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ABSTRACT

EFFECT OF ACRYLIC MONOMERS ON THERMAL STABILITY OF ELECTRON BEAM - CURED POLYESTER ACRYLATE. Effect of acrylic monomers on thermal stability of electron beam (EB) - cured polyester acrylate has been studied by using thermogravimetric analysis. Polyester acrylate oligomer with the trade name of Setacure AP EPS 88/03 was cured by EB-irradiation after being added with acrylate monomers i.e., difunctional monomers (EGDMA, TPGDA, HDDA), and trifunctional monomer (TMPTA). Monomer concentrations in the mixture were 0, 10, 30, and 50 % by weight, whereas irradiation doses for curing were 20, 40, 60, and 80 kGy. The results show that concentration of monomer and irradiation dose do not affect very much the thermal stability of cured polyester acrylate produced, except in the use of TMPTA. In this case, increasing TMPTA concentration and irradiation dose, increase the thermal stability significantly. Initial decomposition temperature and temperature for 10 % weight loss for all samples were between 319 and 376°C. Activation energy of some cured films were also determined using a multiple heating rate method.

ABSTRAK

PENGARUH MONOMER AKRILAT PADA KESTABILAN TERMAL POLIESTER AKRILAT HASIL CURING DENGAN BERKAS ELEKTRON. Percobaan pengaruh monomer akrilat pada kestabilan termal poliester akrilat hasil curing dengan berkas elektron telah dilakukan menggunakan analisis termogravimetri. Oligomer poliester akrilat dengan nama dagang Setacure AP EPS 88/03 diiradiasi menggunakan berkas elektron setelah dicampur dengan monomer akrilat yaitu, monomer difungsional (EGDMA, TPGDA, HDDA), dan monomer trifungsional (TMPTA). Konsentrasi monomer dalam campuran adalah 0, 10, 30, dan 50 % by berat, sedangkan dosis iradiasi dalam percobaan adalah 20, 40, 60, and 80 kGy. Hasil percobaan

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menunjukkan bahwa konsentrasi monomer dan dosis iradiasi tidak banyak berpengaruh terhadap kestabilan termal film yang dihasilkan, kecuali pada penggunaan TMPTA. Dalam hal ini, kenaikan konsentrasi TMPTA dan dosis iradiasi terlihat jelas menaikkan kestabilan termal. Suhu awal terjadinya dekomposisi, dan suhu untuk pengurangan berat 10 % pada semua contoh uji terjadi antara 319 dan 376°C. Energi aktivasi beberapa film ditentukan dengan menggunakan metode multiple heating rate.

INTRODUCTION

Typical components of ultra violet (UV)/electron beam (EB) curable coating usualy contain : a reactive resin of intermediate molecular weight, a multifunctional cross-linking constituent, and reactive diluent (1). The diluents are usually mono- or polyfunctional monomers.

Most of the radiation curable coating systems are based on molecules containing acrylate functional groups and are cross-linkable by both UV and EB. Systems containing acrylic monomers and acrylate-bearing oligomers have given these formulations the major share of the radiation-cured coating market due to the higher curing speed (2-3).

The reactive monomers suitable for UV or EB curing can be mono- or polyfunctional, and their properties vary considerably and are thus having a significant effect on the final film performance. The important properties in selecting any reactive monomer for a particular application are : viscosity, solubility, volatility, flash point, odour, toxicological properties, reactivity, functio-

nality, glass transition temperature, percentage of shrinkage, and surface tension (4).

In considering applications such as for printed circuit boards, solder masks for photoresists, gasket coatings, wire/cable coatings, tapes, and solar collectors. or reflectors, thermal stability of the cured film are important. A comparison of the thermal stability of materials cured via EB, UV, and thermal curings showed that EB curing gave greater thermal stability than UV, and catalyzed or uncatalyzed thermal curings (5).

The objective of this investigation was to determine the relationships, if any, between type and concentration of acrylic monomers i.e., ethylene glycol dimethacrylate (EGDMA), tripropylene glycol diacrylate (TPGDA), hexandiol diacrylate (HDDA), and trimethylol propane triacrylate (TMPTA) on thermal stability of EB-cured polyester acrylate (PA) mixed with those monomers.

MATERIALS AND METHODS

Materials. Polyester acrylate oligomer with the trade name of Setacure AP EPS 88/03 was supplied from AKZO (Netherland), monomer EGDMA and TMPTA from Merck (Germany), HDDA from Cray Valley Product (England), and TPGDA from BASF (Germany). These chemicals were used without further purification.

Equipments. Irradiation was conducted using an electron beam machine from Nissin - High Voltage Co., Ltd., Japan. Maximum operation voltage and current of the machine were 300 kV and 50 mA, respectively.

Methods. Setacure AP EPS 88/03 was mixed with the monomers to get the mixtures of 0, 10, 30, and 50 % by weight of monomer. The mixture were coated on aluminum plates (200 x 100 x 1 mm) by using a glass rod to get a film thickness of around 100 um. The wet films were exposed to electron beam radiation in a nitrogen atmosphere (O_2 conc. < 500 ppm) at various doses, i.e., 20, 40, 60, and 80 kGy. The operation voltage was 300 kV with beam current of 20 mA. Thermogravimetric analysis (TGA) was conducted on the cured materials after stripping them from the aluminum plates. The TGA measurements were carried out in a nitrogen atmosphere at a flow rate of 40 ml/minute, with a constant heating rate of 10°C/minute, and evaluated from 25 to 500°C using a TGA-30 Thermal Analyzer produced by Shimadzu. The weight of the samples were between 5 and 6 mg. In case of activation energy measurement, the heating rate was varied from 5 to 30°C/minute. The weight loss percentages versus temperature were read from the graph.

RESULTS AND DISCUSSIONS

Some properties of acrylic monomers used in the experiment are shown in Table 1. EGDMA, TPGDA, and HDDA have 2 functional groups, but each group has different molecular weight. EGDMA contains methacrylate group, whereas the three other contain acrylate group.

The initial decomposition temperature (T_0) and temperature for 10 % weight loss (T_{10}) are among the main criteria for determining the heat stability of polymers with dynamic heating (6). The higher the value of T_0 and T_{10}, the higher the heat stability of a given polymer. Table 2 shows T_0 and T_{10} of the polyester acrylate (PA)-acrylic monomer cured films which was obtained from thermal decomposition thermograms for various monomer concentrations and irradiation doses. There is no significant difference in thermal stability at low monomer concentration (< 30 %) and low dose (< 40 kGy) between EGDMA, TPGDA, and HDDA. These monomers have the same number of functional group. At a higher monomer concentration (50 %) and low irradiation dose, PA-EGDMA film has a slightly lower T_0 & T_{10} than the other two mixtures. This result is in line with that reported by THALACKER and BOETTCHER (5), that acrylate functional materials are more thermally stable than methacrylate, when cured under such like conditions using EB. The higher concentration of EGDMA (50 %) causes a reduction in curing efficiency as the

final product should now be a mixture of cross-linked copolymer gel plus homopolymer. This is indentical with curing mechanism of polyester - styrene mixture using EB irradiation (7). Since the efficiency of homopolymerization of EGDMA was lower than TPGDA or HDDA, the thermal stability of its film was also lower. Above 60 kGy, the irradiation dose will be sufficient to form PA-EGDMA gelation. SETO, et al. (8) found that percentage of polymerization was higher for oligomers/polymers with greater molecular weight per funotional group. For the same functionality, EGDMA has smaller molecular weight per functional group than TPGDA or HDDA.

Figure 1 shows the thermal decomposition of cured films at 30 % acrylic monomer concentration. The mixtures of polyester acrylate with EGDMA, TPGDA, HDDA, and TMPTA at the dose of 40 kGy exhibit T_0 at 332, 321, 330, and 339°C, and T_{10} at 341, 337, 346, and 352°C, respectively. The residual weight at 500°C were between 6 and 10 % of the original weight. In general, it has been proven that PA-TMPTA gave higher thermal stability than the other three. This is due to the higher funotionality of TMPTA, and can also be seen in the data of T_0 and T_{10} in Table 2. The higher funotionality gave the higher sensitivity toward irradiation, which in turn gave higher cross-link density in the cured polymers. Samples of PA-difunotional

monomers cured at 20, 40, 60, and 80 kGy exhibit nearly identical thermal stability.

Effect of TMPTA concentration on thermal decomposition of PA-TMPTA cured film can be seen in Figure 2. The thermograms indicate that thermal stability increases with monomer concentration. This is not the case for PA-difunctional monomer mixtures as shown by the data in Table 2. The concentration of difunctional monomers (EGDMA, TPGDA, HDDA) does not affect very much the thermal stability of cured films produced as indicated by their T_0 and T_{10}.

Thermal decomposition of PA-EGDMA cured at various irradiation doses is shown in Figure 3. The irradiation dose has no meaningful effect on the thermal stability. However, it appears that at 80 kGy samples have slightly more thermal stable than at lower doses. This fact is probably due to the limited curing level in PA-EGDMA mixture. In case of PA-TMPTA, the effect of irradiation dose on thermal stability is more significant. The thermal stability increases with increasing irradiation dose as indicated by the T_0 & T_{10} in Table 2. The two other monomers (TPGDA & HDDA) follow the same pattern as EGDMA.

Activation energy for decomposition process can be used to determine the thermal stability of a material, whereas material decomposition is influenced by heating rate. Figure 4 shows the weight loss versus temperature at

various heating rate for PA-TMPTA sample. According to the method proposed by OZAWA, at the same weight loss, there is a correlation between heating rate and temperature, which can be expressed by the following equation (9).

$$- \log \beta_1 - 0.457\ E/RT_1 = - \log \beta_2 \quad 0.457\ E/RT_2 = \ldots$$

where,

β = heating rate, $^{o}C/min.$

E = activation energy, cal/mole.

R = gas constant, 1.987 cal/mole ^{o}K.

T = absolute temperature, ^{o}K.

By using a selected weight loss (10, 30, 50, and 70 %), the temperature (in ^{o}K) at that weight loss level can be measured for each thermogram. A plot of the logarithm of the heating rate versus the corresponding reciprocal temperature at constant weight loss is prepared. By assuming that the reaction order is 1, the plotted data should produce a straight line. Figure 4 shows a series of such lines obtained from the four thermograms shown in Figure 3 by plotting data from different weight losses. The slopes obtained from these lines are the values of - 0.457 E/R, and so E can be calculated. Table 3 presents values for the activation energy and the corresponding - 0.457 E/R calculated for four weight loss levels as shown in Figure 3. For different slope, the value of activation energy is also different. Activation energy for PA-TMPTA was between 39.1

and 44.8 kcal/mole at the dose of 40 kGy and TMPTA concentration of 30 %. The average activation energy was 42.5 kcal/mole. By the same method, the activation energy for PA-EGDMA, PA-TPGDA, and PA-HDDA irradiated at the same dose (40 kGY) and monomer concentration (30 %) were found to be 39.1, 40.9, and 40.9 kcal/mole, respectively. This indicate, that PA-TMPTA has better thermal stability than PA-TPGDA, PA-HDDA, and PA-EGDMA.

CONCLUSION

Functionality and molecular weight per functional group of monomer in an oligomer - monomer mixture affect the thermal stability of its film cured by EB irradiation. The thermal stability of cured film from PA-TMPTA mixture is better than that obtained from PA-TPGDA, PA-HDDA, or PA-EGDMA mixtures.

In general, monomer difunctional concentration and irradiation dose, do not affect very much the thermal stability of its film. By increasing the TMPTA concentration (trifunctional monomer) and irradiation dose, the thermal stability will also increase.

The values of initial decomposition temperature and temperature for 10 % weight loss of all samples were between 319 and 376^{o}C. The activation energies for the PA-acrylic monomers at the dose of 40 kGy and 30 % monomer concentration were between 39 and 42 kcal/mole.

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Table 1. Some properties of acrylic monomers

Monomer	Stucture	Molecular weight	Functionality	Molecular weight / functional group
Ethylene glycol dimethacrylate (EGDMA)	$CH_2=CH-CH_2-\overset{O}{\overset{\|\|}{C}}-O-(CH_2)_2-O-\overset{O}{\overset{\|\|}{C}}-CH_2-CH=CH_2$	198	2	99
Tripropylene glycol diacrylate (TPGDA)	$CH_2=CH-\overset{O}{\overset{\|\|}{C}}-O-[CH(CH_2)CH_2-O]_3-\overset{O}{\overset{\|\|}{C}}-CH=CH_2$	300	2	150
Hexandiol diacrylate (HDDA)	$CH_2=CH-\overset{O}{\overset{\|\|}{C}}-O-(CH_2)_6-O-\overset{O}{\overset{\|\|}{C}}-CH=CH_2$	226	2	113
Trimethylol propane triacrylate (TMPTA)	$CH_3-CH_2-C(CH_2-O-\overset{O}{\overset{\|\|}{C}}-CH=CH_2)_3$	296	3	99

Table 2. Initial decomposition temperature (T_0) and temperature for 10 % weight loss (T_{10}) in °C of PA-acrylic monomer cured film. Heating rate : 10°C/min. N_2 : 40 ml/min

Mixture (PA-Acrylic monomer)		Irradiation dose, kGy							
		20		40		60		80	
		T_0	T_{10}	T_0	T_{10}	T_0	T_{10}	T_0	T_{10}
	0	321	333	326	336	327	335	330	339
	10	336	348	328	340	328	340	332	340
% EGDMA	30	332	338	332	341	333	346	336	343
	50	324	329	325	329	326	329	328	338
	10	324	333	323	338	323	331	328	331
% TPGDA	30	322	338	321	337	319	332	320	331
	50	321	335	329	335	332	337	330	338
	10	325	339	333	346	332	344	335	339
% HDDA	30	322	340	330	346	334	349	338	349
	50	330	342	333	346	345	364	360	367
	10	319	339	322	340	327	342	328	345
% TMPTA	30	331	351	339	352	342	351	348	355
" "	50	370	372	371	372	373	376	366	370

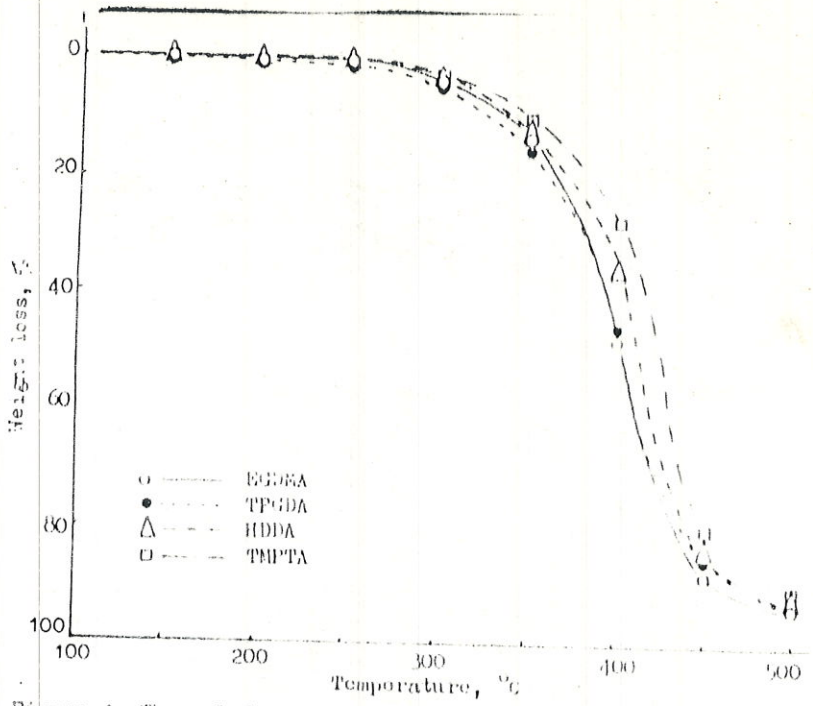

Figure 1. Thermal decomposition of PA-acrylic monomer at 30 % acrylic monomer concentration.
Dose : 40 kGy ; Heating rate : 10°C/min ; N_2 : 40 ml/min.

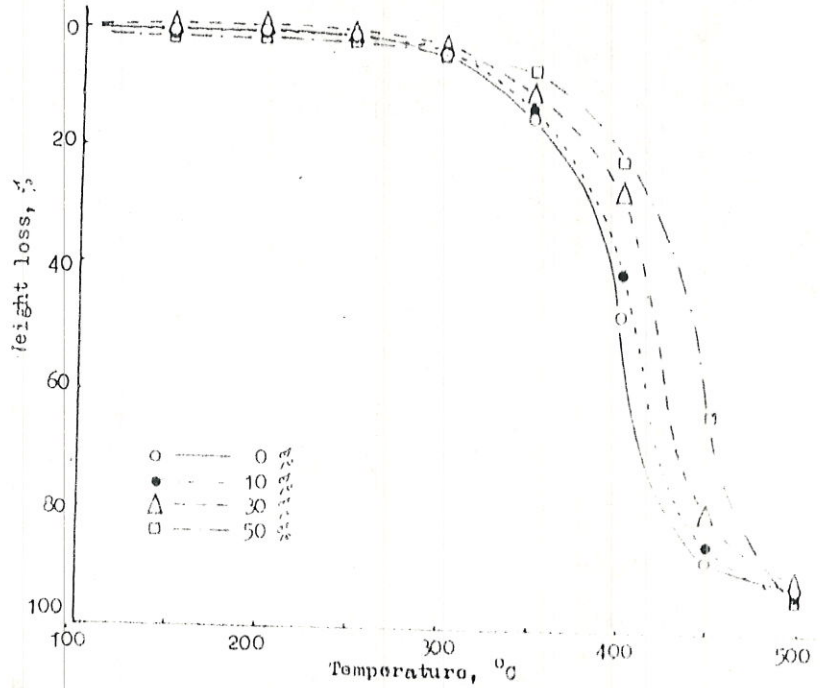

Figure 2. Thermal decomposition of PA-TMPTA at various concentrations.
Dose : 40 kGy ; Heating rate : 10°C/min ; N_2 : 40 ml/min.

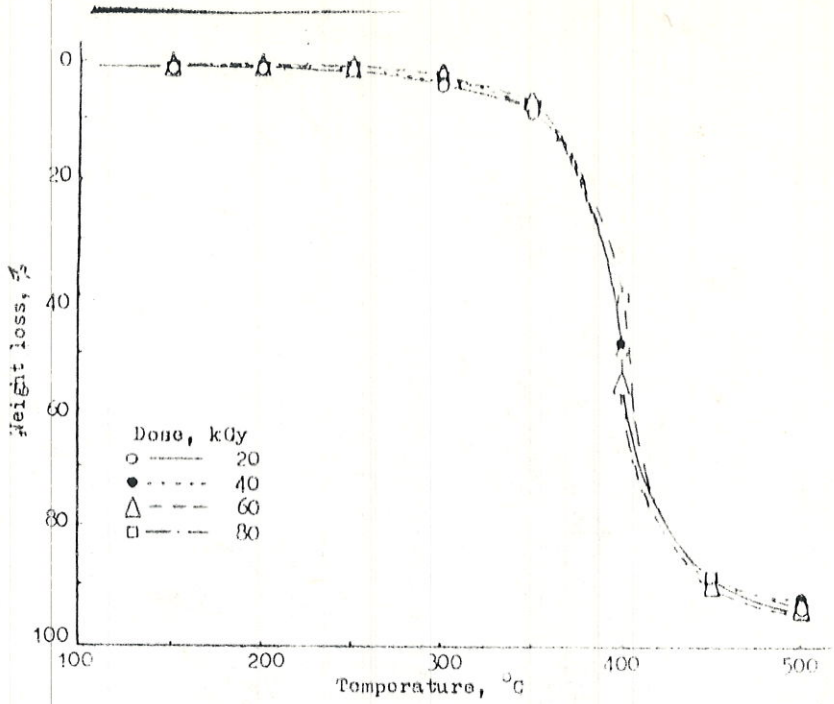

Figure 3. Effect of irradiation dose on thermal decomposition of PA-EGDMA. EGDMA concentration : 30 % ; Heating rate 10°C/min ; N_2 : 40 ml /min.

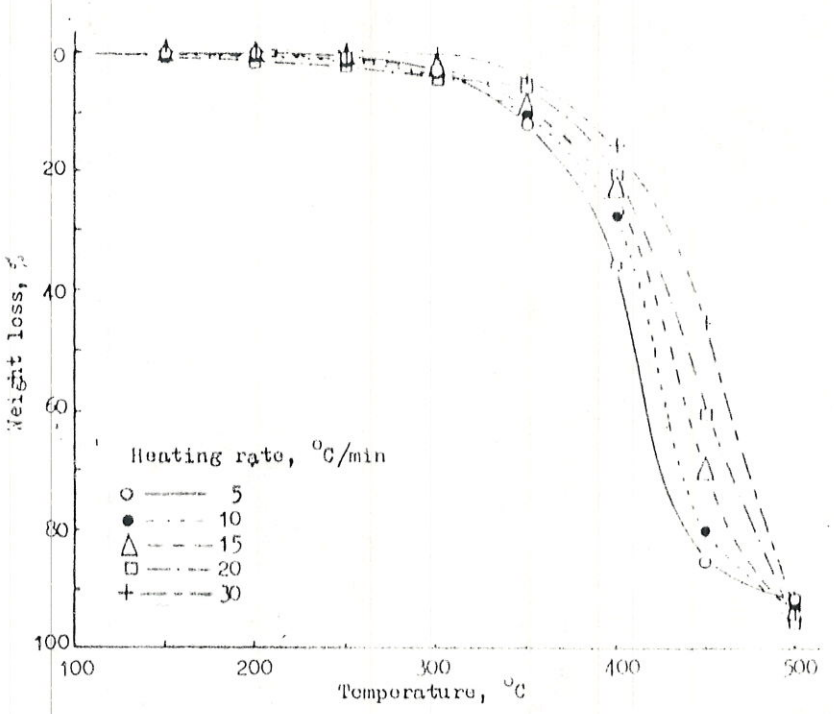

Figure 4. Thermal decomposition of PA-TMPTA at various heating rates. TMPTA concentration : 30 % ; Dose : 40 kGy ; N_2 : 40 ml/min.

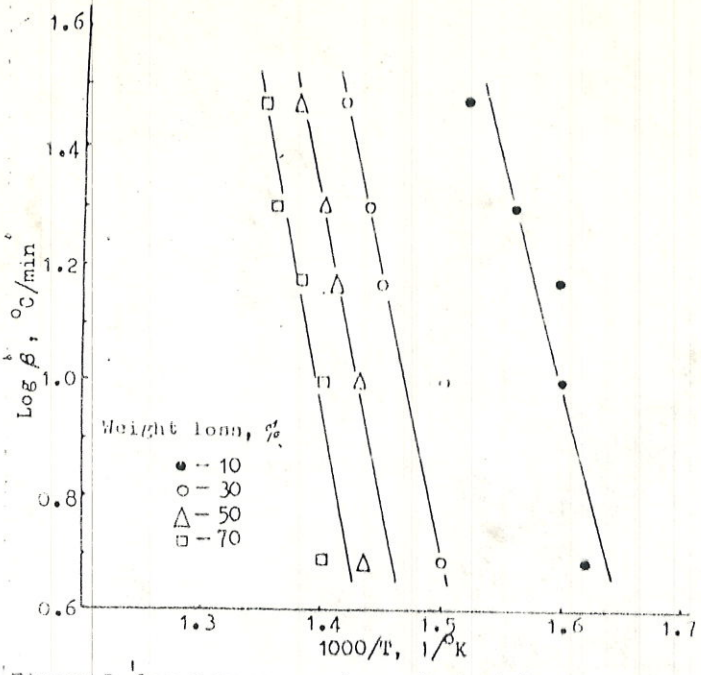

Figure 5. Log β versus reciprocal absolute temperature at different weight loss of PA-TMPTA.
TMPTA concentration : 30 % ; Dose : 40 kGy.

Table 3. Activation energy and 0.457 E/R values of PP TMPTA cured film for various weight loss. TMPTA concentration : 30 %. Dose : 40 kGy.

Weight loss, %	0.457 E/R × 10^{-3}	Activation energy (E), kcal/mol
10	10.7	49.01
30	9.66	44.1
50	9.2	41.7
70	10.1	46.1