8th ARAB INTERNATIONAL CONFERENCE ON
POLYMER SCIENCE & TECHNOLOGY
27 – 30 November 2005, Cairo-Sharm El-Shiekh, EGYPT

Development of radiation curable surface coating based on soybean oil.
Part II. Evaluation of the prepared acrylated resin as surface coatings by using EB or UV sources for radiation curing applications.

M. S. Ibrahim, N.G. Kandile*, Hossam M. Said and I. M. Moussa

National Center for Radiation Research and Technology (NCRRT). Naser City, Egypt, *Women College for Arts, Science, Education Ain Shams University

Abstract

In recent years, there has been a growing trend in using vegetable oils as raw materials in acrylation production that can be cured by UV/EB systems. The acrylated resin formulates by using individually different functional acrylate monomers were prepared and cured by EB or UV sources.

The characterization properties of the cured films were investigated in terms of pendulum hardness, bending, impact, gloss, adhesion and chemical tests. Other formulations were prepared by mixing a constant ratio of different functional acrylate monomers and exposed to UV or EB irradiation. The results showed that the hardness of cured films were increased by increasing the functionality of monomers with excellent adhesion for all formulations but at expense of other properties involving bending and impact tests. Therefore, it can be deduce that the hardness of the curing surface coating by using EB was found to be nearly twice the hardness of the curing surface coating by using UV irradiation. Also, the best formulations which have given good chemical and mechanical properties are (mono-di) functional acrylate monomer resin under EB and (mono-tri) functional acrylate monomer resin under UV irradiation.

Introduction

Radiation curable formulations are essentially solvent free [1,2]. It is found that in order to overcome problems associated with viscosity reduction

of the formulation needed for application purposes, monomers; especially the multifunctional acrylates are useful. The presence of such monomers also influences the degree of cross-linking and the speed of cure in finishing process. The mixtures of unsaturated oligomers and vinyl monomers form the basis for curable formulations; more rarely, mixtures of different oligomers are used. The unsaturated oligomers are generally oligoesters and their acrylates, polyether acrylates, polyurethane acrylates, epoxy acrylates and acrylates of silicon compounds [3]. The base of the formulation of radiation curing on wood surfaces is the oligoester that formed by polycondensation of phthalic and maleic anhydrides and ethylene glycol [4].

The characterization of coating film EB cured by the modified acrylic resin from vegetable oil with high degree of unsaturation level was studied. The new type of EB curable acrylic resin is possessed of pretty characteristics of coating film. It is especially fit for timber surface coatings[5] . The epoxidized palm oil (EPO) can be cured with ultraviolet (UV) radiation using either radical, cationic or hybrid initiation. Cationic curing system has been chosen in this study due to the fact that epoxy groups present in EPO can be utilized directly to form crosslinks [6]. A different formulations of epoxy acrylate oligomer in the presence of *N*-vinylpyrrolidone and trimethylol propane triacrylate and exposed to EB irradiation was prepared. These formulated solutions were coated on a low-grade wood substrate and cured under UV light. Both UV-cured thin films and surface coatings were characterized, and the best formulations for coating wood surface were evaluated [7].

In the present work, acrylated resins were crosslinked by using different functionality of acrylate monomers to form coating films, which curable by using accelerated electron or ultraviolet radiation sources.

Materials, methods and techniques

-Epoxy soybean oil acrylate (ESOLA) was prepared

-Benzophenone and Triethylamine - Pure (99%), are supplied by Prolabo (France).

- Butyl acrylate, 1,6 Hexanediol diacrylate and Trimethylol propane triacrylate (TMPTA) monomers are supplied by Merck Co. 99% , Germany.

Methods and Techniques

-Determination of Percentage Gel Fractions

Samples of the prepared cured films were accurately weighted (W_o) and then extracted with distilled water using Soxhlet system for 3 hours. After extraction, the samples were then removed and dried in a vacuum oven at 80^{o}C to a constant weight (W_1). The soluble fraction was calculated according to the following equation.

Sol. fraction (%) = $[(W_o-W_1) / W_o] \times 100$

Gel fraction (%) = 100- Sol. fraction (%)

- Measurements of Film Hardness : The film hardness was measured by the standard König Rocker Pendulum Hardness **(DIN 531 57)**

-Bending Test : A mandrel of the diameter rang (2-32mm) was used according to **ASTM D 1737 –73**

-Impact Resistance [(8)] : In this work, the round nose steel rod was raised to maximum distance at 120 on the scale i.e., at 3 feet and the distance at which a fracture occurred was recorded.

-Measurements of Gloss : Gloss of cured films was measured according to **ASTM D 523** using NOVO-GLOSS (60^o glossmeter).

-Measurement of Cured Film Adhesion : The apparatus was manufactured by Paul N. Gardner company, INC, Florida, USA

-Automatic Scratch Test : This machine determines the scratch resistance of paint coatings. The machine operate on a 110 volt, 60 Hz Ac, complete set of weight from 100 – 2000 grams, one 1mm tungsten carbide tipped needle supply.

-Alkali Resistance Test : Alkali test was examined according to ASTM D 1647-70.

- Acid Resistance Test : Acid test was examined according to ASTM B 287 -74.

-Electron Beam Irradiation: (Energy 1.5 Mev, Power 37.5 Kw, Beam current 25 mA).

-UV Irradiation:180 w mercury lamp, 220v, 50 Hz (λ=254 nm). Irradiation of samples were carried out using EB or UV at the National Center for Radiation Research and Technology, NCRRT, Naser City, Cairo, Egypt.

Results and Discussion

1- Evaluation of the Prepared Acrylated Resin as Surface Coatings by Using Electron Beam or Ultraviolet sources for Radiation Curing Applications.

There are so many formulations have been found in the literature for those coatings cured by EB or UV. Among of these, sixty percent oligomer and forty percent different functionality of acrylate monomers such as butyl acrylate **BA** (mono-functional) or 1, 6 hexanediol diacrylate HDDA (di-functional) or trimethylol propane triacrylate **TMPTA** (tri-functional) or mixture of different monomers such as mono-di or mono-tri functional acrylate monomers [9, 10, 11].The chosen formula in the present part was 60 % acrylate resin + 40% di-functional acrylate monomer. It was applied on glass, tin and wood substrates and their physico-chemical and mechanical properties of cured films were studied.

This part contains two groups, the first includes the effect of different doses of EB accelerator on acrylate resin formulations while in the second includes the effect of time interval of UV source on acrylate resin formulations. In this regard, several experiments were performed to find out the suitable irradiation dose on curing of acrylate resin formulations by adding di-functional acrylate monomer which acts as solvent and crosslinkable.

1.1 Effect of Irradiation Dose on Curing of the Prepared Coating by Using Electron Beam (EB) Accelerator.

All films of this series were made by using film applicator to give uniform film with thickness (90μm) on glass panels and tin metal substrate.

These films were cured by using EB source at different irradiation doses. The physico-mechanical properties of the cured films were measured to select the optimum curing dose. The obtained results are represented graphically in figure (1). It can be seen from this figure that, the hardness increases gradually until 35 kGy is reached, beyond this dose the hardness increases sharply up to 70 kGy. Further increase in irradiation doses are found to be of no effect. All coating films of this series have excellent appearance and they are colorless, but the impact and bending properties of the films which are exposed to irradiation dose over than 50 kGy, are not good enough due to the increase of hardness of the films (i.e. over cure have been done). The above results leads to the conclusion that the irradiation dose 50 kGy is the optimum dose, thus, it was chosen to cure the films of the next studies.

1.2 Effect of Irradiation Time on Curing of the Prepared Coating by Using Ultraviolet Light.

The same experiments were carried out to study the effect of irradiation time of UV curable source. Hardness, impact and bending tests were taken into consideration to find out the test curing time. The composition of coating formulation was 55 % acrylate resin + 40 % of difunctional monomer + 5 % benzophenone as initiator.

The obtained results of time interval against hardness are represented graphically in figure (2). It can be seen that, the hardness increases gradually until (10 min.) and sharply from 10 min to 30 min, after which the increase in hardness can be neglected. On the basis of the previously obtained results the suitable irradiation time is 30 min. to produce the films of good hardness.

2. Effect of Functionality of Some Monomers on the Coating Formulation Cured By EB Radiation.

All films of this series were coated on the glass, tin, carbon steel and wood panel and cured at 50 kGy by using EB radiation, also, different functionality of monomers were used as solvent and crosslinkable. The compositions of the acrylate formulations and the physico-mechanical and chemical properties are given in table (1) and represented graphically in

figure (3). From the previous results, it can be seen that, the increase the functionality in the cured formulations (the higher the number of acrylate double bonds) is available to produce high yield of radicals during irradiation [12, 13] that increase the crosslinking to make hard films. This behavior may be affiliated with the increasing the gel fraction percent. From table (1), it is interesting to notice that the chemical resistance increases with the increase of functionality of acrylate monomers in the formulation. Also, all films were passed the bending and impact tests. These results clearly indicate that the flexibility increases with decease the functionality as predicted. This behavior is due to the increase of crosslinking process which make the films harder. These results are in good agreement with the decreasing of the gel fraction for different series formulations. Moreover, it can be seen that all the formulations passed the adhesion test to the value (Gt_0) and also, they have very gloss on both wood and metal substrate.

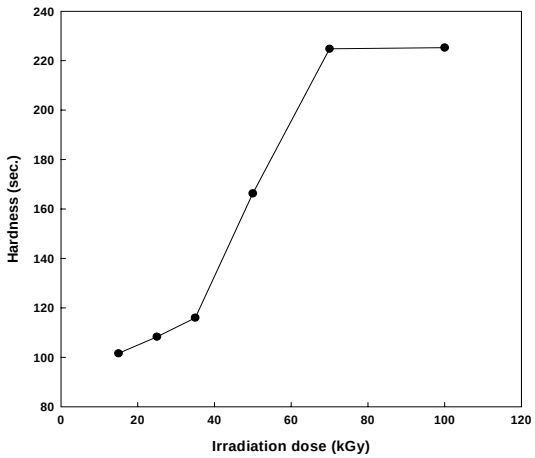

Figure (1): Effect of electron beam irradiation doses on the hardness of cured

films for di-functional acrylate monomer formulations.

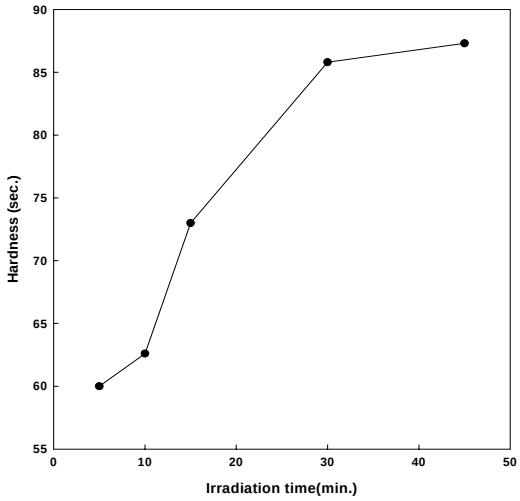

Figure (2): Effect of ultraviolet irradiation times on the hardness of cured films for di-functional acrylate monomer formulations.

2.1 Effect of Mixed Monomers on the Coating Formulations Cured By EB Radiation

The composition of different formulations were prepared by using equal ratios of different monomers as shown in table (2). From this table, it can be seen from this table that, all formulations were passed impact, bending and adhesion tests. Also all films were excellent in appearance, colorless, glossy and they have good chemical resistance (alkali, acid and alcohol media) without considerable defects. Also, the scratch tests for these formulations could not pass scratch test over 1500 gm as a result of increasing the hardness.

Generally, formula (I) has improved bending and impact properties but at the expense of the pendulum hardness. This behavior may be affiliated

with the increase the functionality, the increase the hardness that makes the films brittle.

3. Effect of Functionality of Different Monomers on the Coating Formulation Cured by UV Source.

The composition of the formulations and the physico-mechanical and chemical properties can be shown in tables (3-5). The mentioned table show the effect of a single photointiator (BP) and combination of BP and catalyst (TEA) on the properties of the prepared resins. Also, it can be seen from these tables that the hardness of the prepared films goes inversely with the catalyst concentration. This may be due to the formation of a complex compound between BP and TEA catalyst to generate reactive free radicals that initiate the polymerization of this system. On the other hand, single BP imparts the free radical formation directly that initiates polymerization reaction rapidly. Therefore the formula (I) have good hardness, gel fraction, adhesion and chemical tests than the other formulations. Also, it is found that, all films of different formulations passed the impact and bending tests due to low degree of functionality, which produce low degree of crosslinking density and make the cured films more elastic. Moreover, all films are glossy and have good adhesion on wood and metal substrates. All the prepared films passed alkali, acid and alcohol media tests without considerable defects.

Table (1): Formulations of resin using different monomers and some chemical and mechanical properties under EB irradiation.

Formulations / Properties	Mono-functional resin	Di-functional resin	Tri-functional resin
Acrylate resin, (%)	60	60	60
Monomers, (%)	40	40	40
Dose, (kGy)	50	50	50
P. Hardness, (sec)	80	166.5	172
P. Hardness, (%)	44.5	92.5	95.5
Gel fraction,(%)	97.46	98.5	99.6

Impact test, (inch)	Pass up to 30	Pass up to 10	Pass up to 10
Bending test	Pass at 3 mm	Pass at 5 mm	Pass at 5 mm
Gloss test (W, M)	(80,103)	(80,103)	(80,103)
Adhesiontest(W,M)	Gt_0	Gt_0	Gt_0
Chemical test - HCl, 5% - NaOH, 5% -Ethanol, 95%	 V.good V.good V.good	 V.good V.good V.good	 V.good V.good V.good

Table (2): Formulations of resin using mixed monomers and some chemical and mechanical properties under EB irradiation.

Formulations / Properties	Formula (I) mono, di-functional acrylate resin	Formula (II) mono, tri-functional acrylate resin
Acrylate resin, (%)	60	60
Monomer, (%)-BA -HDDA -TMPTA	20 20	20 20
Dose, (kGy)	50	50
P. Hardness, (sec)	108	136.6
P. Hardness, (%)	60	75.8
Gel fraction, (%)	98.03	98.7
Impact test, (inch)	Pass up to 20	Pass up to 10
Bending test	Pass at 3 mm	Pass at 4 mm
Gloss test (W, M)	(80, 103)	(80, 103)
Scratch test	Pass up to 1500 gm	Pass up to 1500 gm
Adhesion test (W, M)	Gt_0	Gt_0
Chemical test - HCl, 5% - NaOH, 5% -Ethanol, 95%	 V.good V.good V.good	 V.good V.good V.good

Also from the previous Tables (3→5), it is reasonable to suggest that, the relationship between the hardness at different functionality acrylate monomer formulations compositions cured by UV source at 30 min. It is interesting to represent this relation as shown in Fig. (4). We conclude that the hardness of the coating films increases by increasing the functionality of the acrylate monomer. On the other hand, benzophenone imparts higher pendulum hardness and gel fraction to get the best formulation.

A comparison between the hardness of different formulations cured by electron beam at 50 kGy and the optimum formulation (5% BP, 0% catalyst) cured by UV irradiation at 30 min. can be shown in Fig. (5), which shows that the hardness of these formulations increases with increasing the functionality for both EB and UV irradiation. Also the hardness of the prepared films cured by EB was found to be nearly twice the hardness of the same films cured by UV for mono-functional acrylate formulations and di-functional acrylate formulations. This is may be due to EB radiation impart higher energy than UV radiation. This behavior are not seen with tri-functional acrylate formulation taking into consideration that the increasing the functionality increases the hardness of the films but at the expense of other properties such as bending and impact tests.

3.1. Effect of Mixed Monomers on the Coating Formulations Cured by UV Radiation

At the end of this work, it is very interesting to study the behaviour of monomer blends on the properties of the final products under UV irradiation. Thus, two formulations have been done. All the formulations, composition and physico-mechanical and chemical properties are given in table (6). From this table, it was found that, formula (I) and (II) was excellent as surface coating formulations but formula (II) may be better due to the higher value of pendulum hardness and gel fraction. On the other hand, the results obtained from Tables (2, 6) are represented graphically in Fig. (6). This figure shows a comparison between the hardness of the mixed functional acrylate monomer formulations cured by EB at 50 kGy and the optimum formulation (5%BP, 0% TEA) cured by UV irradiation at 30 min. From Fig. (6), it can be deduce that the hardness increases with the increase of functionality for EB or UV irradiation. The pendulum hardness of the (mono-di)-functional acrylate monomer films cured by using UV and EB

Table (3): Formulations of resin using mono-functional acrylate monomer and some chemical and mechanical properties under UV irradiation.

Formulations / Properties	Formula (I)	Formula (II)	Formula (III)
Acrylate resin, (%)	55	55	55
Monomer, (%), BA	40	40	40

Initiator, % (BP)	5	3	1
Catalyst, % (TEA)	0	2	4
Irradiation time, min	30	30	30
P.Hardness, (sec)	40.3	33.2	25
P.Hardness, (%)	22.4	18.4	13.8
Gel fraction, (%)	94.6	94.2	93.6
Impact test, (inch)	Pass up to 60	Pass up to 60	Pass up to 60
Bending test	Pass at 2 mm	Pass at 2 mm	Pass at 2 mm
Gloss test (W, M)	(80, 103)	(80, 103)	(80, 103)
Adhesion test -Wood Plate -Metal Plate	 Gt_2 Gt_2	 Gt_3 Gt_3	 Gt_3 Gt_3
Chemical test - HCl, 5% - NaOH, 5% -Ethanol, 95%	 V.good V.good V.good	 V.good V.good V.good	 V.good V.good V.good

Table (4): Formulations of resin using di-functional acrylate monomer and some chemical and mechanical properties under UV irradiation.

formulations / Properties	Formula (I)	Formula (II)	Formula (III)
Acrylate resin, (%)	55	55	55
Monomer, (%) HDDA	40	40	40
Initiator, % (BP)	5	3	1
Catalyst, % (TEA)	0	2	4
Irradiation time, min	30	30	30
P. Hardness, (sec)	85.5	61	56.3
P. Hardness, (%)	47.5	34	31.3
Gel fraction, (%)	96.9	96.7	94.5
Impact test, (inch)	Pass up to 20	Pass up to 20	Pass up to 20
Bending test	Pass at 3 mm	Pass at 3 mm	Pass at 3 mm
Gloss test (W, M)	(80, 103)	(80, 103)	(80, 103)
Adhesion test -Wood Plate -Metal Plate	 Gt_0 Gt_0	 Gt_1 Gt_1	 Gt_1 Gt_1
Chemical test - HCl, 5% - NaOH, 5% -Ethanol, 95%	 V.good V.good V.good	 V.good V.good V.good	 V.good V.good V.good

Table (5): Formulations of resin using tri-functional acrylate monomer and some chemical and mechanical properties under UV irradiation.

formulations / Properties	Formula (I)	Formula (II)	Formula (III)
Acrylate resin, (%)	55	55	55
Monomer, (%) TMPTA	40	40	40
Initiator, % (BP)	5	3	1
Catalyst, % (TEA)	0	2	4
Irradiation time, min	30	30	30
P. Hardness, (sec)	110	101	88
P. Hardness, (%)	61.1	56.1	48.7
Gel fraction, (%)	97.37	96.9	95.5
Impact test, (inch)	Pass up to 10	Pass up to 10	Pass up to 10
Bending test	Pass at 5 mm	Pass at 5 mm	Pass at 5 mm
Gloss test (W, M)	(80, 103)	(80, 103)	(80, 103)
Adhesion test -Wood Plate -Metal Plate	 Gt_0 Gt_0	 Gt_1 Gt_1	 Gt_1 Gt_1
Chemical test - HCl, 5% - NaOH, 5% -Ethanol, 95%	 V.good V.good V.good	 V.good V.good V.good	 V.good V.good V.good

Table (6): Formulations of resin using mixed monomers and some chemical and mechanical properties under UV irradiation.

Formulations / Properties	Formula (I)	Formula (II)
Acrylate resin, (%)	55	55
Monomer, (%)-BA -HDDA -TMPTA	20 20	20 20
Initiator, % (BP)	5	5
Catalyst, % (TEA)	0	0
Irradiation time, min	30	30
P. Hardness, sec	58	85.5
P. Hardness, (%)	32.2	47.5
Gel fraction, (%)	94.7	96.8
Impact test, (inch)	Pass up to 30	Pass up to 20
Bending test	Pass at 2 mm	Pass at 2 mm
Gloss test (W, M)	(80, 103)	(80, 103)
Scratch test	Pass up to 1300gm	Pass up to 1400gm
Adhesion test (W, M)	Gt_1	Gt_1
Chemical test - HCl, 5%	 V.good	 V.good

- NaOH, 5%	V.good	V.good
- Ethanol, 95%	V.good	V.good

sources were 58, 108 respectively while the hardness of the (mono-tri)-functional acrylate monomer films cured by using UV and EB sources were 85,136.6 respectively.

Therefore, it can be deduce that the hardness of the cured films using EB was found to be nearly twice the hardness of the cured films by using UV irradiation due to the EB accelerator has high energy and more efficient than UV light. From the previous study, it can be conclude that it is preferable to cure the films by EB source in case of high hardness, and by UV source in case of better elasticity.

From the previous study, it may be conclude that, the polyfunctional acrylates as TMPTA produce the most rapid curing but have several drawbacks if used alone: poorer solvent power for oligomers, inferior viscosity lowering ability, a tendency to leave high residual unsaturation in the final product with its associated instability, and a tendency toward excessive crosslink density in the product than mono-functional acrylate monomer. On the other hand, the mono-functional monomer as BA has beneficial effect on the viscosity, flexibility and adhesion, but reacts more slowly. Often the best compromise is secured by blends containing several monomer types in formulations[14,15]**.** Based on the previous results and investigation, it may be conclude that the best formulations which have good chemical and mechanical properties are (mono-di) functional acrylate monomer cured by EB radiation and (mono- tri) - functional acrylate monomer cured UV radiation.

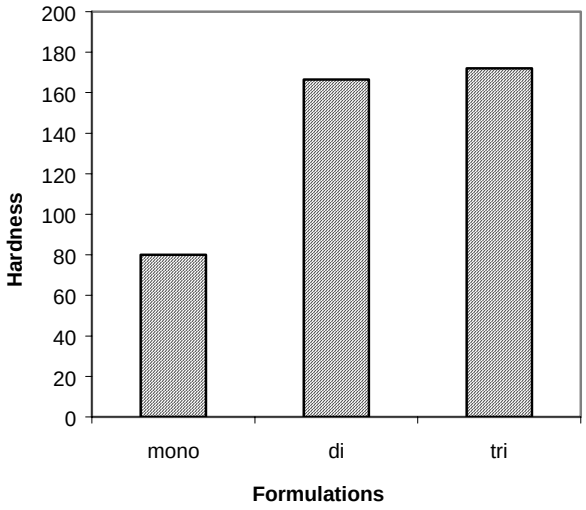

Figure (3): Hardness of cured films with different functional acrylate monomer formulations at 50 kGy of electron beam irradiation

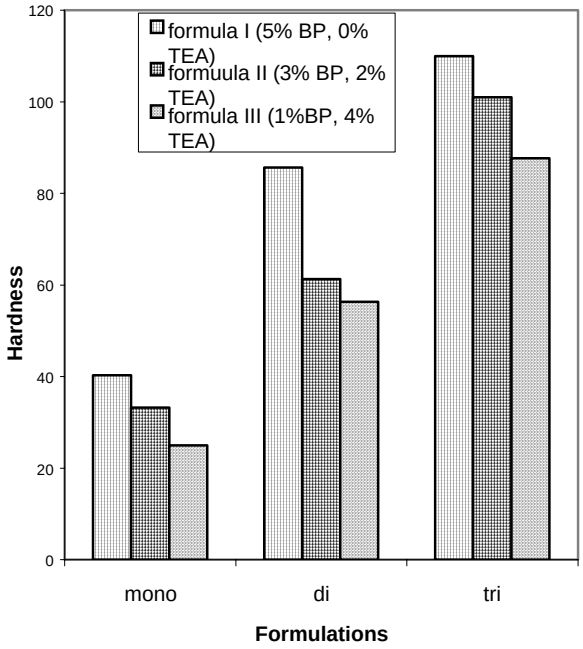

Figure (4): Hardness of cured films with different functional acrylate monomer formulations under UV irradiation at 30 min.

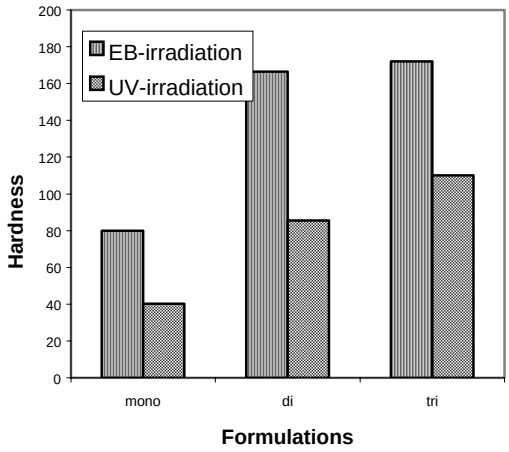

Figure (5): Comparison between the hardness of different functional acrylate monomer formulations cured by EB irradiation at 50 KGy and the optimum formulations cured by UV irradiation at 30min.

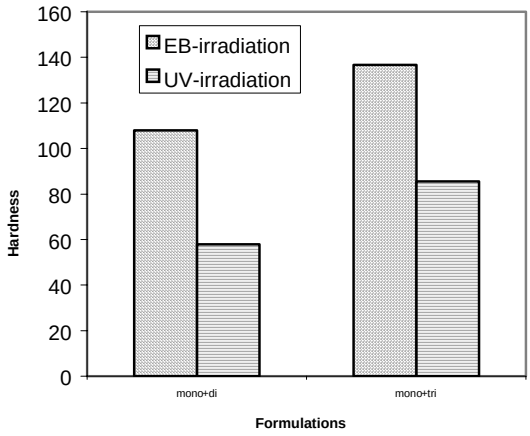

Figure (6): Hardness of cured films mixed with different functional acrylate monomer formulations at 50 kGy of electron beam and UV irradiation at 30min.

References

1. Garnett, J.L., J. Oil Col.Chem.Assoc., 65, 383 (1982)
2. Senich, G.A., and Florin, R.E., Rev. Marcomol.Chem. Phys., 24 (2), 234 (1984).
3. Czvikovzky, T., Radiat. Phys. and Chem., 26, 547 (1985).
4. Ukachi, T., Hega, K., and Matsumura, Y., Radiat. Phys. and Chem., 33, 437 (1989).
5. Jinshan, W., Min, Y., Ruiya, W., Jun, L., and Hongfei, H., Radtech Asia'95 Radiation Curing conference proceedings, Guilin (china), 568 P. P. 227-231 (1995).
6. Wan Rosli, W. D., Kumar, R. N., Mek Zah, S., and Hilmi, M.M., European polymer journal, 39(3), 593 (2003).
7. Idriss, K. M., Mubarak, A.K., Mokhlesur, R., and Mahmuda, G., J. Appl. Poly. Sci., 66 (10), 1997 (1998).
8. Gardner, A., and Sward, G., Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colours, 12th. Edition, Gardner laboratory, INC. Bethesda 14, Maryland U.S.A., (1962).
9. Perry, D.D., Rowe, W., Cirignano, A., and Davis, D.S., "Ultraviolet Light Induced Reactions in Polymers," Ed., Acs.Symp.ser. 25, Am.Chem.Soc., Washington, DC, p.150, (1976).
10. Bayer, W.G., (A Review of UV Curing Tech," Pap. Synth. Conf. (Proc.) of TAPPI, 167 (1978).
11. Prane, J.W., Polym.News, 5 (1), 36 (1978).
12. Nethsinghe, L.P., and Gilbert, M., Polymer, 29, 1935 (1988).
13. Salmon, W.A., and Loan, L.D., J. Appl. poly. Sci., 16, 671 (1972).
14. Jacobi, G.M., Verfkroniek, 50, 75 (1977).
15. Younger, J.R., J .Oil Col. Chem. Assoc., 57, 197 (1976).