), and the latex is stabilized with 0.2 phr KOH. The analysis of residue showed that n-BA disappeared in 2 weeks after irradiation.

APPLICATION OF RVNRL

The introduction of RVNRL to the industries of latex dipped product such as rubber gloves, condoms, rubber thread manufacturer, etc. was initiated in 1985.

Rubber gloves industries

This technology was introduced mainly to technical rubber gloves manufacturer which were mostly home industries. The purpose was to raise the rubber gloves production to meet the local demand. Since they were mostly home industries, this sector was very weak. The quality of the gloves produced in the laboratory scale have meet the consumer’s standard. However, when it was transferred to this sector, their products were very difficult to meet the consumer’s standard due to the lack of dipping skill.

Unlike technical rubber gloves, rubber examination and rubber surgical gloves' manufacturers were large industries. A trial production has been carried out under the cooperation with a manufacturer. The products have met the Indonesian Standard Industry (SII), but the technical problems for producing dipped goods and the market situation were the problems of the introduction to this sector.

The above situation indicates that the problems are not the irradiated latex, but they are more on the technical problem in producing dipped products and the market situation. The same problems are faced if conventional vulcanized latex is used. The competition of the price and quality with the imported products are very tough.

Condoms

The study in using RVNRL for condom production has been carried out in the laboratory and factory scale. While the products have met the BSI and JIS standard in the laboratory scale, the product of the first trial at PT Mitra Banjaran, Bandung in 1987 were totally rejected due to stickiness. After some improvement of the processing, better quality (10% reject) condoms were obtained at the second trial in 1990. The latex was irradiated by using n-BA/CCl₄ sensitizer with a total absorbed dose of 25 kGy.
Table 1 showed the specification and physical properties of the products including those obtained from sulfur vulcanized (SVNRL) one (Sundardi 1990).

<table>
<thead>
<tr>
<th>Specification</th>
<th>RVNRL</th>
<th>SVNRL</th>
<th>ISO 4074 (1992)</th>
</tr>
</thead>
<tbody>
<tr>
<td>thickness (mm)</td>
<td>0.066</td>
<td>0.061</td>
<td>0.045-0.075</td>
</tr>
<tr>
<td>M 300% (MPa)</td>
<td>1.01</td>
<td>1.64</td>
<td>-</td>
</tr>
<tr>
<td>M 600% (MPa)</td>
<td>2.42</td>
<td>5.68</td>
<td>-</td>
</tr>
<tr>
<td>Tb (MPa)</td>
<td>22.06</td>
<td>30.59</td>
<td>min 17.0</td>
</tr>
<tr>
<td>Eb (%)</td>
<td>970</td>
<td>840</td>
<td>min 700</td>
</tr>
<tr>
<td>Bursting vol. (liter)</td>
<td>42</td>
<td>35</td>
<td>min 13.5 (depends on the diameter)</td>
</tr>
<tr>
<td>Color</td>
<td>milky white</td>
<td>milky white</td>
<td>-</td>
</tr>
</tbody>
</table>

Condoms made from RVNRL have lower modulus, higher elongation at break (Eb) and bursting volume than those made from SVNRL. However, the tensile at break (Tb) were lower due to the less crosslink density.

During the laboratory scale the condoms did not stick each other after pilling and drying. However, this problem arose in the factory scale due to the technique of production. To overcome this problem, antistick agent has been added in the rinsing water. Two kinds of commercial soaps have been selected as the antistick agent.

The production of concentrated latex that meets the requirement of condom production decline with the time, whereas the world demand increases. Therefore the R&D for the condom production has become more intensive in the last 2 years. In the cooperation with the R&D group of PT Mitra Banjaran, we carried out the specification of NR latex for the condom production.

Table 2 shows the specification of both concentrated and the irradiated latex. Most of the field latex in Indonesia has relatively high magnesium content. The latex used in the experiments were those after DPA (diammonium phosphate) treatment to reduce the magnesium content.

The radiation vulcanized latex is suitable for condom production, since the specification is in the range of the standard latex for condom. Degradation of proteins by irradiation is assumed to have increased the VFA number.

The interest in the RVNRL as a promising material for condom production has turns up the company and the center to sign a memorandum of understanding in developing this technique. By using RVNRL a chemical free and energy saving process, less probability of pinhole can be obtained so that the products are expected to meet the standard and also the export qualification. The products are free of nitrosamine and protein allergic, because the protein has been destroyed by irradiation.
Table 2: Specification of the concentrated latex (HA) and RVNRL for condom production.

<table>
<thead>
<tr>
<th></th>
<th>Non irrad. Latex *)</th>
<th>RVNRL**)</th>
<th>Standard for Condom</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(HA)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Solid Content (%)</td>
<td>61.44</td>
<td>53.79</td>
<td>min 61.50</td>
</tr>
<tr>
<td>Dry Rubber Content (%)</td>
<td>60.18</td>
<td>52.04</td>
<td>min 60.50</td>
</tr>
<tr>
<td>TSC - DRC (%)</td>
<td>1.26</td>
<td>1.75</td>
<td>1.3 - 1.5</td>
</tr>
<tr>
<td>NH₃ content (%)</td>
<td>1.8</td>
<td>not determined</td>
<td>1 - 2</td>
</tr>
<tr>
<td>Volatile Fatty Acid</td>
<td>0.0176</td>
<td>0.0510</td>
<td>max 0.02</td>
</tr>
<tr>
<td>Viscosity (cp)</td>
<td>115.2</td>
<td>70.4</td>
<td>max 120</td>
</tr>
<tr>
<td>Mechanical Stability Time (sec)</td>
<td>1790</td>
<td>2820</td>
<td>1600 - 1800</td>
</tr>
<tr>
<td>Magnesium content (%)</td>
<td>0.0124</td>
<td>not determined</td>
<td>max 0.005</td>
</tr>
</tbody>
</table>

*) obtained from Jalupang plantation, West Java (tapped during the dry season)
**) 2 phr n-BA, 0.2 phr KOH, 35 kGy

Other industries

Unlike the rubber gloves' industries, other small home industries of dipping goods show more interest in the application of RVNRL. The simple processing and cheaper production cost are the reason for using RVNRL. Those industries are decorated balloons, finger gloves for electrical industries, and a movie industry. For these industries, the center is the RVNRL supplier, and as the consequence therefore it must be able to supply the latex regularly to those companies.

The consumption of the balloon manufacturer was highest among those industries (100 kg/month) at that time. However, this manufacturer stopped its consumption after 7 years due to the market situation. The finger gloves manufacturer consumes less than 50 kg/month, but the center still continuously supplies until now (about 10 years). The movie industry occasionally consumes the latex for making mask, artificial animals, part of human body, etc.

The most regular consumer is a factory producing sealing for cans. This factory's consumption gradually increases from 20 kg/month to 1.5 tons/month within 9 years. The products have supplied the local demand for can sealing. Since 1989, the company itself brings the latex to be irradiated at the center.

So far the evaluation shows that RVNRL is more suitable for small industries with simple or manual processing. Moreover, it gives higher added value to the products, because of the chemical free process and less energy consumption. To apply RVNRL in the large industries such as examination, surgical gloves, and condom factories, modification of the process must be done. For some products the dipping process may need a modification due to the low viscosity of the latex. Any heating during the process must be controlled, because RVNRL does not need high temperature for processing.

More recently we have introduced RVNRL to a baby teat manufacturer in Surabaya, East Java. They produce teats of natural and synthetic rubbers, and the products are mostly for local consumption and partly for export to neighboring countries. Since May 1996 we have sent 3 tons of RVNRL in two batches. They are satisfied with the trial production, but the complain about the process. Unlike SVNRL, RVNRL needs twice as much dipping. Instead of the dipping problem, they have been able to reduce the temperature for drying and get better clarity of the products. They are able to develop a new process to produce the teats from RVNRL. The application of RVNRL by this manufacturer will significantly suppress the nitrosamine content of the products and protein allergic that means high added value of the products.
RECENT R&D TO SUPPORT THE APPLICATION OF RVNRL

The introduction of RVNRL technology to those home industries must be supported by continuous research. The purpose of the research is not only helping the industries to solve their problems, but also to develop new techniques that can be offered in the future.

The low modulus given by RVNRL is one of the merit of this technology in dipping process, because it gives convenience for surgical gloves, condom, baby teats, and balloons. This low modulus is due to low crosslink density. However, low crosslink density results in low tensile strength that is not preferred for surgical gloves, and decorated balloons quickly deflate after blown up. Low crosslink density is also supposed to be the reason of stickiness of the condoms.

All these input have urged us to try to improve the crosslink density. As it has been reported at the previous symposium in Tokyo that high tensile strength of the rubber film will be obtained after irradiation only if the green strength of the latex is high. The latex we use has very low green strength. In order to increase the crosslink density, hydroperoxide or tert-butylperoxide has been added into the latex. The concentration of either peroxide is 0.2 phr, and it is added either before or after irradiation. It is expected that the green strength can be increased before irradiation through peroxidation. The increase of tensile strength is also expected by peroxidation after irradiation through heat treatment of the film.

Blending of RVNRL with latex-g-PMMA is carried out to produce rubber threads. The purpose of blending is to improve the modulus elasticity of the thread. A previous research showed that blending of RVNRL/SVNRL (1/1) produced good quality thread (Utama 1986, Utama and Kusumawati 1991). Since we are going to avoid nitrosamine and protein allergic problems, it has been changed to MMA grafted latex (irradiation grafting). The research is still going on under the cooperation with a national thread company. The results are also presented in this symposium.

We are convinced that RVNRL will be a candidate in the rubber industries in the future. Clean processing is expected, and competition in the international market will force our products to meet the international standard ISO. In order to turn up the role of RVNRL, the radiation technique as well as the RVNRL technology must be improved. We have to concern seriously about the scientific as well as the economical aspects to be able to convince the industries. For this purpose the cooperation of radiation chemist, rubber chemist, and rubber technologist is needed. Through this cooperation, it is expected that the above problems faced by the industries can be solved.

THE IMPACT OF RVNRL TECHNOLOGY ON THE NATIONAL PROGRAM

In spite of those problems, in the past 3 years the institute has offered this technology in participating at the national program to improve the living standard of people in the undeveloped area. The people in that area were trained to produce dipped goods such as gloves, balloon toys, and finger coats either to supply their own needs or their neighboring area. The success of the program depends on each community, those who understand technology are easily stimulated, but those without technology just absorb the knowledge of the training. One example of the success is that a small company in Jakarta (PT. Indrasari) is willing to be a main distributor of the dipped products for a nearby area. These products are consumed by the local cleaning service company, home industries, and the local people as decorating balloons.

The application of RVNRL in the medical rehabilitation is also studied. The price of RVNRL is much cheaper than the silicone rubber for artificial part of human body. It is expected through this technology the low income community can be supported.
ACKNOWLEDGMENT

The authors wish to express their sincere thanks to Mr. Marga Utama, BATAN - PT Mitra Banjaran working group, and Mr. Sundardi for the discussion that enable us to write this paper.

REFERENCES


**QUESTIONS & ANSWERS, and COMMENTS**

**Session III**

<table>
<thead>
<tr>
<th>Q1</th>
<th>Thomas</th>
<th>What is the cause of stickiness in RVNRL films?</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>Yanti Soebianto</td>
<td>The incidence of stickiness occurred when hydrogen peroxide is used as the co-sensitiser which promotes degradation of rubber.</td>
</tr>
<tr>
<td>Q2</td>
<td>Bez</td>
<td>Is it possible to make foam products from RVNRL? This is not possible with SPVL due to instability of the foam.</td>
</tr>
<tr>
<td>A2</td>
<td>Marga Utama</td>
<td>The MST of latex needs to be reduced to 500 seconds to make foam products from RVNRL.</td>
</tr>
<tr>
<td>C3</td>
<td>Thomas</td>
<td>Low modulus RVNRL would be unsuitable for the production of foam products.</td>
</tr>
<tr>
<td>Shukri A. Wahab</td>
<td>It could be used for products such as inner soles of shoes.</td>
<td></td>
</tr>
<tr>
<td>Q4</td>
<td>Tan</td>
<td>Are the dipping parameters for RVNRL similar to that of SPVL?</td>
</tr>
<tr>
<td>A4</td>
<td>Wan Manshol</td>
<td>The dipping parameters are somewhat similar needing only minor modifications.</td>
</tr>
<tr>
<td>Q5</td>
<td>Ken</td>
<td>What is the most suitable antioxidant for RVNRL?</td>
</tr>
<tr>
<td>A5</td>
<td>Wan Manshol</td>
<td>I cannot reveal at the moment.</td>
</tr>
</tbody>
</table>
A SIMPLE AND EFFICIENT GAMMA-IRRADIATOR FOR RVNRL.

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Abstract

This work describes a new design of a gamma irradiator for RVNRL which obeys a reliable operation and an efficient economical equation. Our irradiator is of a nobel design according to present requirements of latex industries and to the state of the art of radiation technology. The irradiator is of a wet storage type, where the radioactive sources are fixed in the reactor vessel, permanently submerged in deionised water. Preformulated latex is pumped from a deposit vessel into the reactor vessel and it is recirculated during the irradiation cycle avoiding turbulences and dose inhomogeneities. The irradiation time per one ton batch with a Co-60 charge of 3.5E15 Bq (100 kCi) is of approximately 4 hours.

INTRODUCTION

Over the past 30 years several pilot, medium and high - capacity Co-60 gamma irradiation facilities were built and installed successfully. The major part of the approximately 160 industrial irradiators are "package irradiators", using standard dimensions for boxes and cartons. These irradiators are very important for sterilization purposes, but are not efficient for treatment of liquid or fluid substances like, enzyme solutions, serum, or as in the present activity the irradiation of NRL for vulcanization. In the past our country was able to build multipurpose irradiators:

a) mobil irradiator (Cancio et al, 1977)

b) package irradiator (Lombardo and Smolko, 1990)

Although several irradiator have been designed and built specially for latex, (Makuuchi et al, 1990; Muhd Noor Bin Muhd Yunus, 1989) we are considering an alternative option. In this occasion the design is a single purpose, wet storage type, with the Co-60 sources submerged and mounted inside the reactor vessel.

DESIGN PRINCIPLES

The facility having a capacity to irradiate more than 100 ton/year can be classified according to Makuuchi (1996) as a single purpose, wet type, batch like process for commercialization work. It consists of a single stainless steel reactor, deposited on the floor of a 6 m deep deionised water pool. The reactor vessel contains a source rack ring shaped, containing 60 independent positions for each Co-60 pencil.
The charge and discharge of the sources is provided as in any other pool for sources interchanging purposes. Latex is pumped from a feed tank to the reactor vessel by a pipe system, and enters the vessel through the central hole of the source rack system in the vessel top covering. This covering is part of the source rack. Latex is flowing continuously during the irradiation time of the batch which could stands up to 4 hours in the reactor and tubing system. The volume of the batch is around 1.5 m$^3$. The RV system consists like in other latex single purpose irradiators facilities of the reactor vessel the emulsification and mixing tanks.

**PROCESS PARAMETERS**

In the study of the gamma irradiator for RVNRL, we considered the main parameters of a facility for commercialization purposes. These parameters are the dose of vulcanization $D_v$ in kGy and the facility scale $M$ in ton/year. With $D_v$ and $M$ we calculated the strength of the Co-60 source $S$ and the efficiency of the facility. The radioactive source of our facility is located in the reactor completely surrounded by the latex fluid in a 360 rad configuration.

**CALCULATION OF THE SOURCE STRENGTH, THE VULCANIZATION TIME AND THE EFFICIENCY**

The absorbed energy $E_a$ of $M$ (ton) of latex irradiated per year with dose $D_v$ (kGy) is,

$$E_a = M \left( \frac{ton}{yr} \right) \cdot D_v \left( kGy \right)$$

The energy emitted by a Co-60 source of $S \ (MCi)$ is

$$E_e = S (MCi) \cdot \prod_{i}^{n} q_i$$

where $q_i$ are adimensional unit equivalences.

The efficiency is

$$\eta \ (%) = \frac{E_a}{E_e} \cdot 100$$

and for $\eta = 100$ the whole emitted energy is absorbed by the material.

$$E_a = E_e$$

When $\eta$ equals to 100% applying (4) we obtain the source strength $S$

$$M \cdot D = S \cdot \prod_{i}^{n} q_i$$
\[ S = \frac{M \cdot D}{\prod q_i} \]

where

\[ \prod q_i = q = q_1 \cdot q_2 \cdot q_3 \]

and

\[ q_1 = \text{power equivalence between MCi and kW} \]
\[ q_2 = \text{energy equivalence between kWh and J} \]
\[ q_3 = \text{annual time equivalence between yr and h} \]

then

\[ q_1 = 14.8 \, (\text{kW/MCi}) \]
\[ q_2 = 3.6 \times 10^6 \, (\text{J/kWh}) \]
\[ q_3 = 8760 \, (\text{h/yr}) \]

In the present case we have \( M = 600 \, (\text{ton/year}) \), \( D_v = 15 \, (\text{kGy}) \)

hence

\[ E_a (\text{J/yr}) = 600 \times 10^3 \times 15 \times 10^3 \times 1 \times 10^{10} \, (\text{J/yr}) \]

\[ E_a (\text{J/yr}) = S \, (\text{MCi}) \times 466 \times 7328 \times 10^9 \]

from (5)

\[ S \, (\text{MCi}) = 0.021427 \text{ or } \]
\[ S = 21.427 \, (\text{Ci}) \]

Without taken in consideration the source decay, self adsorption, geometry, etc. with approximately 22 KCi it is theoretically possible to vulcanize 600 ton/year of latex irradiated at 15 kGy.

If efficiency factors are considered

- annual working time = \( f_1 \)
- 12.3 \% annually decay of the source = \( f_2 \)
- adsorption and geometry = \( f_3 \)

with \( f_1 = 0.7; f_2 = 0.94; f_3 = 0.8 \)

the total efficiency factor

\[ f = \prod f_i \]

then

\[ f = 0.7 \times 0.94 \times 0.8 \]
\[ = 0.5264 \]

The effective source strength for treatment of 600 ton/year results then higher in the following relationship.

\[ S = S' \cdot f \]

where \( S' \) is the effective source strength been equal to

\[ S' = \frac{S}{f} \]
\[ S' = \frac{21.427}{0.5264} \]
\[ S' = 40.704 \text{ Ci} \]

This is the minimum charge of Co-60 for a 600 ton/year facility. The irradiation time of vulcanization for a batch of one ton is

\[ t_v = \frac{6000 \text{ (h/yr)}}{600 \text{ (ton/yr)}} \]
\[ t_v = 10 \text{ (h/ton)} \]

But for a source strength of 100 kCi the \( t_v \) is only 4 (h/ton).

**ACKNOWLEDGEMENT**

The authors wish to express their sincere thanks to the International Atomic Energy Agency for providing support for the incorporation of the RVNRL technology in our Project *MATERIALS FOR BIOMEDICAL AND AGRICULTURAL USE*, ARG/8/011.

**REFERENCES**


THE WORKING OF RVNRL PILOT PLANT OF RUBBER BOARD AND ITS SAFETY DEVICES

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ABSTRACT
A pilot plant for producing radiation vulcanised natural rubber latex (RVNRL) was established at Rubber Board, India in 1992. Irradiation is done by a batch process in the plant. The plant has a versatile safety system for safety of operators and people working in and around the plant.

INTRODUCTION
A panoramic wet storage type gamma irradiator plant with maximum source strength of 3.7 PBq Cobalt-60 was commissioned in April 1992 at Rubber Board, Kottayam for producing radiation vulcanised natural rubber latex. The facility was loaded with 0.37 Pbq Cobalt-60 (8 pencils) initially to standardise the process parameters. The irradiation of rubber latex is done as a batch process in a stainless steel vessel of 1000 litres capacity. Rubber latex is stirred continuously during irradiation using paddle stirrers provided in the product vessel at three locations for ensuring uniform dose distribution. The radiation source is stored in a cylindrical source cage and shielded under water and is brought up to the centre of the product vessel for irradiation by a hydraulic system with two hoist wire ropes. A ventilation system is provided to remove Ozone and Oxides of nitrogen formed during irradiation. A number of safety interlocks are provided to ensure absolute safety of the personnel working in the radiation centre and also to prevent accidental radiation exposure. A concrete biological shield of suitable thickness at different locations are provided all around the irradiation cell. Details of the plant with emphasis on safety aspects are discussed in the paper.

Deminerlised Water Plant
The source storage pool is filled with demineralised water. DM - water is essential for the protection of radiation source. The conductivity of the water in the pool has to be maintained at 10 micro siemens/0.01m. This will reduce the possibility of corrosion of the sealed source. The pool is connected to an emergency water tank of at least half the volume of source storage pool for emergency conditions. The low conductivity of the water is maintained by the use of a suitable DM-water plant fitted with conductivity meter and radiation monitor. If the conductivity is greater than 10 micro siemens per 0.01m for long period, source will be corroded and water will be contaminated. Radiation monitor continuously monitors trace amount of activity, if any, in the pool water.

Control System and Plant Operation
The control system ensure complete safety of the plant and personnel. Radiation source, when not in use, remains in shield condition at the bottom of the source storage pool. Raising the source from the shield condition to source exposed condition is the most important parameter of the facility. Source exposed condition is dangerous for operators and other human beings if accidentally get exposed. Therefore, it is important that source exposed condition must have several safety preconditions. These preconditions are basic requirements of control system. Source lowering can be done without any precondition by operating source lower push button. The source can also be brought down manually or automatically in any one of the several emergency conditions.
Preconditions to be Satisfied to Expose Source

1. Pool water level maintained at required level.
2. Power ON.
3. Hydraulic system ON - oil pressure maintained at working pressure $(6.5 \times 10^5 \text{Kg/m}^2)$
4. Ventilation system ON.
5. Radiation level in the cell at the preset level (<25 micro Sievert per hour)
6. Service keys, trip wire and emergency push button not operated.
7. Product vessel properly aligned.
8. Search operation completed, cell door closed and door interlock cum latch bar pulled.

Source Operation Disable Situations

The following are the conditions under which the source hoist operation is prevented:
1. Pool water below safe level.
2. Radiation level in the cell/labyrinth above normal.
3. Failure of ventilation system.
4. Hydraulic oil level in the tank below minimum required.
5. Hydraulic oil pressure in the system below working pressure.
6. Source disable switch (Service keys) operated.
7. Product vessel not aligned properly.
8. Emergency trip wire pulled.
9. Search operation sequence not fulfilled.

Automatic Source Lowering

The following conditions will bring down the source from exposed condition.
1. Heat sensor/smoke detector inside the cell gets actuated.
2. Power failure.
3. Ventilation system failure.
4. Hydraulic oil pressure below minimum working condition.
5. Fall in pool water level. An illuminated indicator panel is provided on the wall of the control room to identify the source position whether exposed or shielded. Also clearly visible irradiation status indicators are provided at the control console to indicate source in shield, source in transit, source raised, door open, vessel alignment not O.K., exhaust failure etc. Distinct audio alarms operate during search operation, source transit and emergency situations. In addition to the above, an overall general emergency alarm can be activated from the control room by the operator.

The safety of the operation of irradiation facilities depends on the design features on safety incorporated in the facilities. In gamma irradiation facilities four distinctive considerations are included for analysing the safety of the total system. These are

1. Personnel safety against external exposure to radiation.
2. Personnel safety against any radioactive contamination.
3. Exposure to noxious gases.
4. Industrial safety of operations against fire, smoke, explosives etc.

Important technical specifications of the Plant are given in table 1.
Table 1: Important technical specifications

<table>
<thead>
<tr>
<th>Facilities</th>
<th>Technical specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irradiator overall size</td>
<td>20.6m X 15m</td>
</tr>
<tr>
<td>Radiation cell size</td>
<td>4.5m X 4m X 4m (height)</td>
</tr>
<tr>
<td>Source storage pool size</td>
<td>2.6m X 2.0m X 6.3m</td>
</tr>
<tr>
<td>Radiation source shielding</td>
<td>Water</td>
</tr>
<tr>
<td>Biological shield</td>
<td>Concrete wall (2350 Kg./m³) of 1.8m thick (max)</td>
</tr>
<tr>
<td>Roof thickness</td>
<td>1.5m of concrete</td>
</tr>
<tr>
<td>Max. Source capacity</td>
<td>3.7 PBq. of cobalt - 60.</td>
</tr>
<tr>
<td>Product container size</td>
<td>1.2m dia X 1.2m height (Cylindrical vessel)</td>
</tr>
<tr>
<td>Ventilation system</td>
<td>20 Air changes per hour.</td>
</tr>
<tr>
<td>Power supply</td>
<td>440 V, 3 Phase, 10 KW.</td>
</tr>
<tr>
<td>Movement of latex container</td>
<td>Container mounted on a trolley moves on rails</td>
</tr>
<tr>
<td>Safety</td>
<td>Provided with mechanical, electrical and hydraulic interlocks.</td>
</tr>
<tr>
<td>Source Assembly</td>
<td>In the form of a cylindrical cage (0.2m dia) with 12 positions for the source units</td>
</tr>
<tr>
<td>Source specifications</td>
<td>Total length = 0.463m, Total dia = 0.0272m, Active length = 0.4mm, Active dia = 0.0115m</td>
</tr>
<tr>
<td>Cobalt-60 slugs size length rods</td>
<td>0.0064m dia X 0.0254m</td>
</tr>
<tr>
<td>Classification of irradiator</td>
<td>Class III (Wet storage and mobile source)</td>
</tr>
</tbody>
</table>
The design features/safety interlocks at the RVNRL Plant, Rubber Board are summarised in Figure 2.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Cell door interlock</td>
</tr>
<tr>
<td>2.</td>
<td>Pool water level interlock</td>
</tr>
<tr>
<td>3.</td>
<td>Radiation detector</td>
</tr>
<tr>
<td>4.</td>
<td>Cell search</td>
</tr>
<tr>
<td>5.</td>
<td>Exhaust fan</td>
</tr>
<tr>
<td>6.</td>
<td>Fire/Smoke alarms</td>
</tr>
<tr>
<td>7.</td>
<td>Product vessel interlock</td>
</tr>
<tr>
<td>8.</td>
<td>Water treatment system monitor</td>
</tr>
<tr>
<td>9.</td>
<td>Trip wire</td>
</tr>
<tr>
<td>10.</td>
<td>Wire rope tension interlock</td>
</tr>
<tr>
<td>11.</td>
<td>Service keys</td>
</tr>
<tr>
<td>12.</td>
<td>Emergency stop device</td>
</tr>
</tbody>
</table>

**Figure 1:** Design features/safety interlocks at the RVNRL Plant
Radiation Safety Aspects

The use of high intensity gamma sources in the irradiators has a potential for radiation hazards to plant personnel and public in the event of any malfunction or failure of safety systems. It is essential to evaluate the hazards likely to arise under normal working conditions, as also under potential accident conditions (e.g., fire, explosion, corrosion, etc.) in order to avoid high doses to personnel. Personnel monitoring and area monitoring devices are commonly used for the evaluation of external radiation hazard.

Personnel Monitoring

RVNRL Plant is included in the TLD badge service conducted by Radiation Protection Services Division, Bhabha Atomic Research Centre, Mumbai. The thermoluminescence Dosimeter (TLD) cards used by the personnel are routinely read by the TLD - badge section of RPSD, BARC every three months and the reports are sent to us.

The quarterly reports of radiation doses received by the staff members have been analysed from 1992 to 1995. The yearly average dose for the personnel have been computed, the number of persons monitored, the average dose received by the personnel in different years and number of batch irradiations carried out in each year are given in Table 3.

Table 2: The quarterly report of radiation doses from 1992 to 1995

<table>
<thead>
<tr>
<th>Year</th>
<th>Number of batches radiated</th>
<th>Number of persons monitored</th>
<th>Total dose in milli Sievert (mSv)</th>
<th>Average dose in milli Sievert (mSv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1992</td>
<td>7</td>
<td>2</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>1993</td>
<td>13</td>
<td>7</td>
<td>1.00</td>
<td>0.110</td>
</tr>
<tr>
<td>1993</td>
<td>13</td>
<td>7</td>
<td>1.11</td>
<td>0.160</td>
</tr>
<tr>
<td>1994</td>
<td>4</td>
<td>7</td>
<td>1.05</td>
<td>0.150</td>
</tr>
<tr>
<td>1995</td>
<td>6</td>
<td>8</td>
<td>0.60</td>
<td>0.070</td>
</tr>
</tbody>
</table>

Notes:
1) Dose limits recommended by ICRP (1991) for radiation workers:
   Whole body (effective dose) = 20 mSv per year, averaged over defined period of 5 years with no more than 50 mSv in a single year.
2) Dose below measurable level of 0.05 mSv is shown zero.

The analysis indicates that the dose received by personnel are well within the permissible limit. It is found that nobody received any queer dose during the last four years.

Area Monitoring

Routine area monitoring procedure is being adopted in the RVNRL facility during source in shield and source raised condition. Radiation levels at important locations of the facility are tabulated below.
Table 3: Radiation levels at important locations

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Location</th>
<th>Source exposed</th>
<th>Source (micro Sievert/hour)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cell roof</td>
<td>Negligible</td>
<td>0.2</td>
</tr>
<tr>
<td>2</td>
<td>Steel door</td>
<td>&quot;</td>
<td>0.3</td>
</tr>
<tr>
<td>3</td>
<td>Control area</td>
<td>&quot;</td>
<td>0.1</td>
</tr>
<tr>
<td>4</td>
<td>DM-plant room</td>
<td>&quot;</td>
<td>0.3</td>
</tr>
<tr>
<td>5</td>
<td>Service room</td>
<td>&quot;</td>
<td>0.1</td>
</tr>
<tr>
<td>6</td>
<td>No occupancy area</td>
<td>&quot;</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Note: 1) Instrument used for the survey = Digirad
2) Expected accuracy = +/- 15%

From the above table it can be seen that the measured dose rate values are well within the permissible limit, i.e., 25 micro Sievert/hour.

In addition to the radiation survey meters, two radiation detectors called Gamma Area/Zone monitors are installed in the facility which can give warning signal in case of abnormal situations. If the source gets stuck up or not returned to shielded position fully, then there will be higher radiation level in the room. This level will trigger the zone monitor to give audio alarm.

ACKNOWLEDGEMENT

The authors wish to express their sincere thanks to Shri K.J. Mathew, Chairman, Rubber Board for the encouragement and cooperation given in the preparation of this paper and for presenting it at the Second International Symposium on RVNRL at Kuala Lumpur during July, 1996.
THE CRITERIA AND THE DESIGN OF MINT’S LATEX IRRADIATOR

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Wan Abd Hadi, Muhd Noor Muhd Yunus
Malaysian Institute for Nuclear Technology Research (MINT)
Bangi, 43000 Kajang, Selangor
Malaysia.

Abstract

The demand for RVNRL is continually on the upsurge and the present irradiation technique at the present SINAGAMA plant is not sufficient and practical to meet the demand. A number of conceptual designs were evolved to design according to the requirements of cost-effective and highly efficient plant. The number of options are described. In 1994 MINT work with NUKEM to build an automatic continuous latex irradiation plant.
INTRODUCTION

* GAMMA IRRADIATION TECHNOLOGY
* EBM TECHNOLOGY
* ESTABLISHED TECHNOLOGY
* RADIATION PROCESSING
  - STERILIZATION
  - MODIFICATION FOR POLYMER STRUCTURE
* LATEX IRRADIATION
GAMMA IRRADIATOR

* GAMMA RADIATION SOURCE
* BIOLOGICAL SHIELD
* STORAGE - WET OR DRY
* TRANSPORT MECHANISM SYSTEM
* SAFETY SYSTEM
* CONTROL SYSTEM
DEVELOPMENT OF IRRADIATOR PLANT

* PILOT PLANT IN BATAN, INDONESIA

* PILOT PLANT IN INDIA

* USE OF AVAILABLE GAMMA IRRADIATOR - SINAGAMA

- SMALL SCALE

TOWARDS EFFICIENT & ENVIRONMENT FRIENDLY RVRNL PLANT
TRIAL STUDY

CARRIED OUT IN SINAGAMA PLANT, MINT

* ROTATING DRUMS
* ROTARY TABLE
* STATIC IRRADIATION
* BATCH CARRIER IRRADIATION

TOWARDS EFFICIENT & ENVIRONMENT FRIENDLY RVRNL PLANT
SCALE UP IRRADIATION IN SINAGAMA

* STATIC IRRADIATION
  DRINK BOTTLES PLACED IN PARALLEL TO THE SOURCE - 20 LITERS

* REVOLVING BARREL IRRADIATION RIG CONSISTING OF 8 ROTATING DRUMS, PLACED, IN VERTICAL PLANE PARALLELED TO THE SOURCE - QUANTITY - 30 X 8 LITRES

* ROTARY TABLE IRRADIATION
  ROTARY TABLE PLACE AT THE SOURCE.
  CONTAINER OF LATEX PLACED ON TOP

* CARRIER IRRADIATION PLASTIC CONTAINER OF LATEX PLACED IN CARRIER AND FOLLOWS THE AUTOMATIC CARRIER SEQUENCE OF THE SINAGAMA PLANT

TOWARDS EFFICIENT & COST EFFECTIVE RVRNL PLANT
DESIGN CRITERIAS

* COST - ECONOMIC
* HIGH - EFFICIENCY
* SAFETY
* PRODUCTS
* LOGISTIC REQUIREMENTS
  - LOADING/UNLOADING
* FLEXIBILITY/DEDICATED
* DOSE VALIDATION

TOWARDS EFFICIENT & ENVIRONMENT FRIENDLY RVRNL PLANT
## Production Cost Per Kg

<table>
<thead>
<tr>
<th>Milestone</th>
<th>Description</th>
<th>Unit/Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source</td>
<td>kCi</td>
<td></td>
</tr>
</tbody>
</table>

### Enter Your Variables in Boxes Below:

1. **Production**
   - What is your projected annual production capacity (metric tonnes)?
   - What is annual availability (hours)?
   - What is the dose requirement (kGy)?
   - What is the irradiation efficiency (%)?
   - What is the source price per Ci (RM)?

2. **Building and Irradiator Cost**
   - How much did you spend for main building and laboratory (RM)?
   - How much did you spend for shielding (RM)?
   - How much did you spend for pool (RM)?
   - How much did you spend for mechanical and electrical systems (RM)?
   - Other expenses if any?
   - How much did you pay consultation fees (%)?
   - What is the cost of irradiation facilities w/o source (RM)?
   - How much did you allow for contingencies (%)?
   - What is the interest rate (%)?
   - How long do you expect the useful life for the entire facility (yrs)?
   - What will be the ultimate building salvage value (RM)?
   - What will be the irradiator salvage value (RM)?
   - Source salvage value

3. **Operating Cost**
   - Please enter the number of personnel and monthly salary for EACH:
     - Supervisor RM
     - Technicians RM
     - Operators RM
     - General Workers RM
     - Others RM
   - How much do you expect to spend for office supplies (RM)?
   - How much will be required for maintenance per annum excluding source (RM)?
   - How much will you pay for utilities annually (tel., electricity, water, etc.) (RM)?
   - What is the source container rental (RM)?
   - What is the shipping cost for the source/container (RM)?
   - Others: (Please specify) RM
   - Chemicals RM

---

**Cost Economic Analysis of RVRLN Facility**
Co-60 Irradiation Facility
Capital Cost Distribution

- Irradiator cost: 58.8%
- Co-60 Source: 10.5%
- Shieldings: 23%
- Contingency: 0.0%
- Utilities: 2.9%
- Consultant fees: 5.1%
- Building and labs: 11.0%
- Others: 4.3%
- Pool: 4.3%
DESIGN CONCEPT

* DESIGN 1
  WET IRRADIATION

* DESIGN 2
  DRY IRRADIATION - BATCH

* FINAL DESIGN
  MINT & NUKEM DESIGN
  DRY IRRADIATION - CONTINUOUS

TOWARDS EFFICIENT & ENVIRONMENT FRIENDLY RVRNL PLANT
DESIGN 1

WET IRRADIATION

* BATCH TYPE

* FORMULATED LATEX
  PUMP INTO LATEX REACTOR TANK

* BALL DOSIMETERS OF SAME SPECIFIC
  WEIGHT ARE INSERTED INTO THE LATEX

* LATEX REACTOR TANK LOWERED INTO THE POND
  BY MEAN OF GUIDE RAIL ON THE SOURCE
  RACK AT BOTTOM OF CONTAINER

* IRRADIATION - LATEX IS STIRRED TO GET
  HOMOGENOUS DOSE

* AFTER IRRADIATION TIME (DWELL TIME)
  LATEX CONTAINER IS LIFTED FOR
  UNLOADING

* ANOTHER BATCH IS LOWERED FOR IRRADIATION

TOWARDS EFFICIENT & ENVIRONMENT FRIENDLY RVRL PLANT
TYPICAL SECTION FRONT VIEW OF LR FACILITIES

DESIGN 1: BATCH WET IRRADIATION
DESIGN 2

DRY IRRADIATION

BATCH TYPE

* FORMULATED LATEX IN A REACTOR TANK

* REACTOR TANK IS PUSHED INSIDE THROUGH A CONVEYOR SYSTEM INTO RIGHT POSITION IN THE IRRADIATION CHAMBER

* COBALT - 60 SOURCE RAISED FROM POOL STORAGE AND PLACE IN THE VOID CUP OF THE REACTOR TANK FOR IRRADIATION

* AFTER DWELL TIME, SOURCE IS LOWERED

* LATEX REACTOR TANK CART AWAY AND REPLACE WITH A NEW BATCH OF LATEX REACTOR TANK

TOWARDS EFFICIENT & ENVIRONMENT FRIENDLY RVRL PLANT
DESIGN II: BATCH DRY IRRADIATION

SECTIONAL ISOMETRIC VIEW OF LR-II
FINAL DESIGN

* DRY IRRADIATION
* CONTINUOUS
* MATRIX TUBES IN THE IRRADIATION CHAMBER
* PUMPING SYSTEM
* DOSIMETRY BALL
* SCRUBBER
* LATEX FLOW CONTROL BY COMPUTER

PARAMETERS INPUT DURING COMMISSIONING
- DOSE
- FLOW RATE
- SOURCE STRENGTH

* PLANT CAN BE OPERATED ALMOST UNATTENDED

TOWARDS EFFICIENT & ENVIRONMENT FRIENDLY RVRNL PLANT
<table>
<thead>
<tr>
<th>WET</th>
<th>DRY</th>
</tr>
</thead>
<tbody>
<tr>
<td>CATEGORY III (WET)</td>
<td>CATEGORY II (DRY)</td>
</tr>
<tr>
<td>CONSTRUCTION COST HIGH</td>
<td>CONSTRUCTION COST LOWER</td>
</tr>
<tr>
<td>MAINTENANCE COST HIGH</td>
<td>MAINTENANCE COST LOWER</td>
</tr>
<tr>
<td>MAINTENANCE TIME</td>
<td>MAINTENANCE TIME</td>
</tr>
<tr>
<td>LOADING/UNLOADING OF SOURCE</td>
<td>LOADING/UNLOADING OF SOURCE</td>
</tr>
<tr>
<td>DIMINERALISER</td>
<td>HEAT EXCHANGER</td>
</tr>
<tr>
<td>LATEX IRRADIATION</td>
<td>LATEX IRRADIATION</td>
</tr>
<tr>
<td>DIFFICULT OPERATION</td>
<td>SIMPLE OPERATION</td>
</tr>
<tr>
<td>EFFICIENCY</td>
<td>EFFICIENCY</td>
</tr>
</tbody>
</table>

TOWARDS EFFICIENT & ENVIRONMENT FRIENDLY RVRNL PLANT
CONCLUSION

* THE MAIN CRITICAL FACTOR IN DESIGNING THE PLANT IRRADIATOR IS TO MAKE THE RVRNL PLANT A VIABLE VENTURE TO THE INDUSTRY.

* THE PILOT PLANT AND THE VARIOUS DESIGN CONCEPTS PRESENTED WILL FORM THE BASIS FOR THE DESIGN OF FUTURE PLANT.

TOWARDS EFFICIENT & ENVIRONMENT FRIENDLY RVRNL PLANT
TYPICAL SCHEMATIC DIAGRAM OF RVNRL PLANT
(EXISTING PLANT)
LOADING & UNLOADING AREA
FORMULATION AREA
LATEX PUMP
IRRADIATION BUNKER

FACILITIES

TYPICAL SECTION VIEW OF MINT RVNRL FACILITIES
RADIATION VULCANIZATION OF NATURAL RUBBER LATEX (NRL) USING LOW ENERGY ELECTRON BEAM ACCELERATOR

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Department of Material Development
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Abstract

The electron beam induced vulcanization of natural rubber latex has been studied using low energy Electron Beam (EB) accelerators of 300, 250 and 175 keV. The latex was irradiated in a special type stainless steel reaction reactor with a stirrer at the bottom of the reactor. From the results it was found that 300 and 250 keV accelerators could effectively vulcanize NRL. But accelerator of 175 keV is too low energy to vulcanize the latex. At the same time a drum type irradiator where thin layer of NRL was irradiated by accelerator, was used for vulcanization of NRL. This type of irradiator also showed good physical properties of vulcanized latex. The effects of beam current and stirrer speed on vulcanization were studied.

INTRODUCTION

Radiation has been used as a tool to vulcanize NRL for many years. So far Cobalt-60 isotope has been successfully utilized for vulcanization of NRL. But in a number of recently works it was tried to vulcanize NRL using low energy electron beam accelerators. The use of electron beam (EB) radiation is more economical compared to gamma rays, because vulcanization time is shorter than γ-rays and there is no need to use any radiation sensitizer. The only disadvantage of electron beam for vulcanization is their very low penetration capacity.

In the present work NRL has been vulcanized by low energy accelerators of different powers and various beam currents. Stirrer speed was changed to see the effect of stirring on vulcanization. The effect of type of reaction vessels on properties of irradiated latex was also studied. After irradiation physical properties such as tensile strength, elongation at break and swelling ratio of irradiated films has been measured to establish the optimum conditions of vulcanization of NRL by low energy EB.
EXPERIMENTAL

Materials

The latex used in this work was high ammonia centrifuged natural rubber latex concentrate (60%) of Malaysia. To prevent formation of foams during irradiation 0.25 phr BYK-022 manufactured by BYK-Chemie, Japan was used. The main component of BYK-022 is a mixture of silicone resin and polyglycol, density 0.99 g/cm$^3$ at 20° C. During experiment it is used as received. Antioxidants tris(nonylated phenyl)phosphite (TNPP) and (NS-5) were supplied by Ouchi Shinko Chemical Co., Ltd., Japan and used as received.

Electron beam accelerator

For irradiation of latex self-shielded electron beam accelerator of 300 kV manufactured by Nissan High Voltage company was used. Self shielded electron beam accelerators of 175 and 250 kV were manufactured by Iwasaki electric company Ltd. Japan.

The reaction vessels

The stainless steel reactor, diameter of 205 mm and height of 180 mm and a stirrer at the bottom has a holding capacity of 1450 ml latex. A water jacket was used to take off the heat produced during EB exposure to latex. The dimension of the reactor was shown in Figure 1.

The drum type reactor can continuously irradiate latex in a thin layer of 90 µm. The drum moved with a speed of 7 r.p.m. It has a diameter of 165.2 mm and length of 200 mm. The distance between beam window and surface of latex is 55 mm.

Radiation vulcanization of natural rubber latex

For vulcanization by EB natural rubber concentrate (60%) was diluted with 1% aqueous ammonia solution to 50% total solid content (TSC) and prior irradiation defoamer BYK-022 was added to latex.

Irradiated natural rubber latex was cast on leveled glass molds and dried at room temperature until they became transparent. Then the films were immersed in 1% ammonia solution for 24 hours to leach out water soluble components from the films. After drying of the films at room temperature, they finally dried in an oven at 80° C for one hour.

Measurement of physical properties

The tensile properties of the prepared latex films were measured using Strograph RI tension meter (Toyoseki Co. Ltd., Japan). For determination of weight Swelling ratio 20 mm diameter circular sample pieces of rubber films (W1) were weighed and then they were dipped in toluene for 24 hours. The weight of the swollen samples (W2) was determined by blotting the excess solvent. Weight swelling ratio was calculated as follows:

$$S_w, \% = \frac{W_2}{W_1} \times 100$$
RESULTS AND DISCUSSION

Effect of accelerator power and type of irradiation vessel on properties of irradiated latex

The properties of irradiated latex with reaction vessel of 1450 ml capacity are shown in Figure 2 & 3. From Figure 2 it can be seen that with the increase of reaction time tensile strength increases, reaching to maximum value and for beam current 40 mA the tensile strength is maximum. Figure 4 shows that for EB accelerator of 175 keV energy there is only small change of tensile strength with irradiation time. In this case the electrons do not have sufficient energy to vulcanize latex. Where as for accelerators of 300 and 250 keV energy ( Figure 2 & 4) an increase of tensile strength with irradiation time was observed. This change is due to radiation induced crosslinking (vulcanization) of NRL which increases with radiation dose. Accelerators of 175 and 250 keV use drum type reaction vessel for irradiation of latex. Figure 3 &5 shows the effect of beam current on elongation at break and swelling ratio of latex, when the latex is irradiated with accelerator of 300 keV. Effect of beam current on tensile and swelling ratio for accelerators of 175 and 250 keV is shown in Figure 6. With EB accelerator of 175 keV tensile strength increases slowly and at 8 mA of beam current the tensile strength is 27.1 MPa. But for 250 keV EB accelerator the tensile strength increases more rapidly. From these results it can be concluded that the drum type irradiator with beam current above 8 mA, is useful even when low energy EB accelerator of energy 175 keV, was used for irradiation of latex.

Effect of beam current on tensile properties

Beam current of electron beam accelerator corresponds to the dose of irradiation of latex. From the Figure 2 it can be seen that tensile strength of the irradiated films increases with the increasing irradiation time. Maximum tensile strengths at 20,30, 40, 50 and 60 mA beam currents correspond to 25.1, 22.6, 14.2, 12.7 and 9.2 minutes of irradiation times respectively and the tensile strength values are 23.3, 25.5, 28.9, 24.4 and 24.3 MPa respectively. It can be seen that for higher beam current it takes less time to irradiate the latex.

Elongation at break of irradiated latex films at 20, 30, 40, 50, 60 mA beam currents is shown in Figure 3. From the Figure 3 it can be seen that with the increase of beam current the elongation at break for the same period of exposure to radiation is decreasing. With the increase of exposure time of radiation elongation at break decreases for all samples. For beam currents 20, 30, 40, 50 and 60 mA at 30 minutes of exposure time, elongation at break corresponds to 990, 970, 750, 610 and 505% respectively.

According to Figure 5 percent swelling ratio value decreases with increasing radiation time. The same trend is observed for all samples. The swelling ratio drops quickly for irradiated film of higher beam current (60 mA) than film of lower beam current (20 mA) (Figure 5).

Effect of speed of mixing of latex on properties of irradiated latex

Effect of stirrer speed on tensile properties and on swelling ratio are shown in Figure 6, 7 & 8. During irradiation the latex was continuously stirred with a stirrer fitted at the bottom, at speeds 100, 150 and 200 r.p.m. From Figure 6 it can be observed that at speed of 150 r.p.m. the maximum tensile strength is obtained (28.9 Mpa), whereas for 100 and 200 r.p.m. these values are 24.2, 25.2 MPa respectively. It is expected that at higher stirring speed (200 r.p.m.) vulcanization process would take less time and tensile strength would be higher. But it is observed that vigorous stirring cause displacement of some drops of latex on to the aluminium film which absorbs a greater part of energy of electron. As a result partially carbonized latex are formed on the aluminium film and the latex in the reactor at stirring speed 200 r.p.m. gets energy to absorb. Consequently the tensile strength at 200 r.p.m. (25.2 MPa) is less than at 150 r.p.m. (28.9 MPa).
Energy utilization efficiency for vulcanization using low energy electron beam accelerator

For vulcanization of NRL without sensitizer the required dose is 250 kGy (Makuuchi et al.). It was found that using beam current 40 mA it takes 15 minutes to vulcanize 1.45 kg of latex. So the energy used for vulcanization is

\[ 1.45 \text{ kg} \times 250 \text{ kJ/kg} = 362.5 \text{ kJ} \]

While, Electron beam energy to the latex is

\[ 300 \text{ kV} \times 40 \text{ mA} \times 10 \text{ cm/60 cm} \times 15 \text{ min} \times 60 \text{ sec} = 1800 \text{ kJ} \]

Therefore the energy utilization efficiency for vulcanization is

\[ \frac{362.5}{1800} \times 100\% = 20.13\% \]

CONCLUSION

Reaction vessel with stirrer can be used for vulcanization of natural rubber latex using EB accelerator of power above 250 keV. But when vulcanization was carried out in thin layers even lower power accelerator (175 keV) can be used. Properties of electron beam irradiated latex are comparable with those of gamma ray irradiated latex.

Acknowledgment

One of the authors would like to thank the Science and Technology Agency (STA) of Japan for inviting her to Japan Atomic Energy Research Institute and the Iwasaki Electric company of Japan for providing technical assistance.

REFERENCES


Makuuchi K., RVNRL with low energy electron beams, Internal Report, TRCRE, JAERI, Japan.


Figure 1: Diagram of reaction vessel.

Figure 2: Effect of irradiation time on tensile strength.
Figure 3: Change of tensile properties of latex film with irradiation time.

Figure 4: Dependence of elongation at break on beam current.
Figure 5: Effect of beam current on swelling ratio.

Figure 6: Effect of stirrer speed on tensile strength.
Figure 7: Change of elongation at break on stirrer speed.

Figure 8: Effect of stirrer speed on wt. swelling ratio.
THE CONSTRUCTION AND COMMISSIONING OF MINT'S LATEX IRRADIATOR

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Germany

Abstract

The construction and installation of MINT’s automatic continuous latex irradiator is described. MINT co-operated with NUKEM to design the plant. Construction was done by local building consultants and local contractor. The installation of the plant includes local fabrication components and imported components. The plant is automatically controlled by a computer system. Features of plant is described.
CONSTRUCTION

* NORMAL BUILDING CONSTRUCTION

* STRONG FOUNDATIONS FOR THE HEAVY MASS CONCRETE - SHIELDING

* EMBEDDED PIPES

* OUTER SOURCE TANK INNER TANK CONSTRUCTION
LATEX HANDLING & PROCESSING

- Fresh latex storage tank
- Formulation tank
- Pre-irradiated latex tank
- Irradiated latex collection tank
- Chemical tank
- Fresh water tank
- Slurries tank
  (ie. Mixture of soluble oil and water)

FORMULATION AREA

Storage and preprocessing of latex being carried out.

- Fresh latex storage
- Sampling (determine suitable dose required)
- Transfer for formulation
- Formulation
- Transfer to pre-irradiated tank
- Delay
- Start irradiation
- Sampling
- Irradiated latex storage.
MATRIX PUMP

- Function - to transfer formulated latex (ie. Pre-irradiated tank) into irradiation bunker and out (ie. Irradiated latex collection tank), through Matrix pipe.

- Design - Positive displacement by means of piston pump and operated by hydraulic system (ie. approx. 25 litters/stroke).

- Easily regulated - by means of computer setting/control.

- Consist of -
  * Go-devil station (ie. Loading & Recovery Dosimetry ball, Cleaning ball and Separator)
  * Operating valve (ie. Manual & Automatic)

MATRIX PIPE

- Function - latex or liquid piping from Matrix pump to irradiation bunker and back.

- Design - made from Stainless Steel with internally electropolished (ie. Finest surface finish).

- Partly named Irradiation tube which special configuration/ layout, which is placed inside irradiation bunker.

- Irradiated material separated by special sealer named Separator.

- Cleaning by using Rubber foam ball (ie. Nicked name GO-DEVIL)
IRRADIATION BUNKER

- Function - biological shield (ie. to maintain surrounding doserate always at permissible level.

- Design - majority build by heavy density concrete ( ~ 2.3kgs/cm$^3$).

- Design to enclosed - max. 1 MCi of Co-60 radioactive source (ie. Current source strength - 1.4 KCi).

- 5 types of wall penetration;
  - Door - main entrance, equipped with metal cased concrete door plug (ie. Weight ~ 8000 kgs.). Manually operated, since low operation requirement.
  - Pipe labyrinth duct - services duct for matrix pipe and etc.
  - Ventilation duct - embedded below floor level.
  - Source loading & unloading tube - purposely for radioactive source loading & unloading facilities.
  - 4 Nos. Outer tubes - for future additional upgrading.
RADIOACTIVE SOURCE

- Gamma source - Co-60.
- Positioned in horizontal source rack.
- Stored in metal tank surrounded by concrete, embedded below floor level.
- Max. source strength - 1 Mci.
- Current source strength - 1.4 Kci.
- Source rack operation - by means of hydraulic system to raised and lowered by gravity pull.
- Full loaded rack - ~ 3000 kgs.
- Cooled by using cold water circulation system, only during storage position.
RVNRL PLANT

- LATEX HANDLING & PROCESSING
- FORMULATION AREA

IRRADIATION PLANT

BASIC FEATURES
- Category II plant - Dry source storage.
- Source is exposed during irradiation process.
- Automatic - computerised control.

- MATRIX PUMP
- MATRIX PIPE
- IRRADIATION BUNKER
- RADIOACTIVE SOURCE
- CONTROL SYSTEM
CONTROL SYSTEM

- Computerized control system.

- Consist of:
  * PC.
  * Signal interface card.
  * Monitor.
  * LED display board.
  * Contactor block.
  * Power supply.
  * Hydraulic power pack.

- Design:
  * Easily parameter input to operate plant.
  * Several interlock system for safety purposes.
  * Built in feature for fail-safe operation.
  * Plant condition & Operation parameter display.
  * Parallel display and control panel.
DOSIMETRIC MEASUREMENT

* DOSIMETERS

<table>
<thead>
<tr>
<th>TYPE</th>
<th>( \lambda )</th>
<th>RANGE (Kgy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RED 4034</td>
<td>604</td>
<td>5-50</td>
</tr>
<tr>
<td>AMBER 3042</td>
<td>651</td>
<td>1-30</td>
</tr>
</tbody>
</table>

* DOSIMETRY BALL MADE OF HDPE
  fill with latex

* 8 - 15 Kgy

* ABSORBED DOSE

* DOSE DISTRIBUTION IN LATEX

* QUALITY CONTROL

* CALIBRATED AGAINST STANDARD FRICKE DOSIMETER (FERROUS SULPHATE)
DOSE MEASUREMENTS AT THE RVNRL PILOT
PLANT BY MEANS OF AMBER 3042 PERSPEX DOSIMETER

<table>
<thead>
<tr>
<th>Parameters of the irradiation</th>
<th>Measured Dose (kGy)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>First Stroke</td>
</tr>
</tbody>
</table>
| Dose: 12 kGy  
No. of Stroke: 56  
Density: 1 g cm\(^{-3}\) (water)  
Volume: 0.5 m\(^3\)  
Cycle time: 646 Sec.  
Operation time: 10.05 hrs. | 12.21±0.55 | 12.45±0.20 | 12.87±0.35 | 12.51±0.95 | 4.3 |
| Dose: 12.5 kGy  
No. Stroke: 18  
Density: 0.95 g cm\(^{-3}\) (latex)  
Volume: 0.463 m\(^3\)  
Cycle time: 648  
Operation time: 3.24 hrs | 13.58±0.90 | 12.42±0.56 | 13.20±0.24 | 13.07±1.16 | 4.6 |
<table>
<thead>
<tr>
<th>RVNRL PLANT</th>
<th>(COBALT 60)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>INITIAL LOADING</strong></td>
<td><strong>DATE OF LOADING</strong></td>
</tr>
<tr>
<td>144200 CURIES</td>
<td>14-Feb-96</td>
</tr>
<tr>
<td><strong>CURRENT SOURCE STRENGTH</strong></td>
<td></td>
</tr>
<tr>
<td>136462 CURIES</td>
<td></td>
</tr>
</tbody>
</table>
LOADING & UNLOADING AREA
FORMULATION AREA
LATEX PUMP
IRRADIATION BUNKER

SOURCE DRIVE MECHANISM
MATRIX PIPE (IRRADIATION TUBE)
SOURCE PLUG
WATER COOLING PIPE
RADIOACTIVE SOURCE

FINAL DESIGN

TYPICAL SECTION VIEW OF MINT RVNRL FACILITIES
TYPICAL SCHEMATIC DIAGRAM OF RVNRL PLANT

(FINAL PLANT)
## OPERATION TIME BY DOSE REQUIRED

### MANUAL DATE DETERMINATION

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Date of loading</td>
<td>14-Feb-96</td>
</tr>
<tr>
<td>No. of days after loading</td>
<td>147 Days</td>
</tr>
<tr>
<td>Daily decay rate</td>
<td>0.9996324</td>
</tr>
<tr>
<td>Initial source strength</td>
<td>144200 Curies</td>
</tr>
<tr>
<td>Current source strength</td>
<td>136613.2704 Curies</td>
</tr>
<tr>
<td>Datum dose</td>
<td>10 kGy</td>
</tr>
<tr>
<td>Datum cycle time</td>
<td>513 sec.</td>
</tr>
<tr>
<td>Datum density</td>
<td>0.95</td>
</tr>
<tr>
<td>Actual density</td>
<td>0.95</td>
</tr>
<tr>
<td>Source correction</td>
<td>1.055534353</td>
</tr>
<tr>
<td>Density correction</td>
<td>1</td>
</tr>
<tr>
<td>Cycle time</td>
<td>541.4891231 sec.</td>
</tr>
<tr>
<td>Actual cycle time</td>
<td>649.7869477 sec.</td>
</tr>
<tr>
<td>Rounded Actual cycle time value</td>
<td>649 sec.</td>
</tr>
<tr>
<td><strong>Operation time</strong></td>
<td>18.02777778 hrs.</td>
</tr>
<tr>
<td><strong>Rounded Operation time value</strong></td>
<td>18.03 hrs.</td>
</tr>
<tr>
<td><strong>Equivalent operation time</strong></td>
<td>64900 sec.</td>
</tr>
</tbody>
</table>

### AUTO DATE DETERMINATION

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Date of loading</td>
<td>14-Feb-96</td>
</tr>
<tr>
<td>No. of days after loading</td>
<td>150 Days</td>
</tr>
<tr>
<td>Daily decay rate</td>
<td>0.9996324</td>
</tr>
<tr>
<td>Initial source strength</td>
<td>144200 Curies</td>
</tr>
<tr>
<td>Current source strength</td>
<td>136462 6687 Curies</td>
</tr>
<tr>
<td>Datum dose</td>
<td>10 kGy</td>
</tr>
<tr>
<td>Datum cycle time</td>
<td>513 sec.</td>
</tr>
<tr>
<td>Datum density</td>
<td>0.95</td>
</tr>
<tr>
<td>Actual density</td>
<td>0.95</td>
</tr>
<tr>
<td>Source correction</td>
<td>1.056699253</td>
</tr>
<tr>
<td>Density correction</td>
<td>1</td>
</tr>
<tr>
<td>Cycle time</td>
<td>542 0867166 sec</td>
</tr>
<tr>
<td>Actual cycle time</td>
<td>542 0867166 sec</td>
</tr>
<tr>
<td>Rounded Actual cycle time value</td>
<td>542 sec.</td>
</tr>
<tr>
<td><strong>Operation time</strong></td>
<td>15.05555556 hrs.</td>
</tr>
<tr>
<td><strong>Rounded Operation time value</strong></td>
<td>15.06 hrs.</td>
</tr>
<tr>
<td><strong>Equivalent operation time</strong></td>
<td>54200 sec.</td>
</tr>
</tbody>
</table>
CONCLUSION:

* DEDICATED PILOT LATEX IRRADIATOR WAS SUCCESSFULLY COMMISSIONED ON 27th APRIL 1996. SINCE THEN IT HAS BEEN RUNNING SMOOTHLY WITH FEW PROBLEMS. IT MEETS THE REQUIREMENT OF THE RVRNL USER.

* THE PILOT PLANT IS TIMELY LAUNCHED TO TEST THE INDUSTRY AND BUILD THE MARKET DEMAND FOR THE RADIATION VULCANIZED NATURAL RUBBER LATEX.

* PROBLEMS AND IMPROVEMENTS ON THE PLANT OPERATION WILL BE CONTINUOUSLY MONITORED AND UPGRADED TO MAKE IT RELIABLE, SAFE AND EFFICIENT PLANT.

* PLANT DESIGN WILL BE FURTHER DEVELOPED TO REDUCE THE CAPITAL OUTLAY.
PROCESSING COST OF RVNRL

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Kompleks MINT Jalan Dengkil
43000 Kajang, Selangor
Malaysia

ABSTRACT

The main components contributing to the cost of building a pilot plant for RVNRL are highlighted. The fixed cost and operating cost of a pilot plant were determined and the production capacity and the cost to prepare 1 kg of RVNRL were calculated. Two sets of calculations were presented. A set was based on a pilot plant installed with cobalt-60 source of 150 kCi and another set was based on a plant installed with cobalt-60 source of 1 MCi. The effect of different power utilisation efficiencies and the effect of different vulcanisation doses on the production capacities are presented. In general, a small difference in the vulcanisation dose and power utilisation efficiency result in a significant change in the production capacity and the cost for RVNRL preparation. Depending on the production capacity, the cost for preparing RVNRL of 50% total solid content can be as low as RM 0.242 per kilogram.

INTRODUCTION

Though research studies on RVNRL started as early as 1960’s in Europe, the potential applications are identified, and the advantages are well defined and ready for users exploitations. However, until to-day no latex irradiator capable of producing RVNRL on commercial scale is available. The effort to scale up RVNRL preparation in Indonesia and India are limited to pilot plant stage. Moreover, the production rate is very slow and hence the production capacity is very small.

In March 1996 a pilot plant cum commercial latex irradiator was commissioned in MINT. The plant is designed as 1 MCi dry source storage. It is designed to prepare at least 6 000 tons of RVNRL per annum. It is a continuous system, different from those pilot plant latex irradiators available in Indonesia and India which are batch systems.

The major component of MINT’s latex irradiator besides those used for the formulation of natural rubber latex are as follows:

- feeding tank
- hydraulically operated latex pump station
- dosimeter insertion and retrieval station
- irradiation matrix
- biological shielding
- cobalt-60 source
- safety interlocking system
- computer control system.

From the results of RVNRL preparations carried out at the pilot plant scale, it is proven that scale up RVNRL preparation is possible and ready for commercial production. Hence cost analysis on RVNRL processing is very important as this will another factor to determine the commercial prospect of the material.
METHOD

RVNRL processing cost analysis are done based on the MINT's latex irradiator. The processing costs are calculated based on the irradiator being installed with 150 kCi of cobalt-60 and when the irradiator is installed with 1 MCi of cobalt-60.

Estimated Cost of Asset

The estimated cost of asset is the sum of the costs for the land, building, irradiation facilities, latex formulation facilities and cobalt-60 gamma irradiation source. Details are given in Table 1. The cost of the land is not included as the plant is built on an existing premises and government's own.

<table>
<thead>
<tr>
<th>Table 1: Estimated cost of asset for a latex irradiator plant</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cobalt-60 Source</strong></td>
</tr>
<tr>
<td>i) Land</td>
</tr>
<tr>
<td>ii) Building - equipped with biological shielding, a research laboratory, testing laboratory, dosimetry laboratory, administrative room, a common room, wash room, store room, M &amp; E room.</td>
</tr>
<tr>
<td>iii) Irradiation facilities, equipped with latex pumping station, irradiation pipe (350 metres), computerised irradiation control panel.</td>
</tr>
<tr>
<td>iv) Latex formulation facilities include receiving, mixing, storing tanks plus stirrer motors and stirrer blades, electrical fittings etc.</td>
</tr>
<tr>
<td>v) Cobalt-60 source</td>
</tr>
</tbody>
</table>

Cost Calculation

The elements contributing to the cost for preparing RVNRL using the latex irradiator are categorised into two:

i. Fixed cost, appeared in the calculation as depreciation cost, and
ii. Operating cost.

Fixed cost is contributed by the depreciation cost of building, irradiation facilities and formulation facilities. Operating cost is contributed by maintenance service and spares, cobalt-60 replenishment, wages, utilities, telecommunications and administration services, sensitiser water and stabiliser. Details are given in Table 2 and Table 3 respectively.
Table 2: Details of the elements contribute to the fixed cost.

<table>
<thead>
<tr>
<th>Facilities</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>i) Building depreciation (life time of 15 years)</td>
<td>RM 100 000.00</td>
</tr>
<tr>
<td>ii) Irradiation facilities depreciation (life time of 10 years)</td>
<td>RM 350 000.00</td>
</tr>
<tr>
<td>iii) Formulation facilities depreciation (life time of 10 years)</td>
<td>RM 40 000.00</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>RM 490 000.00</strong></td>
</tr>
</tbody>
</table>

Table 3: Operating cost of latex irradiator plant installed either with 150 kCi or 1 MCi of cobalt-60.

<table>
<thead>
<tr>
<th>Cobalt-60 Source</th>
<th>150 kCi</th>
<th>1 MCi</th>
</tr>
</thead>
<tbody>
<tr>
<td>i) Maintenance service and spares for formulation facilities</td>
<td>RM 6 000.00</td>
<td>RM 6 000.00</td>
</tr>
<tr>
<td>ii) Irradiation source replenishment, taken as 12 % of the initial cost annually</td>
<td>RM 42 000.00</td>
<td>RM 560 000.00</td>
</tr>
<tr>
<td>iii) Wages</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a) 1 Plat Manager</td>
<td>RM 233 000.00</td>
<td>RM 233 000.00</td>
</tr>
<tr>
<td>b) 2 QC Managers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c) Plant Operator</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 Senior Technician</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 Technicians</td>
<td></td>
<td></td>
</tr>
<tr>
<td>d) 8 Latex Formulators</td>
<td></td>
<td></td>
</tr>
<tr>
<td>e) 1 Latex/RVNRL Handlers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>iv) Utilities</td>
<td>RM 20 000.00</td>
<td>RM 20 000.00</td>
</tr>
<tr>
<td>v) Telecomunications and administration services</td>
<td>RM 15 000.00</td>
<td>RM 15 000.00</td>
</tr>
<tr>
<td>vi) Sensitiser</td>
<td></td>
<td></td>
</tr>
<tr>
<td>vii) Stabiliser</td>
<td></td>
<td></td>
</tr>
<tr>
<td>viii) Water</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>RM 316 000.00</td>
<td>RM 834 000.00</td>
</tr>
</tbody>
</table>
Estimation of RVNRL Production Capacity

If cobalt-60 source strength is 100 kCi :-

\[
100 \text{ kCi} \quad \xrightarrow{\text{emitted}} \quad 1.48 \text{ kW}
\]

Assumed the irradiation dose required for RVNRL preparation is between 10 to 15 kGy i.e 1 to 1.5 Mrad. 1 Mrad may be defined as:

\[
1 \text{ Mrad} = 10 \text{ kGy} = 10 \text{ kJ per kg} \\
1 \text{ Gy} = 1 \text{ J per kg} \\
100 \text{ rad} = 1 \text{ Gy}
\]

\[
10 \text{ kJ/kg} = 10 \text{ kJ per s x s per kg} = 10 \text{ kWs per kg}
\]

\[
1 \text{ Watt} = 1 \text{ J per s} \\
1 \text{ Mrad} = 10 \text{ kGy} = 10 \text{ kWs per kg} = \frac{10 \text{ kW.hr per kg}}{3600} = \frac{1 \text{ kWhr per kg}}{360}
\]

Production rate, \( M \) may be calculated using the following formula:

\[
M = \frac{360 \cdot f \cdot P}{D} \text{ kg per hr}
\]

where \( f \) = Power utilisation efficiency i.e the efficiency of using the power from the radiation source cobalt-60

\( D \) = Vulcanisation dose, Mrad

\( P \) = Power emitted, kW.

The efficiency of power utilisation may vary, say from 20% to 50% depending on the irradiation system and the irradiation field.

Assuming a pilot plant is installed with 150 kCi of cobalt-60 source, power utilisation efficiency of 25% and vulcanisation dose of 1.2 Mrad (12 kGy), the rate of RVNRL production:

\[
M = 360 \times 0.25 \times \frac{2.22}{1.2} \text{ kg per hr} = 166.5 \text{ kg per hr.}
\]
If the plant is operated 24 hours per day, daily production:

\[ 166.5 \text{ kg} \times 24 = 3996 \text{ kg per day} \]

Monthly production:

\[ 3996 \text{ kg} \times 28 = 111888 \text{ kg per month} \]

Yearly production:

\[ 111888 \text{ kg} \times 12 = 1342656 \text{ kg per year} \]

Irradiation cost:

Cost to irradiate 1 kg of latex (50% t.s.c):

\[
\text{Fixed cost} + \text{Operating cost} = \text{Irradiation cost} \\
\text{Production capacity}
\]

\[
\frac{\text{RM 806000.00}}{1342656} = \text{RM 0.60 per kg.}
\]

Latex as it is may be vulcanised by radiation. However, the irradiation dose required is extremely high, 40 Mrad or above. Therefore, in an effort to reduce the vulcanisation dose and make the process more economical and attractive to the users, prior to irradiation stage latex must first be formulated. The materials used and their cost to formulate latex to prepare a required amount of RVNRL is presented below.

To prepare 1342656 kg of RVNRL the amount and cost of materials required are as follows:

- **Latex (62% t.s.c)** = 1121342 kg (will depend on market price)
- **Sensitiser (5 pphr)** = 33570 kg @ RM 3.60 = RM 120852.00
- **Stabiliser (0.02 pphr)** = 137 kg @ RM 35.00 = RM 4795.00
- **Water** = 187850 kg @ RM 0.003 = RM 563.00

Total cost:

\[
\text{RM 126210.00}
\]

Cost to formulate 1 kg of latex:

\[
\text{Cost of sensitiser} + \text{Cost of stabiliser} + \text{Cost of water} = \text{Cost of Formulation} \\
\text{Quantity of RVNRL}
\]

\[
\frac{\text{RM 126210.00}}{1342656} = \text{RM 0.094 per kg}
\]

Hence, the cost to prepare 1 kg of RVNRL:

\[
\text{Cost to formulate latex} + \text{Cost to irradiate latex} = \text{Cost of RVNRL} \\
\text{RM 0.094 + RM 0.600 = RM 0.694 per kg of RVNRL}
\]
If plant is installed with 1 MCI of cobalt-60 source, assume power utilisation efficiency is 25% and vulcanisation dose is 1.2 Mrad (12 kGy) the rate of RVNRL production:

\[
M = 360 \times 0.25 \times \frac{14.8}{1.2} = 1110 \text{ kg per hour}
\]

If the plant is operated 24 hours per day, daily production:

\[
1110 \text{ kg} \times 24 = 26640 \text{ kg per day}
\]

Monthly production:

Say the plant is operated 28 days in a month:

\[
26640 \text{ kg} \times 28 = 745920 \text{ kg per month}
\]

Yearly production:

\[
745920 \text{ kg} \times 12 = 8951040 \text{ kg per year}
\]

Irradiation cost:

Cost to irradiate 1 kg of latex (50% t.s.c):

\[
\text{RM 1324 000} = \text{RM 0.148 per kg.}
\]

\[
\frac{8951040}{8951040} = \text{RM 0.148 per kg.}
\]

Formulation cost:

Latex = 7474947 kg (will depend on market price)

Sensitiser (5 phr) = 223774 kg @ RM 3.60 = RM 805600.00

Stabiliser (0.02 phr) = 912 kg @ RM 35.00 = RM 31905.00

Water (to dilute to 50% t.s.c) = 1252327 kg @ RM 0.03 = RM 3757.00

\[
\text{Cost to formulate 1 kg of latex:}
\]

\[
\frac{RM 841262}{8951040} = \text{RM 0.094 per kg}
\]

Hence cost to prepare 1 kg of RVNRL:

\[
\text{RM 0.094} + \text{RM 0.148} = \text{RM 0.242 per kg RVNR}
\]
Please note that the price of materials used in these calculations are based on spot purchased using government local order. The price of cobalt-60 is RM 5.00 per Curie, the price of the sensitiser and stabiliser is RM 3.60 per kg and RM 35.00 per kg respectively and water cost RM 0.03 per kg.

Table 4: Cost distribution in RVNRL production

<table>
<thead>
<tr>
<th>Cost</th>
<th>Percentage of Total Cost, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Building and facilities depreciation</td>
<td>RM 490 000.00</td>
</tr>
<tr>
<td>Cobalt-60 source replenishment</td>
<td>RM 560 000.00</td>
</tr>
<tr>
<td>Wages</td>
<td>RM 233 000.00</td>
</tr>
<tr>
<td>Sensitiser, stabiliser and water</td>
<td>RM 839 890.00</td>
</tr>
<tr>
<td>Utilities, administration, maintenance and spares</td>
<td>RM 41 000.00</td>
</tr>
<tr>
<td><strong>Total cost</strong></td>
<td><strong>RM 2 163 890.00</strong></td>
</tr>
</tbody>
</table>

It is shown in the Table 4 that in RVNRL production the cost of purchasing the required amount of sensitiser, stabiliser and water accounted for the highest percentage of the total cost. Any possibility of reducing the amount of these materials use in the process will definitely help to make the cost of RVNRL more attractive to the users.

**Effect of Power Utilisation Efficiency on The Production Capacity**

At a fixed cobalt-60 source of 1 MCI and latex vulcanisation dose of 12.0 kGy the effect of power utilisation efficiency on the rate of RVNRL production is given in Table 5.

Table 5: Effect of plant efficiency on the production capacity of RVNRL

<table>
<thead>
<tr>
<th>Efficiency, %</th>
<th>Production Capacity, kg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hourly</td>
</tr>
<tr>
<td>20</td>
<td>888</td>
</tr>
<tr>
<td>25</td>
<td>1 110</td>
</tr>
<tr>
<td>30</td>
<td>1 332</td>
</tr>
<tr>
<td>35</td>
<td>1 554</td>
</tr>
<tr>
<td>40</td>
<td>1 776</td>
</tr>
<tr>
<td>45</td>
<td>1 998</td>
</tr>
<tr>
<td>50</td>
<td>2 220</td>
</tr>
</tbody>
</table>

From Table 5, it seems that the production capacity increases as the irradiator efficiency increases. More significant increased in the production capacity is observed when efficiency improvement is made to an irradiator of a low efficiency compared to when efficiency improvement is made to a plant of already sufficiently high in efficiency. Furthermore, no proper correlation is observed between the efficiency improvement and the increment in production capacity. The results is presented graphically in Figure 1.
Figure 1: Effect of vulcanisation dose on a production capacity of RVNRL

Figure 2: Effect of plant efficiency on a production capacity of RVNRL
Effect of Vulcanisation Dose on The Production Capacity

At a fixed cobalt-60 source of 1 MCi and plant power utilisation efficiency of 25%, the effect of different vulcanisation doses on the production capacity of RVNRL is given in Table 6.

**Table 6: Effect of vulcanisation dose on the production capacity of RVNRL**

<table>
<thead>
<tr>
<th>Vulcanisation dose, kGy</th>
<th>Production Capacity, kg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hourly</td>
</tr>
<tr>
<td>8</td>
<td>1 665</td>
</tr>
<tr>
<td>9</td>
<td>1 480</td>
</tr>
<tr>
<td>10</td>
<td>1 332</td>
</tr>
<tr>
<td>11</td>
<td>1 211</td>
</tr>
<tr>
<td>12</td>
<td>1 110</td>
</tr>
<tr>
<td>13</td>
<td>1 025</td>
</tr>
<tr>
<td>14</td>
<td>951</td>
</tr>
<tr>
<td>15</td>
<td>888</td>
</tr>
</tbody>
</table>

From Table 6, it shows that the production capacity decreases with the increased in the vulcanisation dose used in RVNRL preparations. Graphical representation of the results is given in Figure 2. Therefore, using latex of right maturity is important to ensure high throughput of the plant and hence reduces the cost of RVNRL processing.

**CONCLUSIONS**

The cost to prepare RVNRL is determined by many factors, among them are the cost of sensitiser and stabiliser, the efficiency of the plant and irradiation vulcanisation dose employed in RVNRL preparation.

The price of RVNRL and the price of sulphur prevulcanised latex can be very competitive especially when RVNRL production is 8 000 tons or more.
QUESTIONS & ANSWERS, and COMMENTS

Session IV

Q1 Yaziz
   How do we establish the homogeneity of the latex in the irradiator so designed?

A1 E. Smolko
   The latex is homogenised through the pumping action and circulation of the latex around the gamma source. The dose distribution problem could be solved using a suitable source design.

Q2
   How do we check the dosimetry?

A2 E. Smolko
   Use solid dosimeters.
IMPROVEMENT OF HARDNESS OF RADIATION VULCANISED NATURAL RUBBER LATEX

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Abstract

Five different methods of sample preparation of radiation induced graft co-polymer using n-butyl acrylate and methyl methacrylate on natural rubber latex have been studied. This work aims to improve some mechanical properties of radiation vulcanised natural rubber latex especially in hardness. Different methods of sample preparation give the different in mechanical properties. Tensile strength in most cases increases up to maximum and then decreases with increasing of monomer. Modulus and hardness increase with increasing of monomer content but elongation at break decreases with increasing of monomer content. The postulated crosslinking and grafting structure of vulcanised latex can be drawn from mechanical properties study.

INTRODUCTION

Radiation vulcanised natural rubber latex (RVNRL) has been developed using effective radiation sensitizer such as n-butyl acrylate (n-Ba) and can be vulcanised at very low radiation dose. This work some attempts were made to prepared graft co-polymer by grafting with methyl methacrylate (MMA) on RVNRL for improving some mechanical properties of RVNRL. Five different methods of sample preparation and their mechanical properties were carried out.

PROCEDURE

Materials

Concentrated natural rubber latex (60% total solid content (TSC)) was obtained from Sri Lanka. Technical grade monomer of n-butyl acrylate (n-Ba) and methyl methacrylate (MMA) were passed through the Alumina Woelm B-Super 1 columns to removed inhibitor before used. Other chemical were analytical grade and used as received.

The optimum dose determination for radiation vulcanised natural rubber latex

Natural rubber latex (60% TSC) was diluted with 1% ammonia solution to be 50% TSC and was stabilized by adding 0.2phr of 10% potassium hydroxide (KOH) before used. Radiation vulcanised natural rubber latex was prepared by adding 5phr of n-Ba into stabilized latex and then the latex was irradiated by gamma rays from Co-60 source at different total dose of 5, 10, 15, 20, 25, 30, 40 and 50 kGy. The irradiation was conducted at constant dose rate of 10 kGy/hr at room temperautre.
Sample preparation and irradiation

Five different methods of sample preparation were carried out as follows:

**Method 1** Natural rubber latex (60% TSC) was diluted with 1% ammonia solution to be 30% TSC. The mixture of n-Ba (5 phr) and different concentration of MMA (25, 50 and 75 phr) was emulsified by using oleic acid (0.5 phr). The mixture of these two monomers were then added to the diluted natural rubber latex while stirring. Stirring was continued for more than one hour and the mixture was left over night. The mixture was irradiated by gamma rays at total dose of 20 kGy.

**Method 2** At first radiation vulcanised natural rubber latex was prepared as described in above procedure of optimum dose determination. The Total dose for vulcanisation was fixed at 20 kGy. The obtained radiation vulcanised latex was diluted with 1% ammonia solution to be 30% TSC. Different concentration of MMA monomer (25, 50, and 75 phr) was emulsified using oleic (0.5 phr) and then was mixed thoroughly with diluted radiation vulcanised latex and kept over night. The mixture was irradiated by gamma rays at total dose of 10 kGy.

**Method 3** Different concentrations of MMA monomer (25, 50, and 75 phr) was proceeded as described in method 2 and then was mixed with rubber latex (30% TSC). The mixture was then irradiated at total dose of 10 kGy. At this step the irradiated latex should be MMA grafted natural rubber latex. The n-Ba was added to the irradiated latex while stirring and then was irradiated again at total dose of 20 kGy.

**Method 4** Radiation vulcanised latex was prepared as described in method 2 and MMA grafted natural rubber latex was prepared in the same way as described in method 3 by fixing the concentration of MMA at 50 phr. The obtained MMA grafted natural rubber latex was mixed with radiation vulcanised latex at different composition of 25, 50 and 75% (v/v).

**Method 5** The emulsion polymerization of MMA was prepared by redox system of (NH$_4$)$_2$SO$_4$/NaHSO$_3$ as initiator and with sodium laurylsulfate as emulsifier at polymerization temperature of 50°C. The procedure of emulsion polymerization was modified from (Egusa and Makunuchi, 1981). Emulsion polymerization was carried out in a 500 ml stainless-steel vessel which was thermostated to desired temperature of 50°C. 180 grams of MMA, 320 grams of deionized water and 1.2 gram of sodium laurylsulfate were poured into the reaction vessel and heated up to the polymerization temperature of 50°C. The mixture was stirred by paddle type stirrer at about 150 rpm with nitrogen gas bubbling and left for about 40 minutes to attain temperature equilibrium and to remove oxygen from the system. 0.2 gram of (NH$_4$)$_2$SO$_4$ and 0.2 gram of NaHSO$_3$ were dissolved in 10 mL of water separately and were added to the system at 30 mins intervals. Immediately after the reaction of 3 hours passed, the temperature of the vessel was lowered to room temperature. The ammonia solution was added to emulsion latex to make a solution of 1% ammonia and the emulsion latex was then mixes with radiation vulcanised latex at different composition of 25, 50, and 75% (v/v).

**Film preparation** Films were prepared by casting about 20 grams of irradiated latex on to glass plate 17cm x 11 cm. and dried at room temperature. The obtained dried rubber films were immersed in distilled water for 24 hours to leach out water soluble components from the films and dried subsequently at room temperature and dried again at 70°C for one hour.

**Measurement of viscosity** The viscosity of the latex was measured at 25°C by a coneplate type rotary viscometer model EMD made by Tokyo Keiki Co. Ltd. Japan.

**Mechanical testing** Tensile strength, modulus and elongation at break of the film sheet were measured by using a Toyoseiki tension meter (STROGRAPH-R1) according to Japan Industrial Standard JIS K6301 method.

**Hardness** Shore-A hardness on the film sheet was measured by plastic hardness tester (ASKER DD2).
RESULTS AND DISCUSSION

Determination of optimum dose for radiation vulcanised natural rubber latex

Figure 1 shows the effect of radiation dose on tensile strength and elongation at break of irradiated film sheet. The tensile strength increases up to maximum and then slightly decreases with increasing of radiation dose. Elongation at break decreases as increasing of radiation dose. The optimum radiation dose is lied between 15 to 20 kGy. The radiation dose of 20 kGy is chosen for vulcanization in this experiment.

![Graph showing tensile strength and elongation at break vs. radiation dose](image)

**Figure 1:** Relationship between tensile strength, elongation at break and irradiation dose.

The viscosity and conversion on monomer

The conversion of monomer and viscosity before and after irradiation of natural rubber latex mixture prepared from method 1 to 3 are given in Table 1 to 3 respectively. The viscosity of NR latex mixture prepared from method I and III shows slightly increasing in viscosity only in method II shows largely increase at 75 phr monomer concentration. Over ninety percent of the conversion of monomer can be obtained from all methods this means radiation dose of 10 kGy enough for polymerization of monomer.

<table>
<thead>
<tr>
<th>MMA content (phr)</th>
<th>Before irradiation</th>
<th>After irradiation</th>
<th>Conversion of monomer (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Viscosity (cp)</td>
<td>Solid content (%)</td>
<td>Viscosity (cp)</td>
</tr>
<tr>
<td>0</td>
<td>3.9</td>
<td>30.8</td>
<td>3.6</td>
</tr>
<tr>
<td>25</td>
<td>4.7</td>
<td>29.4</td>
<td>5.4</td>
</tr>
<tr>
<td>50</td>
<td>5.4</td>
<td>28.5</td>
<td>6.4</td>
</tr>
<tr>
<td>75</td>
<td>7.4</td>
<td>26.2</td>
<td>10.5</td>
</tr>
</tbody>
</table>
Table 2: Latex properties of natural rubber latex mixture prepared by method 2

| MMA content (phr) | Before irradiation | | | | | Conversion of monomer (%) |
|-------------------|--------------------|-------------------|-------------------|-----------------|-------------------|-------------------|-------------------|-------------------|-------------------|
|                   | Viscosity (cp)     | Solid content (%) | Viscosity (cp)     | Solid content (%) |                   |                   |                   |                   |                   |
| 0                 | 3.3                | 30.2              | 3.7                | 30.5             | -                 |                   |                   |                   |                   |
| 25                | 5.1                | 28.9              | 18.1               | 34.7             | 96.9              |                   |                   |                   |                   |
| 50                | 7.4                | 27.1              | 52.0               | 39.0             | 97.7              |                   |                   |                   |                   |
| 75                | 8.8                | 24.9              | 166.0              | 42.7             | 98.2              |                   |                   |                   |                   |

Table 3: Latex properties of natural rubber latex mixture prepared by method 3

| MMA content (phr) | Before irradiation | | | | | Conversion of monomer (%) |
|-------------------|--------------------|-------------------|-------------------|-----------------|-------------------|-------------------|-------------------|-------------------|
|                   | Viscosity (cp)     | Solid content (%) | Viscosity (cp)     | Solid content (%) |                   |                   |                   |                   |                   |
| 0                 | 3.5                | 30.1              | 3.7                | 30.0             | -                 |                   |                   |                   |                   |
| 25                | 4.0                | 28.4              | 6.4                | 35.3             | 98.8              |                   |                   |                   |                   |
| 50                | 5.1                | 26.6              | 14.0               | 39.6             | 99.2              |                   |                   |                   |                   |
| 75                | 6.5                | 25.0              | 16.2               | 43.5             | 99.8              |                   |                   |                   |                   |

Mechanical properties of cast film

Due to the difficulty of making film sheet from MMA grafted latex, prepared by catalyst initiator, because cracking in the film is more easily formed during drying. Table 4 formation of cracking in the film prepared form all methods can only seen from the film prepared by method V at 75% of PMMA emulsion latex in RVNRL.

Table 4: Appearance of film after casting
( Degree of cracking in film: no (O), small (x) large (#) )

| Method of Preparation | Monomer content | | | | | |
|-----------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                       | 0               | 25              | 50              | 75              | 0               | 25              | 50              | 75              |
| 1                     | O               | O               | O               | O               | O               | O               | O               | O               |
| 2                     | O               | O               | O               | X               | O               | O               | X               | O               |
| 3                     | O               | O               | O               | O               | O               | O               | O               | O               |
| 4                     | O               | O               | O               | O               | O               | O               | O               | O               |
| 5                     | O               | O               | O               | #               | O               | O               | O               | #               |

MMA monomer content express in phr for method 1 to 3 and in % (v/v) for method 4 and 5

Figure 2 shows tensile strength of the film sheets. Tensile strength increases up to maximum and then decreases with increasing of monomer content. In case of method 1, 2, 3 and 5, method 5 at 25% of PMMA emulsion latex in RVNRL gives the highest tensile strength of about 350 kg/cm². In method 4, tensile strength decreases with increasing monomer content.
Figure 2: Effect of monomer or polymer contents on tensile strength of irradiated film sheet prepared from different methods.

Figure 3 shows modulus at 600% of irradiated film sheets prepared from 5 methods. Modulus increase with increasing of monomer or polymer content in samples in all methods. Method 2 gives highest modulus value while method 4 gives lowest modulus value.

Figure 3: Effect of monomer or polymer contents on modulus of irradiated film sheet prepared from different methods.

Figure 4 shows elongation at break of irradiated film sheet prepared from different methods. Elongation decreases with increasing of monomer or polymer contents in very cases. For hardness, the hardness increase with increasing of monomer or polymer content and vulcanised rubber latex prepared from method 5 gives highest value of 68 shore A as shown in figure 5.
From different methods of preparation and the results obtained from mechanical properties study, the postulated crosslinking and grafting structure of vulcanised latex can be drawn as shown in figure 6.
Method 1 Mix monomer

Method 2 RVNRL/g-PMMA

Method 3 g-PMMA/RVNRL

Method 4 RVNRL + NRL-g-PMMA

Method 5 RVNRL + emulsion PMMA

Figure 6: Schematic crosslinking and grafting structure of vulcanised latex

CONCLUSION

Tensile strength in most cases increases with increasing of monomer or poly content in vulcanised latex except in method 4. Vulcanised latex prepared from method 5 give highest tensile strength of 350 kg/cm². Modulus at 600% break and hardness increase with increasing of monomer or polymer content in vulcanised latex while elongation at break decreases with increasing of monomer or polymer content. Method 5 also gives highest hardness of 68 shore A.
ACKNOWLEDGEMENT

This work was carried out during scientific exchange program granted by Science and Technology Agency Government of Japan.

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REDUCTION OF RESIDUAL n-BUTYL ACRYLATE SENSITIZER IN RADIATION VULCANIZED NATURAL RUBBER LATEX

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Abstract

Radiation vulcanisation of natural rubber latex needs n-butyl acrylate (n-BA) to lessen required irradiation dose. Considerable amount of n-BA remains in the latex after the completion of radiation vulcanisation and tends to pollute the working environment in a dipping factory. A study has been carried out to reduce the residual n-BA after the radiation vulcanization. About 40% of added n-BA was found in the latex after irradiation to 20 kGy. Hydrolysis of n-BA was effective for reduction of the residual n-BA in the latex. No n-BA was found in the latex when the latex was stored for 4 weeks at room temperature due to its hydrolysis. Heating of the latex was effective to accelerate the rate of hydrolysis of n-BA. Almost all of n-BA in the latex was hydrolysed when the latex was heated for 4 hours at 80°C. Tensile strength of the latex films slightly decreased by heating treatment of the latex, but gradually recovered as storage time extended. Low viscosity was attained by the heat treatment of the latex.
HYDROGEL COATING OF RVNRL FILM BY ELECTRON BEAM IRRADIATION

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Abstract

The tackiness properties of Radiation Vulcanized Natural Rubber Latex (RVNRL) film surfaces coated by various monomers have been investigated in order to understand the suitable hydrogels which reduce the tackiness of the film. In this context, different types of monomers namely, N-vinyl-2-pyrrolidone (NVP), N,N-dimethyl amino ethyl amide (DMAEA), acrylic acid (AAc), N-butyl acrylate (n-BA) and 2-hydroxyethyl methacrylate (HEMA) as well as monomer mixtures have been tried with varying degrees of success. It was found that coating the RVNRL with 80% HEMA/20% n-BA by irradiation at 80 kGy using low Energy Electron Beam gave remarkable reduction in surface tackiness of the RVNRL film. Several other attempts were made such as priming with acid and aluminum sulfate, mixing the aluminum sulfate into the monomer and dipping the partially wet RVNRL film into the monomer to enhance the wettability of the monomers with the film. Studies on surface topography revealed that the decrease in tackiness with coating is due to the increase of the surface roughness at 80 kGy irradiation dose.

Abstrak

Filem yang disediakan daripada lateks getah asli yang divulkanakan dengan menggunakan sinaran (RVNRL) telah disalutkan dengan beberapa jenis monomer dengan tujuan mengurangkan sifat-sifat pelekitan permukaan filem tersebut. Dalam hubungan ini monomer-monomer seperti N-vinyl -2-pyrrolidone (NVP), N,N-dimethyl amino ethyl amide (DMAEA), acrylic acid (AAc), N-butyl acrylate (n-BA), 2-hydroxyethyl methacrylate (HEMA) dan juga campuran monomer tersebut dengan n-BA telah dikaji. Adalah didapati penyalutan permukaan filem RVNRL dengan 80% HEMA/20% n-BA pada 80 kGy dengan menggunakan teknik sinaran alur elektron bertenaga rendah telah berjaya mengurangkan pelekitan permukaan filem RVNRL dengan berkesan. Beberapa percubaan juga telah dibuat untuk meningkatkan pembasahan di antara monomer dengan filem seperti membasah permukaan filem dengan acid dan aluminium sulfate, mencampurkan aluminium sulfate ke dalam monomer dan juga mencelupkan filem RVNRL yang separa basah ke dalam monomer. Kajian permukaan filem dengan menggunakan mikroskop elektron imbasan (scanning electron microscope) menunjukkan penurunan dalam pelekitan pada 80 kGy untuk filem yang disalut dengan 80% HEMA/20% n-BA adalah disebabkan oleh peningkatan di dalam kekasaran permukaan filem.
INTRODUCTION

The radiation vulcanized natural rubber latex (RVNRL) has the following advantages over the conventional vulcanizates (Makuuchi 1996):

1) Absence of N-nitrosamines
2) Very low cytotoxicity
3) Less protein allergy response
4) Degradability
5) Transparency and softness
6) Low emission of SO₂ and less formation of ashes when burned.

These characteristics of RVNRL suggest wide applications of RVNRL in medical field. With regard to this, the first application of RVNR latex was in medical use, optical laser balloon (optical endoscopic balloon) (Shimamura 1989). Indeed, one of the products fabricated from RVNRL are gloves, have been produced successfully from RVNR latex in several countries (Makuuchi et al. 1990; Devendra et al. 1993). However it was found that beside aging, the tackiness of RVNRL film is also inferior to that of sulfur vulcanized one (Haque et al. 1995).

Generally, various methods has been utilized and practiced to reduce the surface tackiness of rubber articles (Waddell et al. 1992). For example, the surface of rubber glove can be halogenated with bromine or chlorine to make it slippery. However, this treatment may result in very poor aging properties, discoloration and embrittlement. Waxes, silicones and powders have been used but this provide only temporary solution as the material rub off in a very short time. Further more, there is always a risk of such lubricants and powders escaping from the interior of the glove to contaminate the surgical field, during donning or if the glove is punctured during an operation. In order to overcome such problem, protective rubber products coated by hydrogel were developed by conventional method using sulfur vulcanized latex (Goldstein et al. 1984; Goldstein et al. 1986). Apart from tackiness, the status of RVNRL film surface including wettability and biocompatibility are important for medical applications. Therefore, surface modification of RVNRL film by suitable hydrogel lining with optimum bulk properties is an efficient way to render it suitable for medical purpose. During past two decades, radiation induced graft co polymerization of monomers onto the surface of polymers using energy sources such as gamma rays, electron beams and UV have been widely developed (Chapiro 1962; Ratner et al. 1974; Muherjee et al. 1985). In this studies attempt was made to graft a combination of hydrophilic and hydrophobic hydrogel onto the RVNRL film by using Low Energy Electron Beam Irradiation.

EXPERIMENTAL

The latex used in this work was a high ammonia centrifuged natural rubber latex concentrates produced by Dunlop of Malaysia. N-butyl acrylate (n-BA), ammonia solution, aluminum sulfate anhydrous, sulfuric acid and hydrophilic monomers such as 2-hydroxyethyl methacrylate (HEMA), acrylic acid (AAc), N-vinyl-2-pyrrolidone (NVP) and N,N dimethyl amino ethyl amide (DMAEA) are products of Japan. The solvents and monomers used were reagent grade and were used without further purification. Inhibitors were removed from the monomers by filtration over aluminum oxide.

RVNRL preparation

The latex, in stainless steel drum was diluted to 50% total solid content, tsc by adding 1% ammonia solution while stirring. This was followed by addition of 0.2 phr of 10% KOH solution and 5 phr n-BA. The stirring continued for more than 2 hours. The irradiation of latex was carried out at a dose rate of 10
kGy / hour for 2 hours at 20°C. After irradiation the latex was tightly covered and kept at room temperature. Films were prepared by casting the latex on glass plates and air drying at room temperature till transparent. Then the films were leached in 1% aqueous ammonia for 24 hours and air dried again until transparent followed by heating in oven at 80°C for complete dryness.

Coating of hydrogel onto RVNRL film.

Various combinations of hydrophilic and hydrophobic monomers (as shown in results and discussions) were coated onto the RVNRL film by dipping the film into the respective monomers and monomers mixtures. The dipped film then irradiated using 300 KeV electron beam accelerator at 150 KeV, 30mA and 20 kGy / pass. Samples were irradiated at 20, 40, 60 and 80 kGy doses. The irradiated films were leached with water in order to wash out the unreacted monomers and followed by air drying at room temperature for 48 hours.

In order to improve the adhesion and wettability between the rubber and the monomers following surface treatments were tried independently prior to dipping.

The RVNRL films were primed by 5% sulfuric acid followed by rinsing in purified water at 20°C.

The RVNRL films were rinsed with 4% aluminum sulfate solution.

0.5% aluminum sulfate was mixed into the monomer mixtures and dipping were carried out in usual manner.

Partially wet RVNRL films (leaching followed by partial drying) were dipped into the monomers mixture prior to irradiation.

Evaluation of tackiness

The tackiness of the films were obtained by using a probe tack tester (Resca Co. Ltd.) with stainless probe at a preload of 10 gf, a press time of 10 seconds and a detach speed of 30mm / min.

Surface Topography

Treated RVNRL film surfaces were prepared in the usual manner for scanning electron microscope (SEM) examination.

RESULTS AND DISCUSSIONS

Tackiness of RVNRL film

In preliminary studies hydrophilic monomers such as NVP, AAe, DMAEA and HEMA were chosen for coating onto the RVNRL film based on the wettability of the respective monomers on the rubber surface by subjective evaluations.
Figure 1 shows the variation in tackiness of the coated RVNRL film with respect to irradiation dose. It is apparent from this figure that the samples coated with AAc show a drastic reduction in tackiness after a dose of 20 kGy. A gradual reduction in tackiness with dose also observed for the film coated with HEMA. This is followed by DMAEA which show only moderate reduction in tackiness compared with the uncoated film. In contrast the samples coated with n-BA show a drastic increase in tackiness with irradiation indicating that polybutyl acrylate formed is rather sticky. Similar trend also observed for samples coated with NVP, suggesting that only AAc and HEMA likely to be suitable for applications require low tackiness. However, films coated with AAc rendered hard surface and peeling of the coated layer on stretching. On the other hand poor wetting of HEMA with RVNRL film surface was observed. Considering above limitations with HEMA and AAc, in order to enhance the compatibility of above chosen hydrophilic monomers with rubber which is hydrophobic, an attempt was made to mix the above individual hydrophilic monomers with a hydrophobic monomer, n-BA which poses Tg approaching that of natural rubber and also used as sensitizer in RVNRL preparation. Referring to Figure 2, it is clear that the film coated with 80% AAc/20%n-BA and 50% AAc/50%n-BA show remarkable decline in tackiness with dose, approaching 0 at 40kGy. Unfortunately, the peeling of the coated layer on stretching coupled with hard and stiff coated surface were not improved. Interestingly, such problems were not observed for films coated with 80% HEMA/20%n-BA mixture and it is noted an improved wetting of HEMA on RVNRL surface with the addition of 20% n-BA. Taking the above criteria into consideration, possible suitable coating material is, 80% HEMA/20%n-BA combinations. Thus from this point further studies were focused on coating of 80% HEMA/20%n-BA.

Results on various other methods which were tried to further improve the quality of the coating were plotted in Figure 3. In this experiment all samples are coated with 80% HEMA/20%n-BA with respective treatments while the control is the dry RVNRL film coating. It is apparent from Figure 3 that each respective treatment give reduction in tackiness in varying extent with irradiation. The improvement with acid treatment could be due to the fact that the hydrophobic RVNRL film surface was made more wettable with the monomers by the acid washing. In addition, the rinsing with aluminum sulfate and the addition of aluminum sulfate into the monomer mixtures also render improvement. This results is in line with the hypothesis for trivalent metal ion which has been described elsewhere (Podell 1986). In relation to this hypothesis it is believed that the trivalent aluminum ion in an acidic solution, form multiplicity of linkages with, on the one hand, the hydroxyl group of PHEMA and on the other hand, the various non rubber constituents in the rubber latex film, in particular with protein substances. Thus an improved adhesion of the PHEMA on the RVNRL surface have achieved.

Finally, the samples which were produced by dipping the partially wet RVNRL film offered the most promising feature with regard to tackiness. Visual observations also confirms that even coating and best homogeneity is achieved. This results could be attributed by the accelerative effect of water on graft polymerization as already indicated by Sasaki et al. (Sasaki et al. 1979) in the similar monomer system. Besides that the improved wetting of HEMA on the rubber surface could be due to the interaction by hydrogen bonding between the water present in the rubber film and OH group of the HEMA at the interface between the RVNRL film surface and the monomer mixture.

Taking the above discussions into consideration, efforts on characterization of the coated surface were focused on RVNRL film coated with 80%HMA/20%n-BA where the wet film dipping technique was employed prior to irradiation.

Surface Topography

SEM photomicrographs of surfaces are shown in Figure 4. It can be noted that the hydrogel coated surface were made to rough whereas the uncoated surface is appear to be smooth. Comparing the coated surfaces which were irradiated at 20kGy and 80kGy, it is apparent that the roughness of the coating increasing
with irradiation dose. Accordingly, a close relation between roughness and tackiness is observed; the decrease in tackiness is due to increase in roughness. This observation is in agreement with report by Takeiro Saito et al. (Saito et al. 1993) who studied on development of anti-stickiness of rubber surface by UV irradiation and sputter-etching treatments.

CONCLUSIONS

Hydrogel coating onto RVNRL film using Low Energy Electron Beam approach in this study was effective in reducing the tackiness of RVNRL film where 80%HMA/20%n-BA found to be the most suitable monomer mixture. Although treatments with acid and aluminum sulfate were studied, these seem unnecessary considering the great improvement in tackiness achieved by dipping the partially wet RVNRL film into the monomer mixtures followed by irradiation. SEM photomicrographs confirms that, 80%HMA/ 20%n-BA coating at 80kGy irradiation dose gave the necessary surface roughness in relation to reduced surface tackiness.

ACKNOWLEDGMENTS

One of us (Ratnam C.T) gratefully acknowledge IAEA for the financial support, MINT for giving permission to work at TRCRE, Japan and JICA for the kind co-operation. A sincere thanks also due to Dr. T. Sasaki for the stimulating discussions, Mr. Shin Hasegawa for his assistance during the experimental work and Mr. Taro Enjoji for his help during the typing of this manuscript.

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Figure 1. Effect of irradiation on tackiness of RVNRL film coated with various monomers.
Figure 2. Effect of irradiation on tackiness of RVNRL film coated with various monomer mixtures.
Figure 3. Effect of irradiation on tackiness of RVNRL film coated with 80% HEMA/20% n-BA.
Figure 4. Scanning electron micrographs of RVNRL film
(a) uncoated RVNRL film (control)
(b) uncoated RVNRL film (irradiated at 80kGy)
(c) coated RVNRL film with 80% HEMA / 20% n-BA (irradiated at 20kGy)
(d) coated RVNRL film with 80% HEMA / 20% n-BA (irradiated at 80 kGy)
THE ROLE OF PROTEINS ON THE THERMAL OXIDATIVE AGING OF RADIATION VULCANIZED NATURAL RUBBER LATEX

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Abstract

The effect of Hevea latex proteins on the aging properties of radiation vulcanized natural rubber latex (RVNRL) was investigated. Unpurified RVNRL films exhibited better aging properties than the purified RVNRL films. A sharp decrease in tensile strength was observed after aging when RVNRL films were leached in 1% NH\textsubscript{3}. However, when these films were soaked in ethanol prior to leaching, the aging properties approximated those of the unleached samples. Kjeldahl and FT-IR analyses of the leached and unleached RVNRL films indicated a higher protein content for both the unleached and ethanol-soaked films than for leached films. Electrophoretic analysis of the proteins present in the NH\textsubscript{3} extracts of leached RVNRL films showed a high concentration of hevein. This protein was not found in the NH\textsubscript{3} extracts of ethanol soaked films. Hevein was shown to improve the aging properties of RVNRL.

INTRODUCTION

Radiation treatment for the vulcanization of natural rubber latex (RVNRL) is a potential alternative to the conventional sulphur vulcanization process. RVNRL utilizes gamma radiation to catalyze the crosslinking of rubber molecules. Various modifications to improve the process and quality of RVNRL products have been developed. Previous studies dealt with the development of sensitizers to enhance crosslinking resulting to a reduction of the required radiation dose, improvement of the properties of the products with leaching, and the use of antioxidants to improve the aging properties of natural rubber latex (NRL). However, certain physical properties of RVNRL are still inferior to those of sulfur-vulcanized rubber. These properties are important factors to consider in the manufacture of dipped rubber goods.

Natural rubber (NR) which contains unsaturated bonds in its chain undergoes thermal oxidation. NR vulcanizates that are conventionally cured with sulphur are not easily affected by this oxidative aging. Sulphur crosslinks are oxidized to sulfoxides, then to the sulphenic acids which are powerful antioxidants\textsuperscript{1}. Radiation vulcanized natural rubber latex (RVNRL), on the other hand, does not have this auto-retarding property. The resistance of RVNRL to oxidation reaction depends on the natural antioxidants present in natural rubber latex. Among these are the tocotrienols, betaines, phenols, phospholipids and amino acids\textsuperscript{2,3,4,5}. The role of proteins in the oxidative aging of NR is still quite unclear. The work of Morimoto indicated that proteins play an important role in the heat resistance of NR compound\textsuperscript{4}. Hasma, on the other hand found that the Hevea proteins do not protect NR significantly against thermal oxidative aging\textsuperscript{3}. This paper presents data to clarify the role of NRL proteins particularly hevein, in the oxidative aging of RVNRL.

MATERIALS AND METHODS

Sri-Lankan latex with the following properties was used for this study. It is a high stability (HS) low ammonia latex with TMPTD-ZnO (LATZ) with a total solid content (TSC) of 60% and viscosity of 17.8 cP.
Extraction and Isolation of Proteins

Natural rubber latex (NRL) was centrifuged at 16,000 rpm for 2 hours at room temperature. A puncture was made on the coagulated rubber portion at the top of the centrifuge tube to run off the serum portion. The serum fraction was placed again in centrifuge tubes and frozen at -25°C. Recentrifugation was done for 2 hours while the serum was still in its frozen state. The bottom clear serum fraction was removed slowly with a pasteur pipette. The pH of the serum was adjusted to pH 6.0 with acetic acid and centrifuged to remove all the precipitated fraction. A portion of this serum was set aside for the isolation of hevein. Ammonium sulphate \((\text{NH}_4)_2\text{SO}_4\) was added to the clear solution to 100% saturation. The precipitated proteins were redissolved in water and reprecipitated again with \((\text{NH}_4)_2\text{SO}_4\). \(\alpha\)-globulin was isolated from the extracted proteins using Archer's procedure. The clarified serum was treated with \((\text{NH}_4)_2\text{SO}_4\) to 65% saturation. The resulting mixture was stored overnight at 4°C. The precipitate was discarded, and hevein was precipitated from the supernatant by saturation (100%) with \((\text{NH}_4)_2\text{SO}_4\). This precipitate was dissolved in water. Desalting was done using the Amicon diaflo ultrafiltration membrane (YM2).

Preparation and Analysis of RVNRL Films

NRL was diluted to 50% TSC with \(\text{NH}_4\text{OH}\) and mixed with 5 phr n-butyl acrylate as sensitizer. NRL was irradiated at an absorbed dose of 15 kGy at room temperature using a \(^{60}\text{Co}\) source at a dose rate of 1 kGy/hr. These were cast into films, and air dried. One set of films was leached in 1% \(\text{NH}_4\text{OH}\) overnight. The films were air dried then oven dried at 70°C for 3 hours to cure. Another set was soaked in ethanol overnight prior to leaching in \(\text{NH}_4\text{OH}\).

Proteins were isolated from the \(\text{NH}_4\text{OH}\) extracts by saturation with \((\text{NH}_4)_2\text{SO}_4\) and analyzed by sodium dodecyl sulphate - polyacrylamide gel electrophoresis (SDS-PAGE). Nitrogen content was measured using the Kjeldahl analysis. FT-IR analyses of the films were carried out using the JEOL (JIR-100D) analyzer.

Determination of the Effect of NRL Proteins on the Aging Properties of RVNRL Films

NRL was purified by centrifuging the latex at 9,500 rpm for 1 hr. The rubber phase was separated from the serum and was redispersed in 5% sodium dodecyl sulphate (SDS) for 24 hrs. This was recentrifuged, rewashed with SDS followed by \(\text{H}_2\text{O}\) before it was finally redispersed in 1% \(\text{NH}_4\text{OH}\). Concentration of the latex was readjusted to 50%.

Extracted proteins were added to purified RVNRL and cast into films. The aging properties of the films were determined by placing these in a gear oven at 70°C for 168 hrs. Tensile strength measurements were taken every 24 hrs.

RESULTS AND DISCUSSION

The aging properties of unpurified RVNRL films was compared to purified RVNRL films. Fig. 1 indicates the aging properties of purified RVNRL films as inferior to that of the unpurified films. Tensile strength retention had gone down to 78% at the end of aging test as compared to the unpurified films which still show a tensile strength retention of 90%. Kjeldahl analysis indicated a decrease in nitrogen content from 0.29% (unpurified) to 0.06%. FT-IR spectra of both films (Fig. 2 & 3) showed differences in absorbance peaks at wavenumbers 3,280 cm\(^{-1}\) and 1,540 cm\(^{-1}\). These peaks are indicative of the protein amide bonds. The absorbance at 3,280 cm\(^{-1}\) was higher for the unpurified film than the purified one. The unpurified RVNRL has an absorbance peak at 1,540 cm\(^{-1}\) which was not present in the purified film.

Differences in the aging pattern of both the unpurified and purified RVNRL film may be associated with their protein content as seen in their FT-IR and Kjeldahl analyses. The removal of the proteins during the purification process of NRL resulted in the deterioration of the aging properties of the RVNRL films.

To confirm the effect of proteins on the aging property of RVNRL, increasing volumes of NRL serum (increasing % Nitrogen) were added to purified RVNRL and their aging properties determined. Fig. 4 indicates that the serum added films were very resistant to aging. Percent tensile strength retention at 0.31%-0.73% Nitrogen were still almost 100% at the end of the aging test. The aging properties of purified RVNRL also improved with the addition of NRL proteins at lower concentration (0.19%) but not quite as much as those films at higher nitrogen concentration. Similarly, extracted proteins from NRL serum which were added to purified RVNRL, also gave the same response (Fig. 5). Percent tensile strength retention decreased only very slightly ranging from 92-99% at the end of aging test. These values are higher than the control (78%).
The aging properties of the leached and unleached films were investigated. Fig. 6 shows two different aging trends for the leached and unleached films. The films which were leached in 1% NH$_4$OH had a very sharp degradation curve. Percent tensile strength retention was reduced to 0% after 96 hours of aging. The unleached RVNRL films on the other hand, still had a tensile strength retention of 74% at the end of aging test. When the films were soaked in ethanol prior to leaching, the aging properties approximated those of the unleached films.

Results of FT-IR and Kjeldahl analyses give strong indications that the observed differences in the aging pattern of the leached and unleached RVNRL films may be associated with their protein content. Kjeldahl analyses of the RVNRL films showed a decrease in protein content from 1.82% to 1.06% after leaching. Ethanol-soaked films had protein content of 1.56% which is close to that of the unleached films. Soaking the films in ethanol before leaching somehow reduces the loss of protein by leaching.

FT-IR data are in consonance with those from the Kjeldahl analyses. The FT-IR spectra of the leached and unleached RVNRL films showed differences in absorbance peak heights at wavenumbers 3,303 cm$^{-1}$ and 1,585 cm$^{-1}$ (Fig. 7) which are characteristic of the protein absorption bonds. Films soaked in ethanol prior to leaching have slightly less absorption at 3,303 cm$^{-1}$ than the unleached films. On the other hand, the absorption peak at the same frequency is hardly discernible in leached films. Likewise, the absorption peak for 1585 cm$^{-1}$ is higher for both the unleached and ethanol soaked films. It may be deduced from the data that proteins in the RVNRL films are extracted during the process of leaching such that the resulting leached films have poor aging properties. Soaking the films in ethanol could have precipitated most of the proteins rendering them insoluble in aqueous NH$_3$. Thus, the proteins are retained in the film and the resulting films have aging properties comparable with those of the unleached films.

To confirm this effect, proteins from the NH$_3$ extracts of both the leached and ethanol-soaked films were isolated and added to purified RVNRL. As shown in Fig. 8, these proteins substantially improved the aging properties of purified RVNRL. The effect of proteins isolated from the NH$_3$ extracts of leached films is the same as that from the total NH$_3$ extract of the leached RVNRL films. Proteins isolated from the NH$_3$ extracts of ethanol-soaked films also improved the aging properties of purified RVNRL but to a much lesser degree than the former.

Proteins from the NH$_3$ extracts of both leached and ethanol-soaked films were analyzed by SDS-PAGE (12.5%). The protein hevein with a molecular weight of 13.5 Kda was found in the NH$_3$ extract of the leached film. This protein was not present in the NH$_3$ extract of ethanol soaked films (Fig. 9). Hevein is soluble in aqueous solutions, thus this protein is easily leached out in 1% NH$_4$OH. The removal of this specific protein from RVNRL may have been responsible for the poor aging property in leached RVNRL films. In as much as hevein is retained in the film when this is soaked in ethanol prior to leaching, these films exhibited good aging properties comparable with those of the unleached RVNRL films. Hevein may have a natural antioxidant property that makes the unleached RVNRL films more resistant to oxidative aging.

While it is ascertained that the NRL proteins could inhibit the thermal oxidative aging of RVNRL, it is not known whether all the NRL proteins would have the same effectivity in improving the aging properties of RVNRL. Two major proteins in NRL, $\alpha$-globulin and hevein were studied for this purpose.

The effect of $\alpha$-globulin to purified RVNRL had improved the aging properties of RVNRL as seen in Fig. 10. Likewise, a deceleration in the aging process of purified RVNRL occurred when hevein was added to it (Fig. 11). Its effectivity in controlling the aging process is greater than the other NRL proteins. Tensile strength deceleration is lesser in purified RVNRL films added with hevein than those which were added with proteins not containing the hevein. Comparing the antioxidant properties of all the proteins studied (Fig. 12), hevein was shown to be the most effective. $\alpha$-globulin and the NRL proteins without the heveins can also protect the RVNRL films against oxidative degradation but not as much as the heveins. This result is further confirmed when a minimum amount of hevein (0.05%) was added to purified RVNRL, and the % tensile strength retention was increased by 26% (Fig. 13).

The antioxidant property of hevein maybe attributed to its amino acid composition. Hevein is rich in cystine containing 16-19% of this amino acid$^{18}$. Cystine could easily be reduced to cysteine. The -SH is a free radical scavenger which could prevent the formation of chain initiating radicals that catalyzes the oxidation reaction steps.

The effect of the amino acids cystine, cysteine and methionine on the aging properties of RVNRL were investigated. Fig. 14 indicates that among the three, methionine exhibited a very good antioxidant property. Percent retention after aging is 26% as compared to the purified RVNRL (control) which has been reduced to an almost zero % retention. Cystine and cysteine on the other hand have very poor aging properties. Their aging curves are only slightly higher than that of the control. Cystine, cysteine and methionine are all S-containing amino acids that can be reduced to an -SH and which could act as good antioxidants. The data however indicated that it is only methionine that has this property. Chemical structures of these amino acids would show that cysteine and cystine have polar ends, -S, H$_2$-NH$_2$, -COOH for cysteine and two -NH$_2$ and -COOH for cystine. Methionine on the other hand has a polar end -COOH and -NH$_2$ on one end and a non-polar -CH$_3$ on the other end. This non-polar end could easily penetrate and interact with the rubber molecule, thus becoming a more effective inhibitor against its oxidative aging.
CONCLUSION

The results of this study show that Hevea proteins exert an inhibitory effect on the oxidative aging of RVNRL. Loss of proteins by leaching results in faster degradation of the RVNRL films. One of the proteins that is leached out by NH₄OH is hevein. Addition of hevein to purified RVNRL improved the aging properties of the RVNRL film. Thus, hevein serves as a natural antioxidant that inhibits the oxidative aging of RVNRL.

ACKNOWLEDGEMENT

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REFERENCES

Figure 1: The Tensile Strength Retention of Purified and Unpurified RVNRL.

Figure 2: FT-IR Analysis of the Unpurified Film
Figure 3: FT-IR Analysis of the Purified Film

Figure 4: The Effect of Serum on the Tensile Strength of RVNPL
Figure 5: The Effect of Proteins on the Tensile Strength Retention of RVNRL

Figure 6: The Effect of Leaching in 1% NH₃ on the Tensile Strength Retention of RVNRL
Figure 7: FT-IR Analysis of the Leached and Unleached RVNRL Film

Figure 8: The Effect of Protein from NH$_4$OH leacheates on the Tensile Strength Retention of RVNRL
Figure 9: SDS-PAGE (12.5%) Electrophoresis of the Protein from the NH$_4$OH Extracts (At Different Concentrations)

Figure 10: The Effect of Alpha Globulin on the Tensile Strength Retention of RVNRL
Figure 11: The Effect of the Havein on the Tensile Strength Retention of RVNRL

Figure 12: Comparison of the Effect of the Different Protein on the Ageing Properties of Purified RVNRL
Figure 13: The Effect of Hevein on the Tensile Strength Retention of RVNRL

Figure 14: The Effect of Amino Acids on the Tensile Strength Retention of RVNRL
STABILITY OF RVNRL UPON STORAGE AND THE DEGRADABILITY OF ITS FILM VULCANISATES

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ABSTRACT

The stability of RVNRL upon storage and the stability of its film vulcanisates towards various ageing conditions were investigated. Within the storage periods of up to 32 weeks employed in the studies, the properties like total solid content, dry rubber content, pH and viscosity generally did not show any significant changes. The MST values decreases with storage periods but remained greater than 1000 seconds. The mechanical properties like tensile strength decreases with storage periods. Under severe ageing conditions RVNRL film vulcanisates showed poor ageing characteristics. The use of a suitable antioxidant helped to protect the mechanical properties but tend to reduce their rates of degradation. This was shown by the results of the studies on the effect of incorporating film vulcanisates in the ground for a period of up to eight months.

INTRODUCTION

RVNRL has many advantages when compared with conventionally vulcanised natural rubber latex (Nakamura, et al., 1990; Pendle, T. D. 1993; Makuuchi et al., 1993; Wan Manshol et al., 1995 a; Wan Manshol et al., 1995 b). Among them is its ability to maintain the properties after a long storage periods. This particular advantage is useful especially when there is any requirement for its long distance shipment and when there is a need to overcome natural rubber latex shortage sometimes experience by the latex based industries especially during the wintering period.

In the previous paper (Wan Manshol, W.Z. 1995) it was described how the properties of RVNRL can contribute to an increasing demand for user-friendly and environment-friendly latex products. This paper present and discussed the results of various ageing conditions done on the samples and how the data can be made useful as further evidence to promote and strongly put the material in the lime light.

EXPERIMENTAL METHOD

High ammonia latex of known properties and maturity period was formulated in a quantity of approximately 250 kg per batch according to the method as previously described (Wan Manshol et al., 1993) The latex mixture was placed in Jerry-can containers of 25 litres capacity and irradiated with gamma rays from a Cobalt-60 source to a dose of about 12 kGy. After the irradiation stage, the latex is called RVNRL (Radiation Vulcanised Natural Rubber Latex).

Irradiation dose absorbed by the samples were measured by using ceric-cerous dosimeters. The latter were placed on the sample containers during the irradiation stage. Due to small differences in the irradiation dose absorbed by the samples, RVNRL from different containers were combined before it was stored at room temperature in 205 litres capacity metal drums for further analysis. RVNRL preparation was repeated using the same procedure but latex of different maturity periods.
i) Effect of storage on the properties of RVNRL.

Properties of the RVNRL were monitored at known intervals. These were done according to the methods as previously described. The mechanical properties of the RVNRL films vulcanisates were determined on coagulant dipped films prepared using 15% calcium nitrate in industrial grade methylated spirit plus water.

ii) Degradability of RVNRL film Vulcanisates.

The studies were carried out on RVNRL film vulcanisates. The latter were prepared by coagulant dipping method using RVNRL taken from one of the batches use in the studies on the effect of storage on its physical properties. Five sets of film vulcanisates were prepared from RVNRL added with antioxidants and a set of film vulcanisate was prepared from RVNRL without any added antioxidant. The antioxidant employed were Arbestab Z, Irganox 1010, Irganox 1520 and Ralox LC and the amount used were 1 pphr. All films vulcanisates were about 0.2 mm to 0.5 mm thick. The films were cut into dumb bell shaped test pieces according to BS 6746 and the thickness recorded. The samples were then subjected to the following conditions:

a) Accelerated ageing test in a Geer oven at 70 °C for three days and had the mechanical properties evaluated after the samples were reconditioned to the ambient temperature and pressure for 24 hours.

b) Accelerated ageing test in a Geer oven at 70 °C for seven days and had the mechanical properties evaluated after the samples were reconditioned to the ambient temperature and pressure for 24 hours.

c) Incorporated in the ground approximately a foot deep and had their mechanical properties determined at monthly intervals for a period of eight months.

d) Kept in a room at ambient temperature and normal atmospheric pressure and had their properties evaluated at monthly intervals for a period eight months.

Mechanical properties evaluations were done according to ASTM standard using a universal testing machine, Instron model 4301 at a cross head speed of 500 mm per minute.

Any differences in the tensile strengths of the samples compared to their initial values were taken as the degradation caused by the treatment described above.

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<th>Batch D</th>
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Table 2: RVNRL Properties with respect to storage time (I)

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Table 3: RVNRL Properties with respect to storage time (ii)

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<td>21.6</td>
</tr>
<tr>
<td>Modulus at 500 %</td>
<td>2.16</td>
<td>2.01</td>
<td>2.08</td>
<td>2.04</td>
<td>2.03</td>
</tr>
<tr>
<td>Modulus at 700 %</td>
<td>8.21</td>
<td>7.51</td>
<td>7.92</td>
<td>7.36</td>
<td>7.56</td>
</tr>
<tr>
<td>Elongation at break, %</td>
<td>910</td>
<td>930</td>
<td>960</td>
<td>930</td>
<td>930</td>
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</tbody>
</table>

RESULT AND DISCUSSIONS

As shown in table 1 to 3, in general there were no significant change in the physical properties of RVNRL with respect to their storage times, except for their MST readings which tends to decrease as the storage time increases. In contrast, the tensile strengths of their film vulcanisates decreases with storage times. Moreover, the decreased in the tensile strengths seems to varies between the batches of RVNRL, this is shown by the difference in the slopes of the graphs of tensile strengths versus storage times presented in Figure 1.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile Strength, MPa</th>
<th>Modulus @ 500, %</th>
<th>Modulus @ 700 %, MPa</th>
<th>Elongation @ Break, %</th>
<th>Tensile Strength, MPa</th>
<th>Modulus @ 500, %</th>
<th>Modulus @ 700 %, MPa</th>
<th>Elongation @ Break, %</th>
<th>Tensile Strength, MPa</th>
<th>Modulus @ 500, %</th>
<th>Modulus @ 700 %, MPa</th>
<th>Elongation @ Break, %</th>
<th>Tensile Strength, MPa</th>
<th>Modulus @ 500, %</th>
<th>Modulus @ 700 %, MPa</th>
<th>Elongation @ Break, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>RVNRL</td>
<td>26.2</td>
<td>2.5</td>
<td>7.7</td>
<td>950</td>
<td>3.8</td>
<td>1.2</td>
<td>3.3</td>
<td>714</td>
<td>0.5</td>
<td>24.8</td>
<td>2.3</td>
<td>7.9</td>
<td>940</td>
<td>25.8</td>
<td>2.0</td>
<td>6.1</td>
</tr>
<tr>
<td>RVNRL + Arbestab Z</td>
<td>24.1</td>
<td>2.3</td>
<td>7.8</td>
<td>930</td>
<td>30.5</td>
<td>2.4</td>
<td>8.3</td>
<td>976</td>
<td>24.8</td>
<td>2.3</td>
<td>7.9</td>
<td>940</td>
<td>25.8</td>
<td>2.0</td>
<td>6.1</td>
<td>990</td>
</tr>
<tr>
<td>RVNRL + Ralox LC</td>
<td>27.8</td>
<td>2.2</td>
<td>8.7</td>
<td>950</td>
<td>27.5</td>
<td>2.0</td>
<td>6.2</td>
<td>1070</td>
<td>17.8</td>
<td>1.8</td>
<td>4.9</td>
<td>850</td>
<td>22.7</td>
<td>2.0</td>
<td>6.1</td>
<td>990</td>
</tr>
<tr>
<td>RVNRL + Irganox 1520</td>
<td>23.5</td>
<td>2.1</td>
<td>7.3</td>
<td>950</td>
<td>25.2</td>
<td>2.1</td>
<td>7.8</td>
<td>950</td>
<td>22.7</td>
<td>2.0</td>
<td>6.1</td>
<td>990</td>
<td>25.8</td>
<td>2.1</td>
<td>6.9</td>
<td>1000</td>
</tr>
<tr>
<td>RVNRL + Irganox 1010</td>
<td>24.6</td>
<td>2.2</td>
<td>7.7</td>
<td>950</td>
<td>27.3</td>
<td>2.3</td>
<td>8.2</td>
<td>970</td>
<td>25.8</td>
<td>2.1</td>
<td>6.9</td>
<td>1000</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

Table 4: Tensile Strengths of Film Samples after Ageing 3 and 7 days at Geer Oven at 70°C
Assuming the steeper the slope the greater were the changes in the tensile strength with respect to the storage times, the RVNRL prepared using latex of two, three and seven weeks maturity seems to show more significant dropped in their tensile strength of their film vulcanisates compared to those samples taken from the RVNRL prepared from the same batch of latex but of five and six weeks maturity periods.

From the results there is a strong suggestion that the maturity of the latex used in RVNRL preparation may influence the mechanical properties like the tensile strength of its film vulcanisate. Within the storage time employed in this study, RVNRL may be stored up to about six months. Within the storage period the latex was found to retain all the properties which make it useful for the production of dipped goods like examination glove and surgical glove.

The result of accelerated ageing test carried out on RVNRL films vulcanisates contained added antioxidant and without antioxidant are presented in table 4. As shown in table 4 the ageing properties of RVNRL film vulcanisates subjected to accelerated ageing test at 70°C were determined to be very poor. It could be improved by addition of suitable antioxidants. Among the antioxidant used in this study, except for Ralox LC, others were found effective and managed to retain the tensile strengths of the leached samples to an acceptable values.

Table 5 and 6 summarises the tensile strength of film samples kept at the room temperature and the tensile strength of film samples incorporated in the ground respectively. Graphical representations of the results are given in Figures 2 to Figure 6. As shown in Figures 2 to 6, under both circumstances, the tensile strengths initially increased with time before start to decreased again. In this study, any decrease in tensile strengths of film samples kept at room temperature are assumed to be an effect of oxidative degradation, and the decrease in tensile strengths of the film samples incorporated in the ground are assumed to be an effect of biodegradation. Based on the slopes of the graphs, under both circumstances films samples with no added anti oxidant seems to degrade faster than those film samples contained added anti oxidants. Hence, the rate of samples degradations may be reduced by an addition of a suitable antioxidant. Moreover, it is also observed that the effectiveness of an antioxidant in protecting a sample from degradation was influenced by the conditions surrounding the samples. For example, the samples added with an anti oxidant Ralox LC seems to be able to retain their tensile strength at high value under both circumstances, whether the samples were kept at room temperature or incorporated in the ground. In contrast, the samples added with an antioxidant Irganox 1520 were found to have lost only a small percentage of their tensile strengths when kept at room temperature even up to 240 days, but were fast to degrade once in the ground.

Figure 2 shows that RVNRL film samples contained no added antioxidant were fast to degrade when incorporated in the ground under normal conditions. The samples were almost fully degrade after about 240 days. For comparison results of similar treatment done on commercially available medium modulus sulphur vulcanised film vulcanizate is given in figure 7. The test method employed is not a standard method. However, the data obtained can be made useful especially in making a rough estimation of how long it may take for a product made from RVNRL to degrade should it being thrown on the ground and how RVNRL applications in producing latex dipped goods like surgical glove, examination glove, balloon may contribute to solve the those problems related to environmental pollution.

Theoretically, treating films samples at 70°C for seven days is equivalent to keeping the samples at room temperature for six months. Therefore the decrease in tensile strength of the samples kept for six month at the room temperature should be similar to the decrease in tensile strengths of samples subjected to accelerated ageing test at 70°C for seven days. However, the results obtained were not in agreement with the theory. From the results of the accelerated ageing test given in Table 4, it is learned that adding a suitable anti oxidant to RVNRL is a prerequisite otherwise products made from RVNRL will easily degrade and may not be kept even up to six months under normal storage conditions. In contrast, the results shown in Table 5 and Figure 2 indicate that within a period of about seven month the change in the tensile strengths of the RVNRL film samples kept at room temperature were only about ± 10% of the initial value. In fact as shown in the same table, at any fixed time within the period employed in the study, the tensile strengths of the film samples contained no added antioxidant were similar to the tensile strengths of the films samples contained added antioxidant.
### Table 5: Tensile Strengths of Film Samples Kept at Room Temperature up to 240 Days

<table>
<thead>
<tr>
<th>Sample</th>
<th>Storage time, days</th>
<th>Tensile Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>30</td>
</tr>
<tr>
<td>RVNRL</td>
<td>26.2</td>
<td>27.5</td>
</tr>
<tr>
<td>RVNRL + Arbestab Z</td>
<td>24.1</td>
<td>27.4</td>
</tr>
<tr>
<td>RVNRL + Ralox LC</td>
<td>27.8</td>
<td>31.2</td>
</tr>
<tr>
<td>RVNRL + Irganox 1520</td>
<td>23.5</td>
<td>26.8</td>
</tr>
<tr>
<td>RVNRL + Irganox 1010</td>
<td>24.6</td>
<td>27.5</td>
</tr>
</tbody>
</table>

### Table 6: Tensile Strengths of Film Samples Incorporated in the Ground up to 240 days

<table>
<thead>
<tr>
<th>Sample</th>
<th>Storage time, days</th>
<th>Tensile Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>30</td>
</tr>
<tr>
<td>RVNRL</td>
<td>26.2</td>
<td>29.3</td>
</tr>
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<td>RVNRL + Arbestab Z</td>
<td>24.1</td>
<td>30.0</td>
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<tr>
<td>RVNRL + Ralox LC</td>
<td>27.8</td>
<td>29.6</td>
</tr>
<tr>
<td>RVNRL + Irganox 1520</td>
<td>23.5</td>
<td>26.7</td>
</tr>
<tr>
<td>RVNRL + Irganox 1010</td>
<td>24.6</td>
<td>27.5</td>
</tr>
</tbody>
</table>

### Figure 1: Graphs of tensile strength versus storage time of RVNRL prepared using latex of different maturity
Figure 2: Graphs of tensile strength versus time for RVNRL film vulcanisates without added antioxidant kept at room temperature and incorporated in the ground.

Figure 3: Graphs of tensile strength versus time for RVNRL film vulcanisates added with 1 phr of an antioxidant Arbestab Z, kept at room temperature and incorporated in the ground.
Figure 4: Graphs of tensile strength versus time for RVNRL film vulcanisates added with 1 phr of an antioxidant RALOX LC, kept at room temperature and incorporated in the ground.

Figure 5: Graphs of tensile strength versus time for RVNRL film vulcanisates added with 1 phr of an antioxidant IRGANOX 1520, kept at room temperature and incorporated in the ground.
Figure 6: Graphs of tensile strength versus time for RVNRL film vulcanisates added with 1 phr of an antioxidant IRGANOX 1010 kept at room temperature and incorporated in the ground.

Figure 7: Graphs of tensile strength versus time for film vulcanisate of medium PVMM without added an antioxidant incorporated in the ground.
CONCLUSIONS

Within the limit of the experimental errors and the storage times employed in this study, RVNRL prepared using latex of a suitable maturity period may be stored up to six month in a normal storage conditions at room temperature without any addition of antioxidant. RVNRL film samples contained no added antioxidant are fast to degrade when expose to the normal ground conditions. The samples are almost fully degrade after 240 days.

RVNRL film samples contained no added antioxidant may be kept at room temperature up to six months and no serious deterioration to the tensile strength were observed. Adding a suitable antioxidant to RVNRL helps to improve the shelf life of its film samples and hence any products made from it.

ACKNOWLEDGEMENTS

The authors are grateful to their coworkers in Rubber Processing Group in MINT for their excellent effort in making this project a success. The authors are also grateful to the Malaysian Government for providing generous fund for this project under the programme Intensification of Research in Priority Areas.

REFERENCE


Wan Manshol W. Z., Norjanah, M. and Meor Yahaya,
QUESTIONS & ANSWERS, and COMMENTS

Session V

C1 J. Anand

There are advantageous reasons why proteins are present in NR latex. There is technology available to reduce extractable proteins whilst keeping the proteins in the latex films.

Q2 Yaziz

Is the coating technique compatible in the production of powderless latex products?

A2 Chantara T. Ratnam

Coating compounds comprising 80% HEMA and 20% acrylic acid are compatible with RVNRL.

Makuuchi

A low-cost self-shielding electron beam machine that costs an equivalent of 2 centrifuge machines is suitable for hydrogel coating of RVNRL films.

Q3

How was the tackiness of films determined?

A3 Chantara T. Ratnam

The tackiness of the films was determined using a Rascatackiness meter.

Q4

Is there any separation between the hydrogel coating and the rubber film?

A4 Chantara T. Ratnam

There was no peeling off observed when using the HEMA acrylic acid in the 80/20 weight ratio.
Malaysia

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<th>Contact</th>
<th>Fax</th>
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