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Coating performance and characteristics for EB–curable aliphatic urethane acrylate coatings containing difunctional monomer on wood surface

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ABSTRACT

Electron beam (EB) was used to cure coatings of aliphatic urethane diacrylate (AUA) diluted with tripropylene glycol diacrylate monomer (TPGDA). Cured coating films were characterized by Fourier transformed infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), gel fraction and swelling properties. The wood surfaces that cured at different irradiation doses were tested for their end use performance properties like gloss, pencil hardness, adhesion, chemical resistance, steam resistance and cigarette burn resistance. FTIR studies indicated that the density of acrylate functionality and degree of curing increased with increasing irradiation dose. This observation was supported by gel content and swelling investigation as well. The thermal stability, pencil hardness, adhesion and chemical resistance properties were improved by increasing the radiation doses. However, there was a significant decrease in gloss at higher radiation doses. The cured coating passed the steam and stain resistance test but not passed the cigarette burn resistance test.

Keywords, Electron beam curing; Aliphatic urethane diacrylate; Tripropylene glycol diacrylate monomer; Adhesion; Pencil hardness; Wood

1. INTRODUCTION

Radiation curing is a polymerization/cross-linking process, initiated by high-energy radiation, to convert a reactive liquid chemical system into a non-tacky solid cross-linked network at room temperature with virtually zero

emission of volatile organic compound since these systems are 100% reactive and usually contain no solvents [1-7]. EB curable formulations typically consist of an oligomer or prepolymer and reactive monomers. The oligomer is mainly responsible for the performance properties of the cured film. Because of the high viscosity of radiation curable oligomers or pre-polymers, reactive diluents are incorporated in the formulations to make thin film applications possible. They are also required for the production of pre-polymers, to facilitate processing and bulk handling of raw materials [8, 9]. Reactive diluents or modifiers are typically acrylates or methacrylates, with functionalities ranging from one to six, usually more than one, which are capable of reducing the viscosity of the pre-polymers and being incorporated into the structure of cured films. Monomers have traditionally been classified as either monofunctional or multifunctional [10].

Recently much attention has been paid to radiation curing of urethane acrylate resins for surface coating applications. Various types of resins in combination with different reactive diluents were cured and examined for end performance properties of the coatings [7, 11, 12, 13]. Urethane acrylate resins hold pride position in coating industry because of its low cost and many desirable properties like flexibility, hardness, gloss, chemical resistance, etc. Wood coating applications typically demand high gloss, which can be obtained from urethane acrylate oligomers. Tripropylene glycol diacrylate monomer (TPGDA) has a low viscosity and offers a much-appreciated combination of solvency, flexibility, adhesion, reactivity, toughness and outdoor stability in the cured film. The curing behaviour and performance of the EB curable coatings largely depends on their chemical formulations. In the present work, we have investigated the EB curing behaviour and end use performance properties of aliphatic urethane diacrylate (AUA) coating containing a reactive diluent monomer (TPGDA) at different irradiation doses.

2. EXPERIMENTAL

2.1. Materials

The oligomer aliphatic urethane diacrylate (AUA) and reactive diluent tripropylene glycol diacrylate (TPGDA) were supplied by Cytec Surface Specialeties (Drogenbos, Belgium) and were used as received without further purification. The plywood composite samples were purchased from local suppliers.

2.2. Methods

2.2.1. EB curing of urethane acrylate resin

Urethane acrylate oligomer and reactive diluent (TPGDA) were mixed at a ratio (80/20) (wt%) with continuous stirring at ~40 ^{o}C to get homogeneous mixture to be used as formulations for coating. These formulations were applied onto wood samples by using film applicator with thickness of ~100 μm. The coated samples were irradiated using electron beam accelerator (Energy1.5 MeV, power 37.5 kW, Beam current 25 mA and scan width variable up to 90 cm), to get cured coating film. In the present work, the required doses of electron beam radiation are 5, 10, 15, 25 kGy.

2.2.2. Fourier Transform Infrared Spectroscopy (FTIR)

Cured films were measured by ATI Mattson, Genesis series, Fourier Transform Infrared Spectroscopy was used. FTIR spectra were recorded in the range from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} and averaged over 25 scans.

2.2.3. Thermogravimetric analysis (TGA)

TGA studied were carried out using TGA – 30 apparatus (shimadzue, Kyoto, Japan), at heating rate of 10^{o}C/min in air and temperature range from room temperature to 600 ^{o}C.

2.2.4. Gel fraction

Gel fraction of the EB-cured films were determined by soxhlet extraction for 10 hour using acetone as the solvent. Insoluble gel fraction was dried in vacuum oven at 40 ^{o}C to constant weight and then the gel fraction was calculated as follows:

Gel fraction (%) = w_1/w_O x 100

w_O: the weight of cured film before extraction

w_1: the weight of cured film after extraction

2.2.5. Swelling of cured film in acetone

Cured films of known weight were dipped in acetone for 48 hour and weighed after blotting the excess solvent from the surface to estimate the swelling ratio of the cured film using following relation:

Swelling ratio = swelled weight / initial weight

2.2.6. Performance tests 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), gloss at 60^o angle (ASTM: D 523-99), pencil hardness (ASTM: D 3363-00), alkali resistance test (ASTM D 1647-89), acid resistance test (ASTM B 287 -74), stain/chemical resistance conducted for seven different staining agents (EN 438-2: 1991), steam resistance (EN 438-2: 1991), and cigarette burn resistance (IS12823: 1990).

3. RESULTS AND DISCUSSION

3.1. FTIR

FTIR can be effectively used to follow the curing behavior of coating formulation[14, 15] and also to estimate the degree of curing. The FTIR spectra of uncured and cured AUA coating at different doses are shown in Fig. (1). Certain characteristic peaks corresponding to different functional groups present in the formulations clearly appeared in the FTIR spectra. The absorption peaks at 3300-3500 cm^{-1} belonged to –NH (hydrogen bonded), at 2855-2955 cm^{-1} were assigned to CH_2 and CH_3. However, the absorption peak at 1720 cm^{-1} were ascribed to carbonyl group, C=O. While, NCO stretching absorption appeared around 2130 cm^{-1}. Most important are the peaks at 1630, 804 cm^{-1} that are characteristic peaks of unsaturated double bond of acrylate group of oligomer. A comparison of the FTIR spectra of uncured and cured coating formulations at different dose (5, 10, 15, 25 kGy) showed that the characteristic peaks of acrylate double bonds almost disappeared after EB curing. The percentage conversion of double bonds in the EB cured coating was found to be more than 98 % which suggested a very high degree of curing of resin via EB curing process resulting in formation of high performance coatings. The estimation of the double bond conversion was made by comparing the reduction in the intensity of the C=C and at 1630 cm^{-1} relative to the carbonyl group peak at 1720 cm^{-1}, which was assumed to remain constant during the curing reaction.

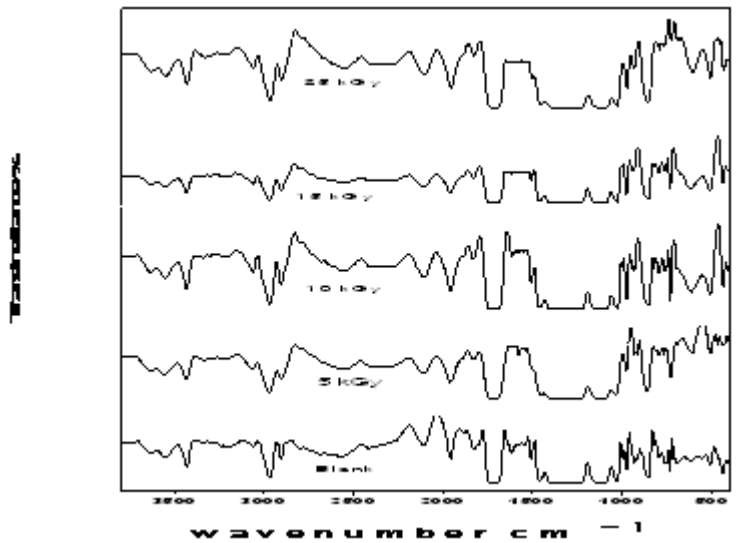

Fig. 1: FTIR of uncured and cured AUA coating at different irradiation doses

3.2. Gel fraction

Gel fraction determination is an important property of any coating, as it is directly measures the extent of crosslinking of the cured film, which in turn determines the final properties of the coating. The results of gel fraction measurements are shown in Fig. (2). The gel fraction increased with the increase of radiation dose and finally gets saturated at 15 kGy. The gel fraction results were supported by the degree of curing estimated by FTIR. The increase in the gel fraction is due to the increase in the density of Crosslinking that produces from high irradiation doses.

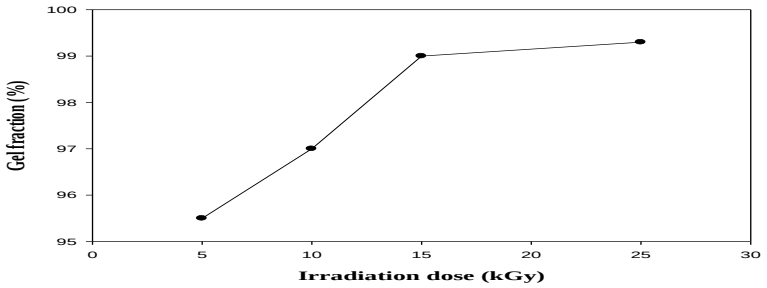

Fig. 2: Effect of irradiation dose on gel fraction of AUA coating

3.3. Swelling measurements

Coating formulations containing fixed amount of TPGDA at different irradiation doses were investigated for swelling in acetone for 48 h. The results

of swelling experiments are given in Fig. (3). It could be seen that the swelling ratio of cured films decreased with the increase in the radiation dose, which was again supported by the gel fraction results showing enhanced crosslinking with the irradiation dose. The reason for decrease in the swelling with the increase of irradiation dose is due to increase in the gel fraction and crosslink density of the coating. Therefore, the coatings with higher crosslinking density are expected to show better swelling resistance against chemicals or solvents.

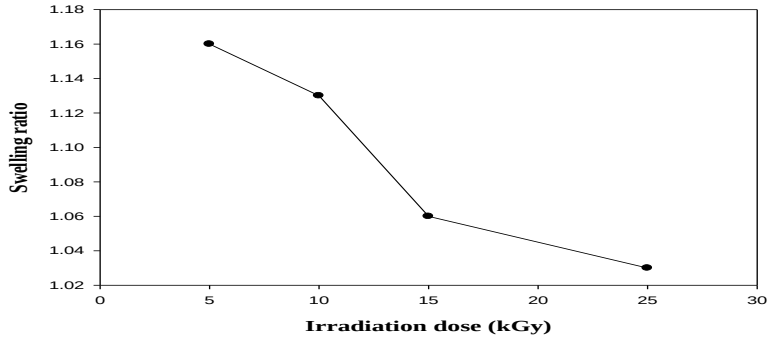

Fig. 3: Effect of irradiation dose on swelling ratio of AUA coating

3.4. Thermogravimetric analysis (TGA)

Thermal stability of the cured coatings was investigated by thermogravimetric analysis of the EB cured coating film. The thermograms of AUA formulation at different doses are given in Fig. (4). It can be seen that the cured AUA coating was stable up to ~300 ^{o}C. The EB cured coatings showed weight loss in two steps; first major weight loss in the temperature range of 300-400 ^{o}C was due to thermal decomposition of organic coating and second weight loss in temperature range 400-500 ^{o}C was referred to the oxidation of the residual formed from the thermal decomposition of coating. The details of the TGA data for EB cured coatings are presented in Table (1), showing the temperatures for different percentage weight losses (10%, 40%, 80%, 90%) of the coatings under different irradiation doses. TGA results showed that the increase in radiation doses increase the thermal stability of AUA coating due to the increase in crosslink density. The data obtained from Table (1) were confirmed by Fig. (5) which shows the variation of rate of decomposition (dw/dt) as a function of heating temperature for AUA coating at different doses. From the Table (1) and Fig. (5), it can be seen that the temperatures of the maximum rate of reaction (T_{max}), taken from the TGA thermogram, shifted to higher temperature by ~14 ^{o}C with increasing the irradiation doses indicating higher thermal stability at higher doses.

Table (1): Decomposition temperature at certain percentage weight loss and temperature of the maximum rate of reaction (T_{max}) of different coating films cured at different doses.

Sample wt/wt	Dose kGy	Decomposition temperature at different weight loss				T_{max}
		10%	40%	80%	90%	
AUA / TPGDA 80/20	5	295	335	438	476	342
	10	303	340	446	485	348
	15	310	362	452	499	356
	25	316	370	460	510	356

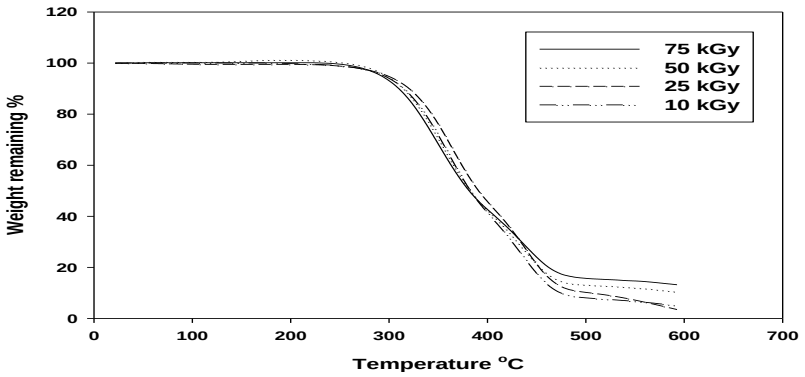

Fig. 4: TGA thermograms of EB cured AUA coatings at different irradiation doses with temperature.

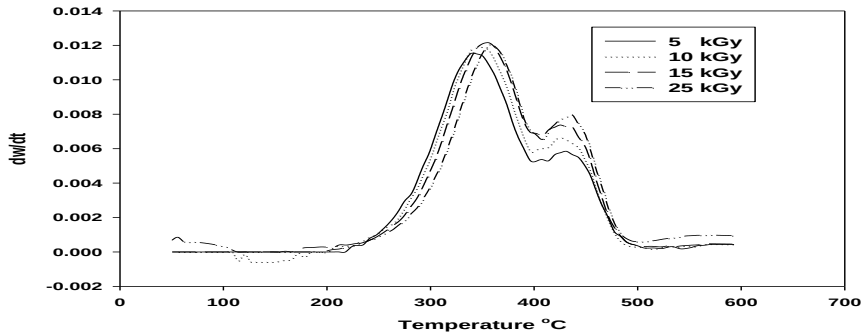

Fig. 5: Rate of decomposition of EB cured AUA coatings at different irradiation doses with temperature.

3.5. Pencil hardness

Pencil hardness property of coating was determined using pencil hardness tester (BYK Gardner) with a calibrated set of drawing leads (Mars

Lumograph, Germany) ranging from 6B (the softest) to 6H (the hardest). The sharpened pencil with circular flat lead end was fixed to the pencil hardness tester and pushed away in a 6.5 mm stroke on to the coated surface. The process was started with the hardest pencil and continued down the scale of hardness to the two end points: one, the pencil that will not scratch the film reported as "pencil scratch hardness", and, two, the pencil that will not cut into or gouge the film reported as "pencil gouge hardness". Results of pencil hardness test of cured surfaces are shown in Fig. (6). It was observed that the pencil scratch hardness of the AUA coating was 2H at low doses. By increasing the irradiation dose up to 25 kGy the scratch hardness of coating improved by two hardness scale to 4H. The pencil gouge hardness of cured surfaces of all the coating formulations was greater than 4H hardness.

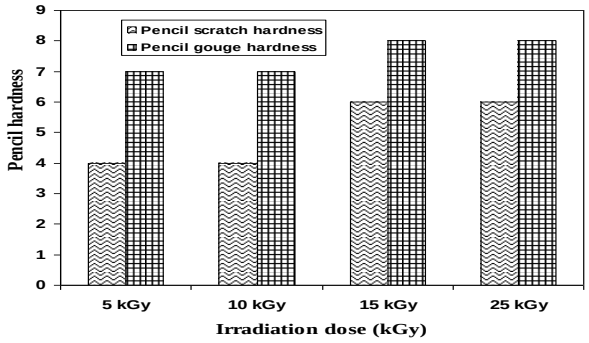

Fig. 6: Effect of irradiation dose in AUA oligomer on the pencil scratch hardness and pencil gouge hardness properties of the EB cured wood samples. Rating for pencil hardness: 1, HB; 2, F; 3, H; 4, 2H; 5, 3H; 6, 4H; 7, 5H; 8, 6H.

3.6. Gloss

Gloss is a measure of the reflecting light from coated surface and it is an important property of coating when the purpose is to provide aesthetic or decorative look to the surface. Gloss of the cured samples was measured at 60^{o} angle of reflectance using a digital mini gloss meter calibrated against internal standard of known refractive index (BYK Gardner) and the results are reported in gloss unit (GU). The gloss values of cured surfaces are plotted as a function of irradiation dose in Fig. (7). It could be seen that the gloss of the plywood surface is enhanced by more than 30 times after curing with AUA resin. The gloss of the coating decreased gradually with the increase in the radiation dose, which may be attributed to micro distortions such as waviness caused by

shrinkage generated on the coating at higher doses due to higher crosslinking caused by TPGDA. The micro distortions in the coating surface scatter the reflected light in other direction and resulted in low gloss values at 60^o angles.

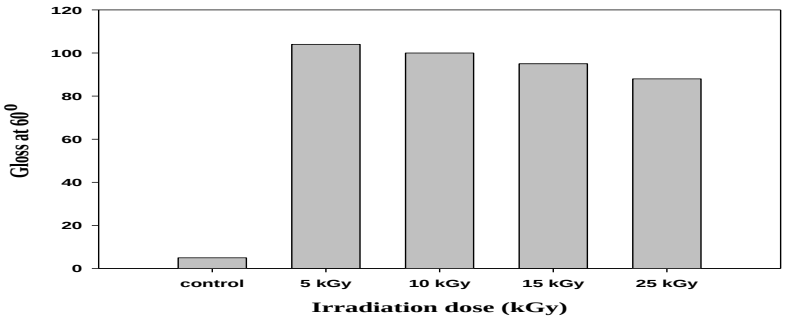

Fig. 7: Effect of irradiation dose in AUA oligomer on the gloss of the EB cured wood samples.

3.7. Adhesion properties

Organic coatings are very useful tools to protect the aesthetic appearance of wood surface. The adhesion properties to wood substrates were investigated by crosscut adhesion (tape adhesion). For the crosscut adhesion analysis, adhesion is classified from 0B, poor adhesion, to 5B, good adhesion (5B>4B>3B>2B>B>0B). It was found that, although highly crosslinked polyurethane acrylates prepared from high doses at (15, 25 kGy) exhibited good mechanical properties such as scratch resistance and hardness in addition to enhanced chemical resistance, they showed moderate adhesion (2B, 2B) to wood substrates. It is known that the moderate adhesion of EB curable coatings to wood is related to low flexibility most often due to the high crosslink density of the polymeric network, the rapid and relatively large cure shrinkage of acrylated binders, and insufficient wetting of the substrate **(16)**. On the other hand, at low doses (5, 10 kGy) the crosslinked AUA give high adhesion (4B) with wood surface due to hydrogen bond formation with hydroxyl group of cellulose structure for wood surface.

3.8. Chemical resistance

The cured coatings were tested for acid and alkali chemical resistance by immersing the coated glass panels to half-length in an aqueous solution containing 5 gm of anhydrous sodium carbonate per 100 ml distilled water and 5 % HCl (32%) for 24 hours. The panels were removed, washed thoroughly and the immersed portions of the films were examined after drying for two hours for

any defects and any change in hardness. It was found that all cured panels of all formulations containing TPGDA in acid or alkali media did not show any visible discoloration and any change in hardness measurements.

3.9. Stain resistance

The coated and uncoated samples were tested for seven staining chemicals list of these and the performance of AUA resin at different irradiation doses is provided in Table (2). Drops of staining agents were pipetted out onto 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 if any. It was found that all coating composition showed excellent stain resistance against the staining agents taken for the test.

Table (2): Stain resistance test of EB cured coating on wood

Reagents	Time of contact	Control	Formulations at different irradiation doses			
			5 kGy	10 kGy	15 kGy	25 kGy
30 % AcOH	10 min	5	6	6	6	6
25% NaOH	10 min	3	6	6	6	6
20% H_2O_2	10 min	6	6	6	6	6
Boric acid	10 min	4	6	6	6	6
ammonia 10%	16 h	3	6	6	6	6
Coffee (Nescafe)	16 h	1	6	6	6	6
Tea (lepton)	16 h	2	6	6	6	6

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.

3.10. Steam resistance

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 results are reported in Table (3), which indicated that the all cured films at different irradiation doses showed excellent steam resistance property.

3.11. 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 (3), it was found that all

cured films at different irradiation doses did not perform satisfactorily against cigarette burns and suitable additives have to identified and incorporated in formulations to provide cigarette burn resistance to coatings.

Table (3): Steam resistance and cigarette burn test of EB cured coating on wood

Property	Control	Formulations at different irradiation doses			
		5 kGy	10 kGy	15 kGy	25 kGy
Resistance to steam	4	4	4	4	4
Resistance to cigarette* burn	1	2	3	2	2

The rating for steam resistance test and cigarettes burn 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.

***Marlboro.**

CONCLUSION

The EB curing behavior and end use performance properties of aliphatic urethane diacrylate (AUA) coating containing 20 % of reactive diluent (TPGDA) at different irradiation doses were investigated. It was found that, at higher irradiation dose some properties of coatings like crosslinking density, thermal stability, pencil hardness, and chemical resistance properties were improved. However, higher irradiation dose results in micro distortions on the coating surfaces and induces brittleness that adversely affects gloss and adhesion properties of the coating.

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مجلة البحوث الإشعاعية
والعلوم التطبيقية
مجلد ٥ عدد ٢ ص ص ٢٤٣ ـ٢٥٥ (٢٠١٢)

خواص وصفات دهانات البولى يوريثان أكريلات المعالجة بالحزم الالكترونية والمحتوية على مونيمر ثنائى الفاعلية وتطبيقاتها على السطوح الخشبية

عيسى محمد محمد

قسم كيمياء الإشعاع- المركز القومى لبحوث وتكنولوجيا الإشعاع ـ هيئة الطاقة الذرية – مصر ـ القاهرة

يهدف هذا البحث الى تحضير ودراسة خواص بعض الدهانات القائمة على اليوريثان اكريلات بإضافة مونيمر ثنائى الفاعلية مثل تراى بروبلين جليكول داى اكريلات ومعالجة هذه الدهانات بجرعات إشعاعية مختلفة تحت تأثير المعجل الالكتروني وتطبيقاتها على الأسطح الخشبية والزجاجية. وقد تم قياس الأشعة تحت الحمراء والتحليل الحرارى والانتفاش لجميع الأفلام المعالجة بالإشعاع. وقد تم أيضا على الأسطح الخشبية والزجاجية قياس جميع الخواص الفيزيائية والكيميائية والميكانيكية مثل اللمعان , الصلادة , اللصوقة والمقاومة للأحماض والقواعد وأيضا المقاومة للبخار واحتراق السجائر. وقد وجد أن الثبات الحرارى واللصوقة والصلادة لجميع الأفلام تتحسن بزيادة الجرعة الإشعاعية إلى أن تصل الى ٢٥ كيلو جراى ولكن وجد نقص طفيف فى اللمعان عند زيادة الجرعات الإشعاعية.