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A Comparative Study of Ultraviolet and Electron Beam Irradiation on Acrylate Coatings

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RADIATION curing is the polymerization of a chemical system which is initiated by ultraviolet (UV) or electron beam (EB) irradiation. The curing, the transformation from a liquid into a non-tacky solid, is very fast and occurs in less than one second. In this work, the optimum irradiation time on curing urethane acrylate coating by using UV and the best cured dose by using EB irradiation was studied. Coating formulations were prepared by physical mixing of aliphatic urethane acrylate (AUA) and tripropylene glycol diacrylate (TPGDA) at different ratio (60:40), (70:30), and (80:20) to choose the optimum concentration. Cured coating films were characterized by Fourier transform spectroscopy (FTIR), and swelling properties. The wood surface that cured by UV or EB were tested for their end use performance properties like pencil hardness, adhesion, bending, chemical resistance, steam resistance, stain resistance, and cigarette burn resistance test. superior results and excellent mechanical performance of acrylate films on the surface of wood induced by EB were found compared with those induced by UV irradiation.

Keywords: Ultraviolet irradiation, Electron beam, Acrylate coatings, Wood surface

Introduction

Acrylic coatings are among the most broadly used ones in various industrial applications [1]. Polyurethane is considered as an important part in many industries due to their widely mechanical properties and its ability to be easily machined [2-5].

Polyurethane acrylate is a type of UV curable prepolymer with excellent properties such as excellent flexibility, low temperature resistance, good weatherability, and optical property [6]. Polyurethane acrylate coatings combine high toughness with elasticity. However, some difficulties in application of urethane acrylate resins were found due to relatively high viscosity. hydrogen bridges between functional urethane groups are the main reason of high viscosity and superior mechanical properties.

In recent years UV curing coatings have developed rapidly because of their excellent economic benefits and environmental performance [7]. Many reports are available in the literature on radiation cured coating including UV and EB curing [8- 11]. The EB-induced free radical polymerization of acrylic monomers is considered to follow the same reaction scheme as for UV-induced polymerization. The main difference between the two initiation (UV and EB) processes lies in the energy deposition and the pathway for free radical generation [12]. The UV-curing technique is based on the polymerization of a multifunctional system induced by an incident UV radiation to obtain a three-dimensional network. UV-curing technique represents a major improvement in the development of the coating, adhesive and ink industries [13]. UV-curing provides many advantages such as drying, broad formulating range, reduced energy consumption, coating of heat sensitive substrate, high curing rate and capital principal for curing equipment [14, 15]. The wide expansion interest for UV systems can be explained by several reasons such as their rapid polymerization, which can be controlled by light intensity, and their very

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low energy Consumption. Polymers cured by UV light usually exhibit properties such as mechanical, chemical and heat resistance because of their higher cross-linking density [16]. Unfortunately, the use of EB curing is more limited because of higher complexity and investment cost. Major advantages of the EB curing processes are as follows: a solvent free system, less energy consummative, a much higher production rate, and a processing ability at ambient temperature. Electron beam radiation is better than UV radiation in terms of efficiency and throughput. The aim of this work is to compare between PU coatings cured by UV and EB-irradiation on different substrates and their evaluation by different measurements like hardness, adhesion, chemical (acid and alkali) resistance, and bending.

Material and Experimental

Material

Ebcryl 284 is an aliphatic urethane diacrylate oligomer diluted with 12% of 1, 6 hexanediol diacrylate monomer. It was delivered from Cytec Surface Specialties, Drogenbos, Belgium.

Tripropylene glycol diacrylate (TPGDA) was a monomer difunctional and with a branched alkyl polyether backbone. The molecular weight of TPGDA was 300.4g/mol. Polymerization occurs when TPGDA was exposed to sources of free radicals. It was delivered from Cytec Surface Specialties, Drogenbos, Belgium

Benzophenone (bp) was used as a photo initiator in UV-curing applications. The molecular weight was 182.22g/mol. It was delivered from Sigma-Aldrich from Egypt.

Measurements and experimental techniques

Preparation of polyurethane acrylate

The mixtures of polyurethane, 3% photo initiator (benzophenone) and tripropylene glycol diacrylate (TPGDA) as reactive diluent were heated slightly above an ambient temperature to ensure a homogeneous mixing. The mixtures were deposited on the glass and tin substrates with thickness of 100 µm using a bar coater. These films were cured by using UV- irradiation at different doses to measure the mechanical and chemical properties.

UV irradiation

The curing of coatings was carried out by UV irradiation. The detailed description of standard UV lamp was [(type: EMLTA Vp-60) (made in Poland), 180W mercury lamp, 220V, 50Hz and monochromatic filter (λ =320nm)]. In this work the distance between the samples and UV irradiation was constant distance (10cm).

EB irradiation

The irradiation processes of coated samples are carried out at ambient temperature using electron beam accelerator (Energy 3 MeV, power 90 kW, Beam current 30 mA, conveyer speed 16m/min (50HZ) and scan width up to 90 cm) and refunded in the National Center for Radiation Research and Technology (NCRRT), Cairo, Egypt.

Fourier transforms infrared (FTIR) spectroscopy

The infrared analysis carried out using an FTIR spectrometry model Vertex 70, made by Bruker Optic, Germany, over the range 200-4000cm $^{-1}$ for quantitative analysis.

Performance of cured wood panels

The cured wood samples were tested for different end performance properties, as per guidelines of standard test methods: film adhesion (ASTM D 3359-97), pencil hardness (ASTM: D 3363-00), alkali resistance test (ASTM D 1647-89), acid resistance test (ASTM B 287 -74), bending test (ASTM D 522-93a), stain resistance for different staining agents (EN 438-2: 1991), steam resistance (EN 438-2: 1991), and cigarette burn resistance (IS12823: 1990).

Results and Discussion

Characterization

FT-IR characteristics

The infrared spectra are used to check the conjunction of the polymerization reaction. Figure (1a & 1b) represents the IR spectra of AUA and the UV-cured urethane acrylate coating. The characteristic absorption bands of AUA and UV-cured coating are assigned at 1719cm^{-1}, 1524cm^{-1}, and 1234cm^{-1}. These bands confirm that the urethane acrylate coating network represents the bending vibration C=O, N-H, and C−N, respectively. The peak at 3368cm^{-1} represents the free hydroxyl (−OH) groups in the system. Additionally, the peaks at 2920cm^{-1} and 2852cm^{-1} represent the stretching vibration of aliphatic C−H asymmetric and symmetric. The band of C=C of AUA which appeared at 1630

cm^{-1} was disappeared in cured PU films after UV-irradiation. This is due to C=C bonds in the reactive monomers instill the crosslinking reaction by photopolymerization [17]. This is indicated that the AUA/TPGDA was converted into completely cured films under irradiation.

Effect of UV exposure time on the properties of cured urethane acrylate coatings

This part is carried out to study the effect of irradiation times of UV curable source on urethane acrylate oligomer. Hardness, adhesion, bending and swelling tests were taken to find out the tests curing time. The coating formulation was prepared (57 % urethane acrylate oligomer + 40% of difunctional monomer (TPGDA) + 3% benzophenone as initiator). The formulation was then applied as a thin film on different substrates such as glass, tin, and wood with film applicator with thickness 100µm. The curing of coating films was carried out by using the standard UV mercury lamp at different irradiation times (10, 15, 20 & 30 min). Table (2) showed the mechanical and chemical properties of the urethane acrylate films cured at different UV exposure times. Both hardness and adhesion results under UV irradiation at different times (10, 15, 20 & 30min) are plotted in Figure (2).

The cured film at 10 min is tacky and so, tests were not applicable on it. As the time of cured films increased up to 30 min. the hardness increased from (**3H → 6H**) and adhesion increased from (**1B → 2B**). Cured films at different time (15- 30 min.) passed bending and chemical resistance tests. The best cured time is 30 min. at which the best hardness, adhesion, and the flexibility results.

Swelling measurement

Coating formulation containing fixed amount of AUA/TPGDA (60/40) (57 % urethane acrylate oligomer + 40 % of difunctional monomer (TPGDA) + 3 % benzophenone as initiator) at different cured times (15, 20, and 30 min) under UV- radiation were investigated for swelling in acetone for 48h and weighed after blotting the excess solvent from the surface to estimate the swelling ratio of the cured film using the following relationship [18].

Swelling ratio = Swelled weight / Initial weight

The results of swelling test are shown in Table (3). The results are illustrated that the swelling ratios of cured films decrease with increasing the time of radiation dose due to the high crosslink density of the coating films. Therefore, the coatings with higher cross-linking density are expected to show better swelling resistance against chemical or solvent.

The performance of AUA/TPGDA (60/40) induced by EB irradiation

The electron beam (EB) irradiation is become more and more important as a curing technique in an industrial coating, for example on substrates like wood, paper, metal, and plastic. This part is carried out to study the effect of irradiation dose of EB curable source on urethane acrylate. Oligomer formulations parameters observed that hardness, adhesion, bending, and chemical resistance tests were taken to find out the best curing dose. The coating formulations were prepared (60:40) urethane acrylate oligomer and di functional monomer (TPGDA). The formulations were then applied as a thin film on different substrates, such as glass, tin, and wood with film applicator with thickness 100µm. The curing of coating films was carried out by using the EB-irradiation at different irradiation doses (5, 10 & 15 kGy). Table (4) showed the mechanical and chemical results of curing doses on urethane acrylate formulations. Both hardness and adhesion results under EB irradiation at different irradiation doses (5, 10 & 15 kGy) are plotted in Figure (2).

It was found that highly crosslinked polyurethane acrylates prepared from high dose at (10, 15kGy) exhibited good mechanical properties such as hardness, adhesion, and enhanced chemical resistance. The result showed that the pencil hardness of the acrylate coating was 2H at the low dose (5kGy). By increasing the irradiation dose to (10, 15kGy) the hardness of coating improved from 6H to 7H. The result showed that the moderate adhesion of the acrylate coating was 2B at the high dose (15kGy). It is known that the moderate adhesion of EB curable coatings is related to low flexibility most often due to the high crosslink density of the polymeric network. But, at low doses (5, 10kGy) the crosslinking gives high adhesion (4B). All cured panels of coating formulations at different doses pass bending and chemical resistance tests. The best cured dose is 10kGy at which the best hardness, adhesion, and flexibility results.

Preparation and curing of different AUA/TPGDA formulations by UV irradiation

The preliminary study of three coating formulations based on aliphatic urethane acrylate oligomer resin was evaluated. The formulations comprised oligomer/monomer (AUA/TPGDA) with

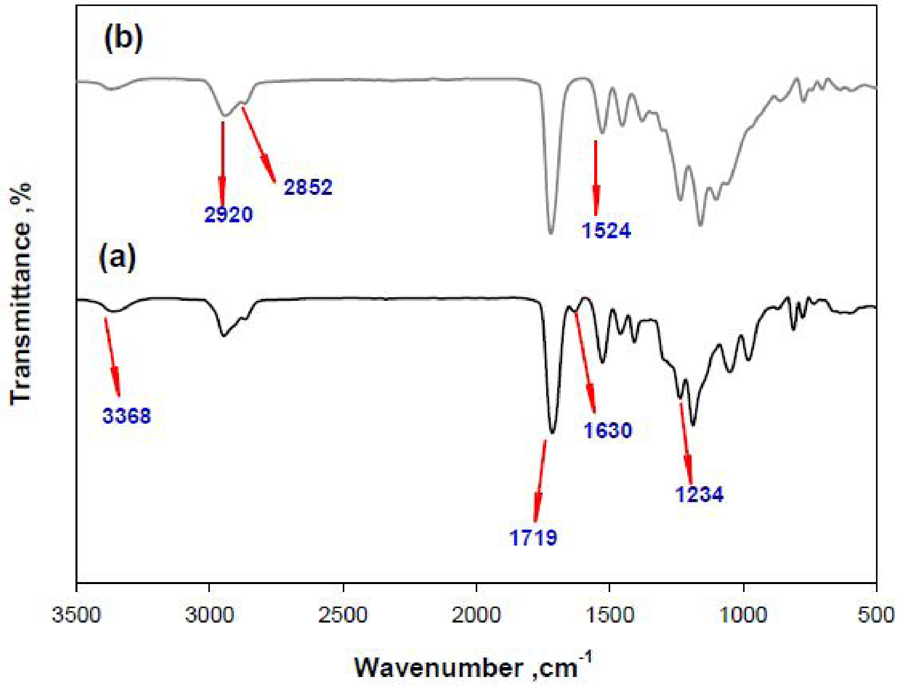

Figure (1): FT-IR spectra of (a) AUA and (b) UV-cured PU

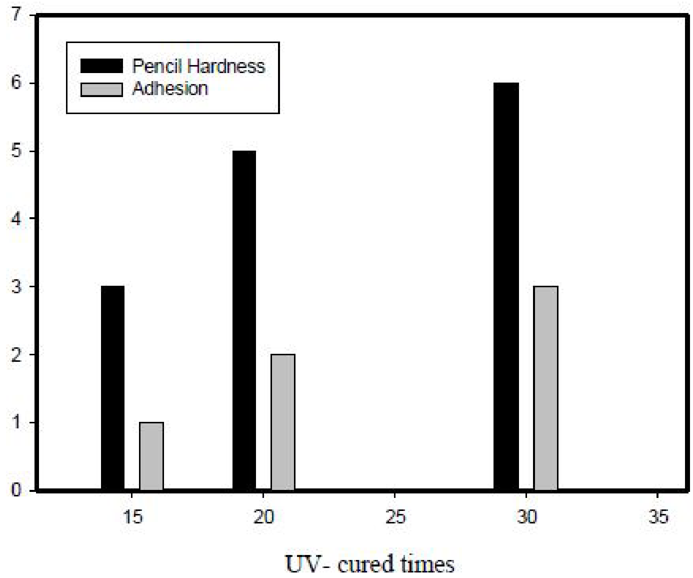

Figure (2): Effect of irradiation time on hardness and adhesion of urethane acrylate coatings

different concentrations [60/40, 70/30, 80/20]. Benzophenone was added as the initiator with 3 wt%. The formulations were then applied as a thin film on different substrates such as glass, tin, and wood with film applicator with thickness 100μm. All samples were cured by UV-radiation to choose the best mechanical and chemical results of the cured films. Mechanical characteristics such as hardness, adhesion and bending results in addition to alkali and acid resistance results were summarized in Table (1).

The results indicated that, there is a direct relationship between the concentrations of AUA/TPGDA (60/40, 70/30, 80/20) and the hardness is increased from (5H →9H). However, the relationship is reversible between the adhesion and AUA/TPGDA concentration the adhesion is decreased from (3B→1B). TPGDA-based AUA acrylates seem to have a higher degree of crosslinking [19]. The hardness of coated films increases by increasing number of double bonds in oligomer (AUA) is available for crosslinking leading to increase the hardness but decrease adhesion. The all concentrations are pass bending and chemical resistance (very good). So, the chosen concentration of AUA/TPGDA is (60/40) due to the hardness, adhesion and the flexibility is very good.

A comparative study of UV and EB irradiation on acrylate coating formulations

The aim of this part is to compare polyurethane acrylate samples that exposed to 10kGy under EB irradiation with those induced to 30 min. under UV irradiation. The mechanical characteristics such as hardness, adhesion and bending results in addition to chemical resistance results were summarized in Table (5). It is clear from Table (5) that, the obtained results under EB irradiation are satisfied and goes hand in hand with those of UV-cured samples.

Moreover, the hardness and adhesion of coating induced by EB irradiation were higher than the coating induced by UV irradiation and this is due to the higher crosslinking density and more uniform polymeric film in case of coating films cured by EB process [20]. Although, all samples of polyurethane acrylate coatings that cured by EB have high hardness and very good chemical resistance, they showed moderate adhesion to substrates. the adhesion of EB curable coatings was decreased because of the low flexibility as a result of high crosslink density of their polymeric films. Finally, all cured coating panels did not show any visible change in chemical resistance such as acid or alkali media for all cured films.

Application of acrylate coatings on the plywood surface

The plywood samples were cut into small pieces and dried in an oven at 100°c to remove the free moisture from plywood until constant weight. The surface of the plywood sample was polished smoothly with the help of suitable sandpaper (240 & 320 mesh). Then it was treated under UV radiation. After treatment the plywood samples were coated with coat formulation and cured under UV and EB irradiation.

The basic structural component of wood is cellulose and contain (OH) group. Aliphatic urethane acrylate contains (NH) group so urethane acrylate with (OH) group in wood substrate formed hydrogen bond. After UV and EB curing formed strong chemical bond between AUA and wood substrate so the hardness is increased. The mechanical characteristics such as hardness and adhesion results were summarized in table (6). It was observed that the pencil hardness of the acrylate coatings cured by UV and EB irradiation was 5H and 7H, respectively. Whereas the adhesion of the AUA coating cured by UV and EB irradiation on plywood was the same, 4B.

Stain resistance test

The cured films of acrylate coatings were tested for four staining chemical list as shown in Table (7). Drops of staining agents were pipette out on the coating surfaces and covered with glass cup to prevent evaporation. After specified time of contact, the staining agent was wiped off with tissue paper and cleaned with water and then coating surface was examined for discoloration or change in appearance.The ratings for stain test: 1, dark brown stain; 2, light brown stain; 3, absorbed at surface, yellow stain; 4, white rim; 5, faint rim; 6, no effect [21].

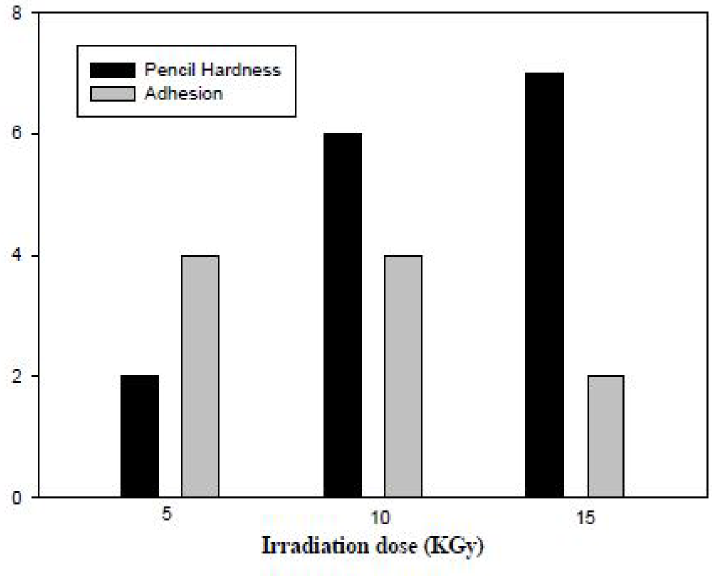

Figure (3): Effect of irradiation dose on hardness and adhesion of ur acrylate coatings

TABLE (1): Mechanical and chemical characteristics of different AUA/TBGDA formulations

Formulations / Tests	AUA/ TBGDA 60/40	AUA/TBGDA 70/30	AUA/TBGDA 80/20
Hardness	5H	8H	9H
Adhesion	3B	1B	1B
Bending	Pass	Pass	Pass
NaOH 5 %	Very good	Very good	Very good
HCl 5 %	Very good	Very good	Very good

TABLE (2): The mechanical and chemical characteristics of curing times on urethane acrylate

Irradiation time / Tests	10 min	15 min	20 min	30 min
Hardness	-	3H	5H	6H
Adhesion	-	1B	2B	2B
Bending (2mm mandrel)	-	Pass	Pass	Pass
NaOH 5 %	-	Very good	Very good	Very good
HCl 5 %	-	Very good	Very good	Very good

TABLE (3): The swelling ratio against curing time of AUA/TPGDA (60/40)

Weight(gm) / Time(min)	Initial wt (g)	Swelling wt (g)	Swelling ratio%
15 min	0.056	0.0624	1.114
20 min	0.0744	0.084	1.102
30 min	0.057	0.062	1.087

TABLE (4): The mechanical and chemical characteristics with different curing doses on urethane acrylate

Irradiation doses / Tests	5 KGy	10 KGy	15 KGy
Hardness	2H	6H	7H
Adhesion	4B	4B	2B
Bending	Pass	Pass	Pass
NaOH 5 %	Very good	Very good	Very good
HCl 5 %	Very good	Very good	Very good

TABLE (5): Physical, mechanical and chemical properties of cured polyurethane acrylate coatings by UV and EB irradiation

Type of radiation / Tests	UV	EB
Hardness	4H	6H
Adhesion	3B	4B
Bending (2mm mandrel)	Pass	Pass
NaOH, 5 %	Very good	Very good
HCl, 5 %	Very good	Very good

TABLE (6): Hardness and adhesion of acrylate coatings on plywood, induced by UV and EB irradiation

Tests \ Type of radiation	UV	EB
Hardness	5H	7H
Adhesion	4B	4B

TABLE (7): Stain resistance test of cured coating on plywood induced by UV and EB irradiation

Reagents \ Type of irradiation	Time of contact	UV	EB
25% NaOH	10 min	6	6
Boric acid	10 min	6	6
Coffee (Nescafe)	16 h	6	6
Tea (lepton)	16 h	6	6

TABLE (8): Steam resistance and cigarette burn test of cured coatings on plywood induced by UV and EB irradiation

Test \ Type of irradiation	UV	EB
Resistance to steam	4	4
Resistance to Marlboro cigarette burn	2	3

It was found that all coating composition showed excellent stain resistance against the staining agents taken for the test.

Steam resistance test

The samples were exposed to steam for 1 h and then the samples were examined for any visible changes on the coating surfaces due to steam. The rating for steam resistance test and cigarettes burns test: 1, sample charred with surface damaged, black coloration; 2, blisters with severe mark with black colour in the core and brown at periphery; 3, moderate brown stain with no blisters;4, no visible change.

The results were reported in Table (7), which indicated that, all cured films showed excellent steam resistance properties.

Cigarette burn test

A lit cigarette was placed horizontally on the specimen for 1 min. The tested area was cleaned with water and suitable solvent and then examined. From results of the cigarette burn test given in Table (8), it was found that all cured films did not perform satisfactorily against cigarette burns.

Conclusion

According to the obtained results it can be concluded that, the optimum condition of curing acrylate coating with UV-irradiation was 30 min, whereas the best curing condition by EB irradiation was 10KGy. At this condition, the preliminary study of three coating formulations based on urethane acrylate were evaluated. FTIR was done for AUA and UV cured polyurethane acrylate and this showed that, crosslinking of AUA/TPGDA under irradiation was occurred and converted completely to cured acrylate coatings. The performance of acrylate coatings which cured by UV or EB irradiation were studied and evaluated. The evaluation results of of cured coatings by EB goes hand in hand with UV irradiation with better results. The hardness of EB cured coatings were higher than the UV cured coatings. This may be due to, EB curing process produce a more uniform polymeric film. while, the adhesion of all samples cured by EB is the same or less than those cured by UV irradiation due to low flexibility as a result of high crosslinking density.

The application of cured acrylate coatings on plywood by UV or EB irradiation was succeeded and their properties like hardness, adhesion, chemical resistance, steam resistance test were satisfied.

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