

Photopolymerization and Thermal Behavior of Phosphate Diacrylate and Triacrylate Used as Reactive-Type Flame-Retardant Monomers in Ultraviolet-Curable Resins

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ABSTRACT: Tri(acryloyloxyethyl)phosphate (TAEP) and di(acryloyloxyethyl)ethyl phosphate (DAEEP) were used as reactive-type flame-retardant monomers along with commercial epoxy acrylate and polyurethane acrylate oligomers in ultraviolet (UV)-curable resins. The concentrations of the monomers were varied from 17 to 50 wt %. The addition of the monomers greatly reduced the viscosity of the oligomers and increased the photopolymerization rates of the resins. The flame retardancy and thermal degradation behavior of the UV-cured films were investigated with the limiting oxygen index (LOI) and thermogravimetric analysis. The results showed that the thermal stability at high temperatures greater than 400°C and the LOI values of the UV-cured resins, especially those containing epoxy acrylate, were

largely improved by the addition of the monomers. The dynamic mechanical thermal properties of the UV-cured films were also measured. The results showed that the crosslink density increased along with the concentrations of the monomers. However, the glass-transition temperature decreased with an increasing concentration of DAEEP because of the reduction in the rigidity of the cured films, whereas the glass-transition temperature increased with the concentration of TAEP because of the higher crosslink density of the cured films. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 185–194, 2005

Key words: flame retardance; photopolymerization; thermogravimetric analysis (TGA)

INTRODUCTION

Ultraviolet (UV)-curing technology has been widely used for protective coatings, electronics, adhesives, and inks because of its high cure speed, energy conservation, pollution reduction, and cost effectiveness.¹ Important types of oligomers and monomers commonly used in UV-curable formulations include acrylated compounds, such as acrylated epoxies, acrylated polyurethanes, acrylated polyesters (or polyethers), trimethylolpropane triacrylate, and neopentylglycol diacrylate. However, the cured films of these materials generally are flammable, and this demands the development of flame-retardant systems to reduce fire hazards for some applications, such as the matrices for optical fibers and flame-retardant wood coatings.^{2,3}

Flame retardants are used in blends with resins as additives and in resins during curing as reactive components. Although the required level of fire retardancy can normally be attained via blending with

resins as additives,⁴ because the high concentration of additives leads to curing difficulties and severe degradation, such additives are not optimal for UV-curable systems.⁵ To overcome these problems, some halogen-based reactive-type monomers and oligomers have been prepared and used with some common acrylate resins to reduce their flammability.^{4,6} However, halogen-type flame retardants give rise to toxic gases and corrosive smoke during combustion.⁷ Therefore, the search for halogen-free reactive-type flame retardants, such as phosphorus-containing materials, has drawn much attention.^{8–10} In our previous work, two kinds of UV-curable phosphorus-containing monomers, tri(acryloyloxyethyl)phosphate (TAEP) and di(acryloyloxyethyl)ethyl phosphate (DAEEP), were synthesized, and they had the limiting oxygen index (LOI) values of 29 and 36, respectively. Their molecular formulas are shown in Figure 1.¹¹

In this study, DAEEP and TAEP were blended with commercial epoxy acrylate (EB600) and polyurethane acrylate (EB270) in different ratios to obtain UV-curable flame-retardant resins. The effects of the two monomers on the viscosity and photopolymerization rates of their resins were investigated. The flammability and thermal behavior of the UV-cured films were also determined.

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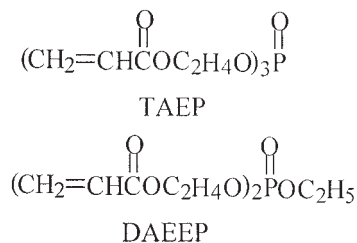


Figure 1 Molecular formulas of TAEP and DAEEP.

EXPERIMENTAL

Materials

EB600, an epoxy acrylate with a unsaturation concentration of 4.00 mmol g^{-1} and a molar mass of 500 g mol^{-1} , and EB270, an aliphatic polyurethane acrylate with a unsaturation concentration of 1.33 mmol g^{-1} and a molar mass of 1500 g mol^{-1} , were supplied by UCB Co. (Brussels, Belgium). DAEEP and TAEP were synthesized by the reaction of phosphorus oxychloride and dichloroethylphosphate with hydroxyethyl acrylate, respectively. The unsaturation concentration of difunctional acrylated monomer DAEEP, with a molar mass of 322 g mol^{-1} , was calculated to be 6.21 mmol g^{-1} through 2 divided by the molar mass. That of trifunctional acrylated monomer TAEP, with a molar mass of 392 g mol^{-1} , was calculated to be 7.65 mmol g^{-1} through 3 divided by the molar mass. 2-Hydroxy-2-methyl-1-phenyl-1-propanone (Darocur 1173), kindly supplied as a gratis sample by Ciba-Geigy (Basel, Switzerland), was used as a photoinitiator.

Sample preparation

All resin formulations were UV-cured with UV irradiation equipment (80 w cm^{-2} ; Lantian Co., Beijing, China) in the presence of 2 wt % Darocur 1173.

Measurements

The viscosity of the resins was measured with a QNX spinning viscometer (Tianjin Instrument Co., Tianjin, China) at a speed of 750 rpm at 30°C .

The photopolymerization rate was monitored with a CDR-1 differential scanning calorimeter (Shanghai Balance Instrument Co., Shanghai, China) equipped with a BHG-250 UV spot cure system (Mejiro Precision Co., Tokyo, Japan). Photopolymerization was carried out in an N_2 atmosphere. The sample was placed in an uncovered aluminum pan.¹² The incident light intensity at the sample pan was measured to be 2.14 mW cm^{-2} with a UV power meter. The unsaturation conversion (P_t) was calculated as follows: $P_t = H_t/H_\infty$, where H_t is the heat effect within t seconds and H_∞ is

the heat effect of 100% unsaturation conversion. The differential scanning calorimetry (DSC) curves were unified by the weights of the samples (g). The polymerization rate was defined by $\text{mmol}_{\text{C}=\text{C}} \text{ g}^{-1} \text{ s}^{-1}$, that is, the variation of the unsaturation concentration ($\text{mmol}_{\text{C}=\text{C}} \text{ g}^{-1}$) per second. For calculating the polymerization rate and the heat effect of 100% unsaturation conversion, the value for the heat of polymerization of 86 J mmol^{-1} per acrylic unsaturation was taken.¹³

The thermogravimetric analysis (TGA) was carried out on a Shimadzu TG-50 apparatus (Kyoto, Japan) at a heating rate of $10^\circ\text{C min}^{-1}$ in air. Concerning the thermal analyses of the EB600 and EB270 formulations, the curves of the weight differences between the experimental and theoretical thermogravimetry (TG) curves were computed as follows:¹⁴

$W_{\text{exp}}(T)_{\text{oligomer}}$: TG curves of the UV-cured pure commercial oligomer (EB600 and EB270) films.

$W_{\text{exp}}(T)_{\text{monomer}}$: TG curves of the UV-cured pure monomer (DAEEP and TAEP) films.

$W_{\text{exp}}(T)_{[\text{oligomer}/\text{monomer}]}$: TG curves of the UV-cured oligomer/monomer blend films.

$W_{\text{th}}(T)_{[\text{oligomer}/\text{monomer}]}$: theoretical TG curves computed by a linear combination of the TG curves of the resins and monomers [$W_{\text{th}}(T)_{[\text{oligomer}/\text{monomer}]} = xW_{\text{exp}}(T)_{\text{oligomer}} + yW_{\text{exp}}(T)_{\text{monomer}}$, where x and y are the weight percentages of the oligomer and monomer in the blend, respectively, and x plus y is 1].

$\Delta(\text{Weight})_{[\text{oligomer}/\text{monomer}]}$: curves of the weight difference [$\Delta(\text{Weight})_{[\text{oligomer}/\text{monomer}]} = W_{\text{exp}}(T)_{[\text{oligomer}/\text{monomer}]} - W_{\text{th}}(T)_{[\text{oligomer}/\text{monomer}]}$].

The $\Delta(\text{Weight})$ curves allowed the observation of an eventual increase or decrease in the thermal stability of the formulations in comparison with the combination of components analyzed separately.

The LOI values of the cured films were measured with a ZRY-type instrument (Nanjing, China) on $120 \times 60 \times 3 \text{ mm}^3$ sheets according to ASTM D 2863-77. The vertical burn test was performed on a CZF-1 type instrument (Nanjing, China) on $127 \times 12.7 \times 3 \text{ mm}^3$ sheets according to ASTM D 635-77.

The tensile storage modulus (E') and tensile loss factor ($\tan \delta$) of the UV-cured films were measured with a dynamic mechanical thermal analyzer (Rheome Tric SCI Apparatus, Ltd., New York) at a frequency of 1 Hz and a heating rate of 2°C min^{-1} in the range of 0 – 200°C on $20 \times 5 \times 1 \text{ mm}^3$ sheets.

RESULTS AND DISCUSSION

The compositions of the formulations containing EB600, EB270, DAEEP, and TAEP are listed in Tables I and II.

TABLE I
Viscosity and Flammability of the Resins of DAEEP and TAEP Blends with EB270

Resin	Formulation (wt %)			Viscosity (cps)	Flammability	
	EB270	DAEEP	TAEP		LOI	UL-94
EB270	100	0	0	3000 (60°C)	19.5	Fail
EB270-0.17DAEEP	83	17	0	7000	22	Fail
EB270-0.25DAEEP	75	25	0	3200	23	Fail
EB270-0.33DAEEP	67	33	0	1800	25	Fail
EB270-0.50DAEEP	50	50	0	540	25.7	Fail
DAEEP	0	100	0	21	29	V ₀
EB270-0.17TAEP	83	0	17	9000	22	Fail
EB270-0.25TAEP	75	0	25	4800	23	Fail
EB270-0.33TAEP	67	0	33	2800	25.2	Fail
EB270-0.50TAEP	50	0	50	825	26	Fail
TAEP	0	0	100	23	36	V ₀

The viscosity of a resin formulation is one of the most important parameters because it affects its flow ability, air release rate, and photopolymerization rate and the final properties of the cured film. Reactive monomers and sometimes organic solvents¹⁵ are generally added to adjust a formulation's viscosity. As EB600 and EB270 are viscous oligomers, the addition of modifiers as diluents is necessary to reduce the viscosity. As shown in Tables I and II, the viscosity of the samples sharply decreased with the addition of DAEEP and TAEP, and this resulted from the lower viscosity of DAEEP and TAEP. Moreover, the rapid viscosity reduction further indicated that DAEEP and TAEP had good miscibility with EB600 and EB270.

Photopolymerization kinetics

The properties of a UV-cured film, which are very important to its applications, depend not only on the resin's composition but also on its photopolymerization kinetics. The most important parameters characterizing the curing kinetics of a resin are the rate at the peak maximum (R_p^{\max}) and the final degree of double-bond conversion (P^f). Figures 2 and 3 show the photopolymerization rates and the unsaturation conver-

sions of resins obtained from photo-DSC measurements at 50°C.

The photopolymerization rate of each sample showed a steep increase at the start of reaction; it reached R_p^{\max} and then dropped rapidly. R_p^{\max} increased with increasing DAEEP and TAEP concentrations in the EB600 and EB270 resins. The higher R_p^{\max} values were attributed to the high concentration of double bonds and low viscosity. Moreover, narrower peaks for the polymerization rates were obtained as more DAEEP or TAEP was added. A shorter irradiation time to the leveling off of the unsaturation conversion curves was obtained with increasing concentrations of DAEEP and TAEP, as shown in Figure 3. This occurred because the reactivity of the acrylic groups was promoted by the viscosity reduction of the resins. The photopolymerization occurred not only among oligomers (EB600 and EB270) but also between oligomers and monomers (DAEEP and TAEP). The final unsaturation conversion of double bonds decreased as more monomers were added. It may be concluded that the preformation of a gel with a certain crosslink density (V_c) restricted the polymeric radicals for further photopolymerization.

TABLE II
Viscosity and Flammability of the Resins of DAEEP and TAEP Blends with EB600

Resin	Formulations (wt %)			Viscosity (cps)	Flammability	
	EB600	DAEEP	TAEP		LOI	UL-94
EB600	100	0	0	3000 (60°C)	21	Fail
EB600-0.17DAEEP	83	17	0	1300 (60°C)	26	Fail
EB600-0.25DAEEP	75	25	0	4500	27	Fail
EB600-0.33DAEEP	67	33	0	2000	27.7	V ₂
EB600-0.50DAEEP	50	50	0	550	28.3	V ₀
EB600-0.17TAEP	83	0	17	1300 (60°C)	26	Fail
EB600-0.25TAEP	75	0	25	8100	27.3	Fail
EB600-0.33TAEP	67	0	33	3200	28.3	V ₁
EB600-0.50TAEP	50	0	50	900	31.5	V ₀

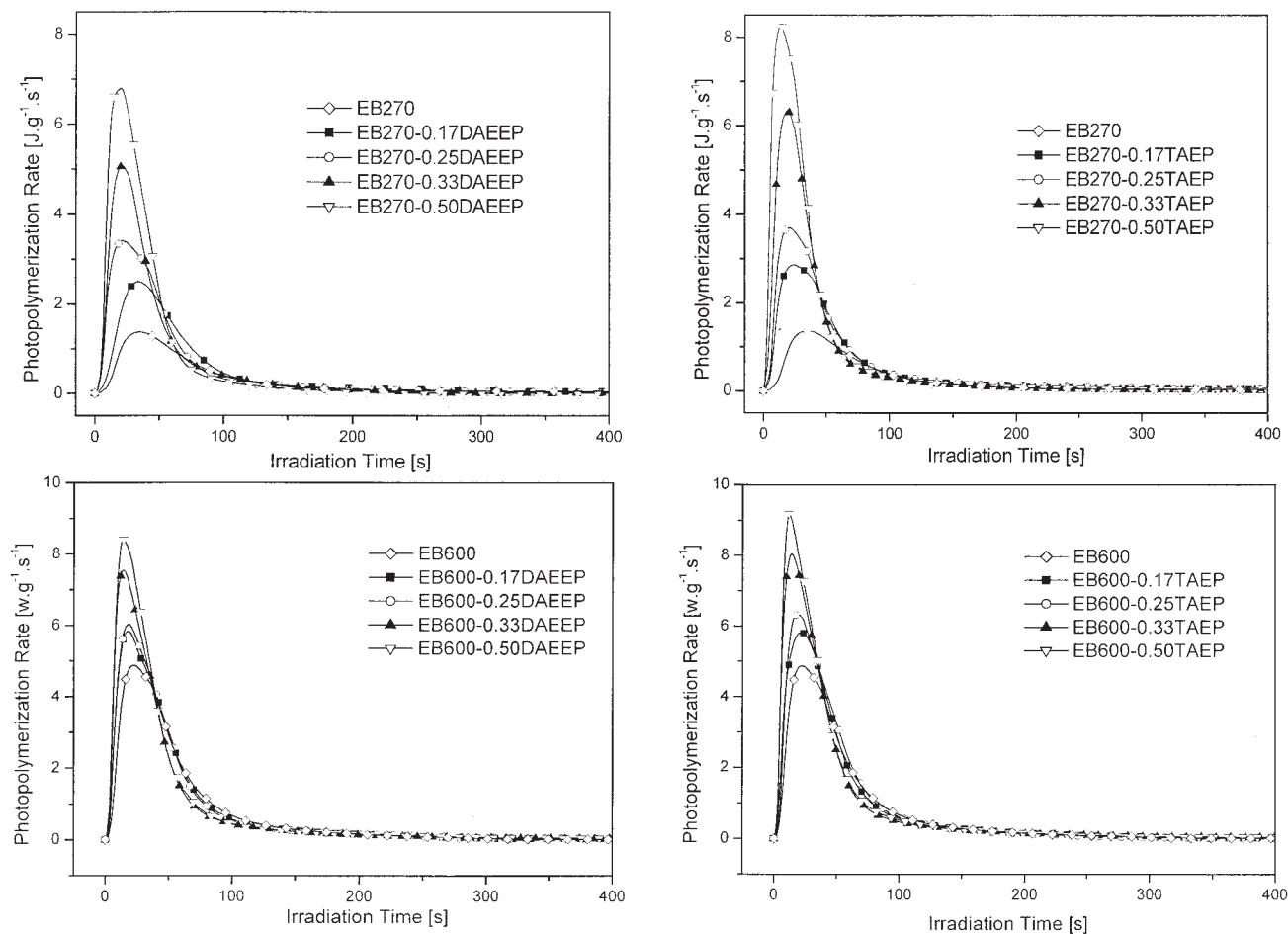


Figure 2 Photopolymerization rates of the resins.

Figures 2 and 3 also show that R_p^{\max} of the resins with the addition of TAEP was higher than that of the resins with the addition of DAEEP, whereas P^f of the former was lower than that of the latter. The higher R_p^{\max} values could be due to the higher double-bond density of TAEP. The lower P^f values were attributed to the higher V_e values of TAEP, which were due to its trifunctionality (vs the difunctionality of DAEEP).

Thermal degradation behavior

The thermal behaviors of the UV-cured DAEEP and TAEP films have been reported elsewhere.¹¹ The degradation of the UV-cured DAEEP and TAEP films could be divided into three steps. From 160 to 270°C, the degradation was mainly due to the fast degradation of phosphate groups. From 270 to 350°C, poly(phosphoric acid) formed, and it catalyzed the breakage of carbonyl groups to form polynuclear aromatic structures. When the temperature was increased beyond 500°C, some unstable structures in the char decomposed, and this resulted in the formation

of phosphorous oxides and some volatilizable aromatic molecules.

The TG curves of the UV-cured EB270 samples containing different concentrations of DAEEP or TAEP are shown in Figure 4. The UV-cured pure EB270 sample without the addition of DAEEP or TAEP degraded in two main steps. The first one started at 180°C with a derivative thermo-gravimetry (DTG) peak at 350°C, and the second one started at 489°C with a DTG peak at 558°C. No residue was observed at 610°C. The degradation process of all other UV-cured samples could also be divided into two stages. The temperature ranges of the different stages, the temperatures of the fastest degradation (peak temperatures), and the mass loss in each stage are listed in Table III. During the thermal degradation, the samples with higher DAEEP concentrations began to degrade at a lower temperature with less mass loss in the first stage, whereas a broader temperature range with a higher mass loss was observed in the second one. This can be explained by the fact that the phosphorus-containing moieties, which degraded at low temperatures, could react further with the polynuclear aro-

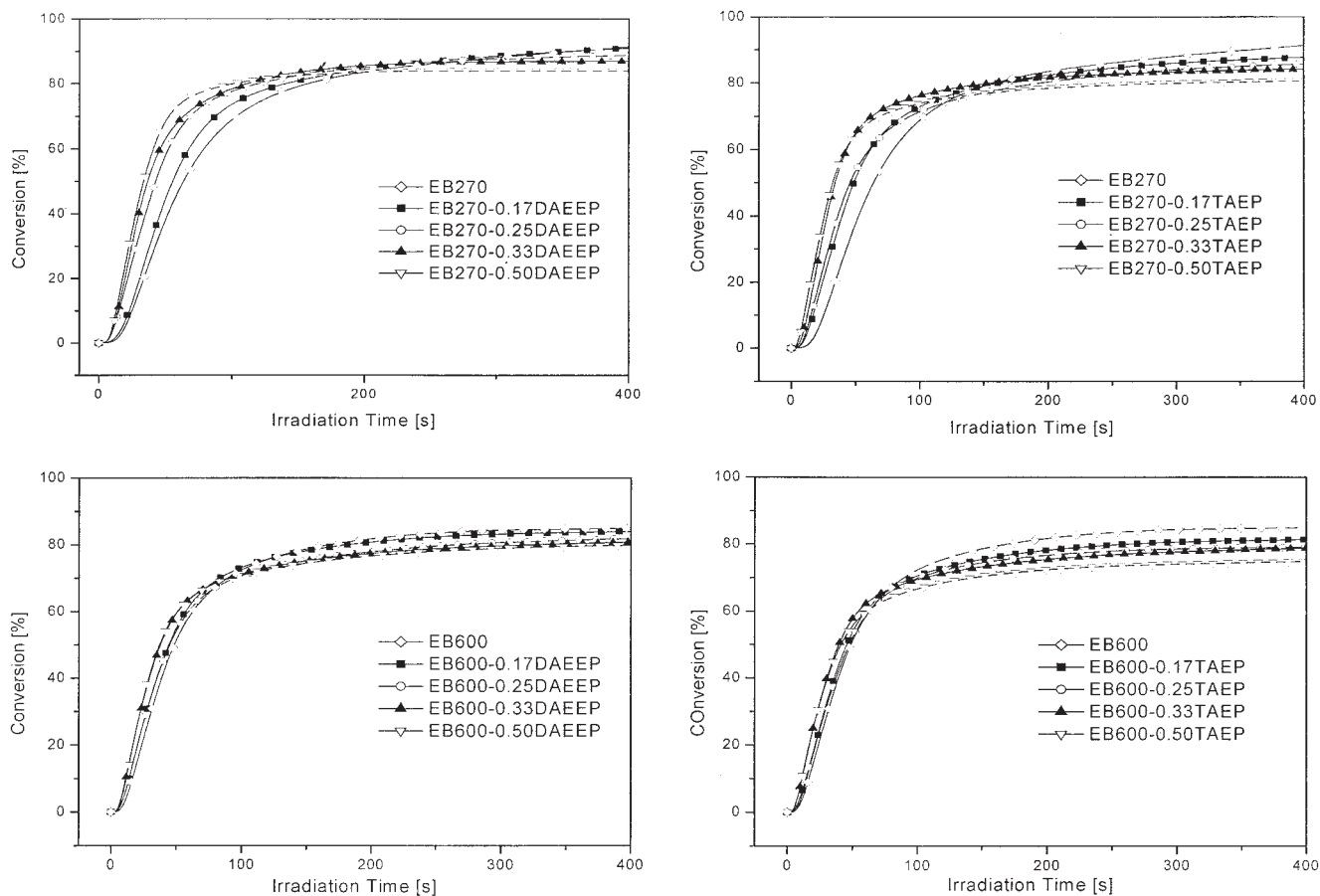


Figure 3 Unsaturation conversion versus the irradiation time of the resins.

matic carbon formed during degradation and produce thermally stable phosphorus-carbon structures by grafting or linking different aromatic carbons.¹⁶ The thermal behaviors of EB270 samples with different TAEP concentrations were similar, except that their higher V_e values may have slightly improved the thermal stability during the first degradation stage of the

samples. This can be proved by the fact that the samples with the addition of TAEP experienced less mass loss in the first stage than the samples with the same loading level of DAEEP. Moreover, Table III shows that EB270-0.50DAEEP had a char yield of 11%, which was higher than that of 9% for pure DAEEP. EB600-0.33TAEP and EB270-0.50TAEP had char

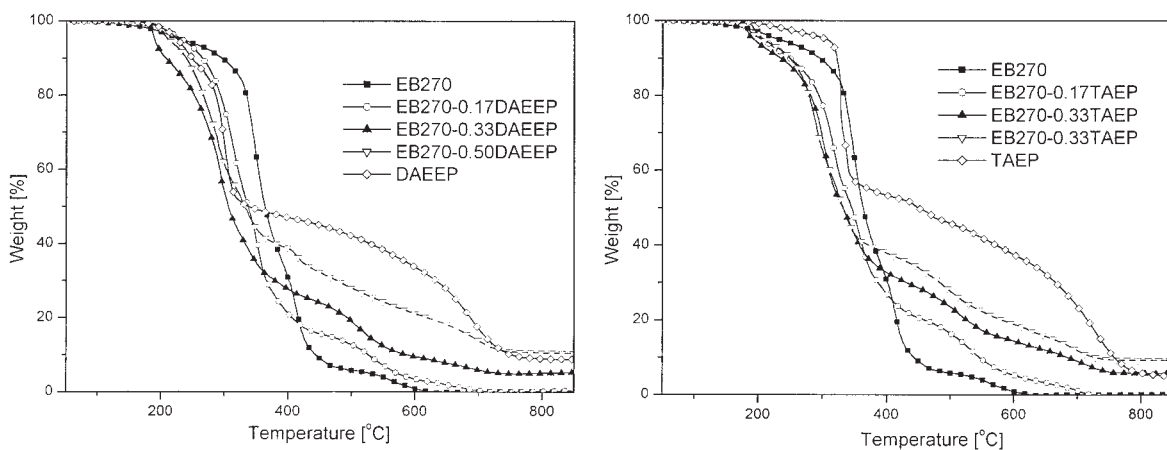


Figure 4 TGA curves of the cured EB270 resins with the addition of DAEEP or TAEP.

TABLE III
TGA Data of the UV-Cured Resins of DAEPP and TAEP Blends with EB270

Resin	First degradation temperature (°C)			Second degradation temperature (°C)		Char yield (%)
	Range	DTG peak	Mass loss (%)	Range	Mass loss (%)	
EB270	180–489	350	94	489–610	6	0
EB270–0.17DAEPP	177–448	312	84	448–737	16	0
EB270–0.33DAEPP	175–407	294	73	407–731	22	5
EB270–0.50DAEPP	174–382	287	60	382–743	29	11
DAEPP	171–335	303	50	335–772	41	9
EB270–0.17TAEP	176–448	316	79	448–747	21	0
EB270–0.33TAEP	174–404	298	68	404–764	26	6
EB270–0.50TAEP	175–376	292	60	376–752	31	9
TAEP	181–363	331	44	363–822	51	5

yields of 6 and 9%, respectively, which were also higher than that of 5% for pure TAEP. These results imply that there were some interactions between the degradation products of the phosphorus-containing monomers and those of EB270.

To investigate the interactions, we present the weight difference curves of the samples in Figure 5. For all the samples, the destabilization behavior in the temperature range of 180–410°C (peak around 320°C) and the stabilization behavior in the temperature range of 410–520°C can be observed. This is because the decomposition product of DAEPP and TAEP, poly(phosphoric acid), catalyzed the degradation of EB270 and then further reacted with the decomposition products of EB270; this reduced the production of inflammable volatile compounds and promoted the formation of crosslinked char at higher temperatures. Therefore, the samples with the addition of DAEPP or TAEP had higher char yields than pure DAEPP or TAEP samples.

The TG curves of the UV-cured films of EB600 with different concentrations of DAEPP or TAEP are shown

in Figure 6. The degradation process of all the UV-cured samples could also be divided into two stages. The temperature ranges of the different stages, the temperatures of the fastest degradation (peak temperature), and the mass loss in each stage are listed in Table IV. During the thermal degradation, the samples with the addition of DAEPP or TAEP began to degrade at lower temperatures with less mass loss in the first stage, whereas a broader temperature range with a higher mass loss was observed in the second one. However, the UV-cured EB600 samples had less mass loss in the first stage than the EB270 samples with different DAEPP or TAEP concentrations. This indicated that the former were more thermally stable than the latter. Moreover, EB600–0.33DAEPP had the least mass loss in the first stage and the highest mass loss in the second one among the samples of EB600 with different DAEPP concentrations; this was similar to the situation for EB600–0.33TAEP. Moreover, EB600–0.50DAEPP had a higher char yield than pure DAEPP. Similarly, EB600–0.33TAEP and EB600–0.50TAEP had higher char yields than pure TAEP. This implied

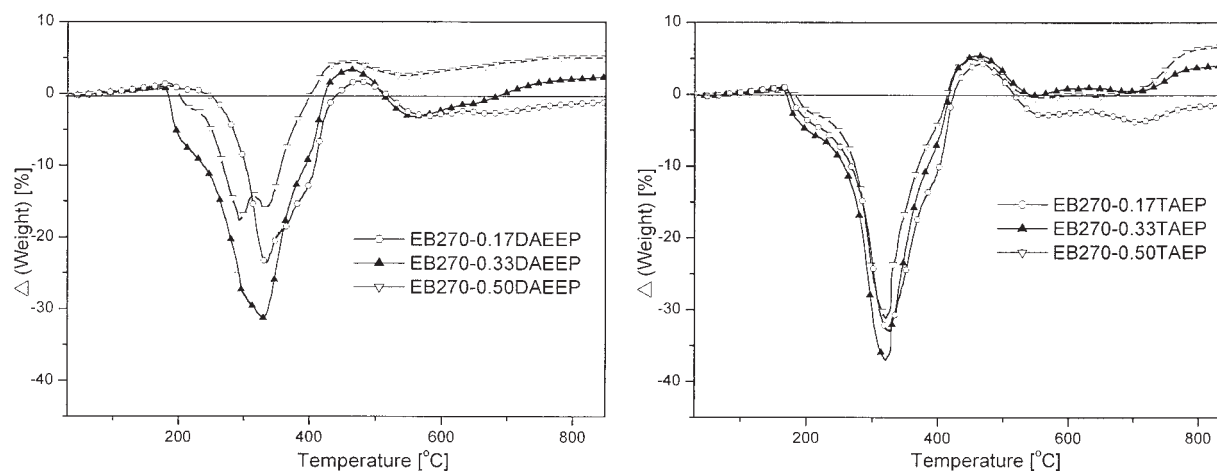


Figure 5 Curves of the weight difference for the EB270 resins with the addition of DAEPP or TAEP.

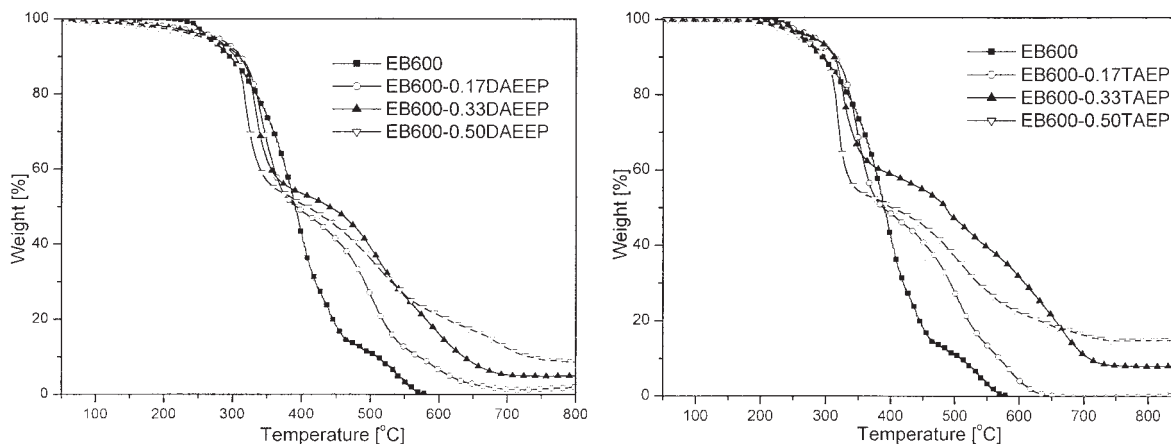


Figure 6 TGA curves of the EB600 resins with the addition of DAEAP or TAEP.

that there were also some interactions between the degradation products of the phosphorus-containing monomers and those of EB600.

The weight difference curves of the samples are shown in Figure 7. The weight-loss difference for the UV-cured EB600–DAEAP blends in the temperature range of 240–340°C was positive, whereas that for the EB600–TAEP blends was negative. This was because the quantity of C_2H_4 and $(HO)_3POC_2H_5$ resulting from the decomposition of DAEAP in the first temperature range was smaller because it was partially retained by the cured EB600 network because of its high V_c value. The UV-cured EB600–DAEAP and EB600–TAEP samples showed an important zone of destabilization in the temperature ranges of 340–380°C and 280–380°C, respectively. These could be attributed to the fact that poly(phosphoric acid) catalyzed the degradation of EB600 and the intumescent formulation was developed. Then, the UV-cured samples were stabilized over 380°C with an important quantity of thermally stable char produced from the reactions between the decomposition products of EB600 and DAEAP or

TAEP. Moreover, the maximal difference weight around 460°C for EB600–0.33DAEAP was the biggest, and this was similar to the situation for EB600–0.33TAEP. This may imply that the reaction at this loading level between the decomposition products for EB600 and DAEAP or TAEP was more sufficient than that at other loading levels. However, the higher loading level could improve the final char yield, as shown in Table IV.

Figures 5 and 7 show that the UV-cured samples of EB600 with the addition of DAEAP or TAEP had smaller destabilization peaks and bigger stabilization peaks than EB270 with the addition of DAEAP or TAEP. This indicates that DAEAP and TAEP were less effective at developing char around 400°C for EB270 than for EB600.

Flammability

The LOI and UL-94 tests are widely used to evaluate the flame-retardant properties of materials and to screen flame-retardant formulations. UL-94 is a testing method for flame-retardancy. During the test, the

TABLE IV
TGA Data of the UV-Cured Resins of DAEAP and TAEP Blends with EB600

Resin	First degradation temperature (°C)			Second degradation temperature (°C)		Char yield (%)
	Range	DTG peak	Mass loss (%)	Range	Mass loss (%)	
EB600	235–470	387	86	470–570	14	0
EB600–0.17DAEAP	191–408	342	51	408–697	46	3
EB600–0.33DAEAP	182–391	334	45	391–706	49	6
EB600–0.50DAEAP	176–370	318	45	370–760	45	10
DAEAP	171–335	303	50	335–772	41	9
EB600–0.17TAEP	187–399	344	52	399–679	48	0
EB600–0.33TAEP	183–394	325	40	394–752	51	9
EB600–0.50TAEP	182–362	317	47	362–743	38	15
TAEP	181–363	331	44	363–822	51	5

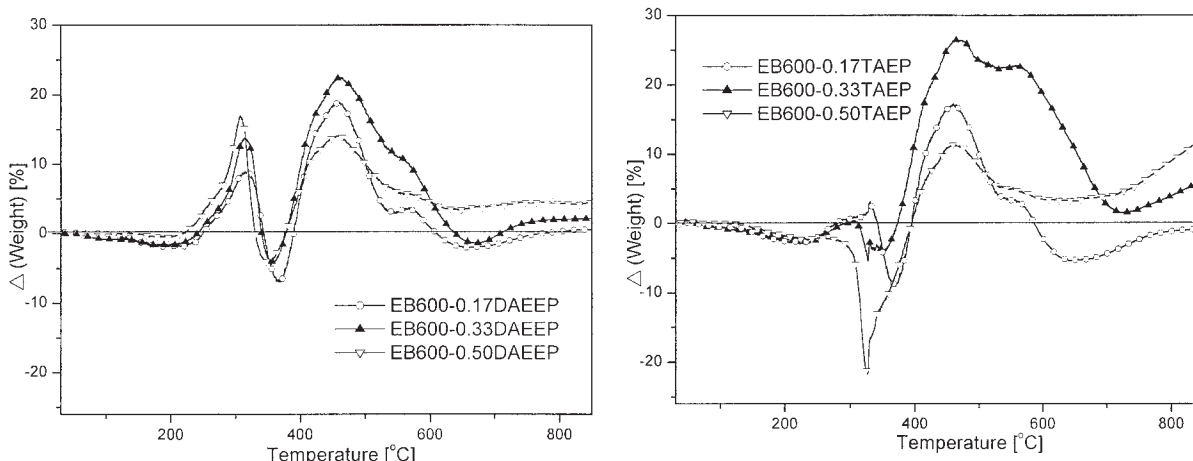


Figure 7 Curves of the weight difference for the EB600 resins with the addition of DAEEP or TAEP.

polymer specimen was subjected to two 10-s ignitions. After the first ignition, the flame was removed and the time for the polymer to self-extinguish (t_1) was recorded. Cotton ignition would be noted if polymer dripping occurred during test. After cooling, the second ignition was performed on the same sample and the self-extinguishing time (t_2) and dripping characteristics were recorded. If t_1 t_2 is less than 10 s with no dripping, it is considered to be a V-0 material, an industrial standard for flame-retardancy. Tables I and II list the LOI and UL-94 data for the samples. The LOI values increased as the DAEEP or TAEP concentration increased in the EB600 and EB270 resins. Moreover, DAEEP and TAEP were more available to increase the LOI values for EB600 than for EB270. This was attrib-

uted to their thermal behaviors. The EB600 resin with 33% DAEEP or TAEP reached the V₂ or V₁ grade in the UL-94 tests, and this resulted from the greater efficiency of the monomers for developing char around 400°C for EB600 than for EB270.

Dynamic mechanical thermal properties

Dynamic mechanical thermal analysis (DMTA) provides information about the microstructure of a cured film. The E' and $\tan \delta$ curves of the UV-cured EB600 samples with DAEEP or TAEP are shown in Figures 8 and 9. The softening point (T_s) is defined as the extrapolated onset of the drop of E' . The glass-transition temperature (T_g) is defined as the peak of the $\tan \delta$

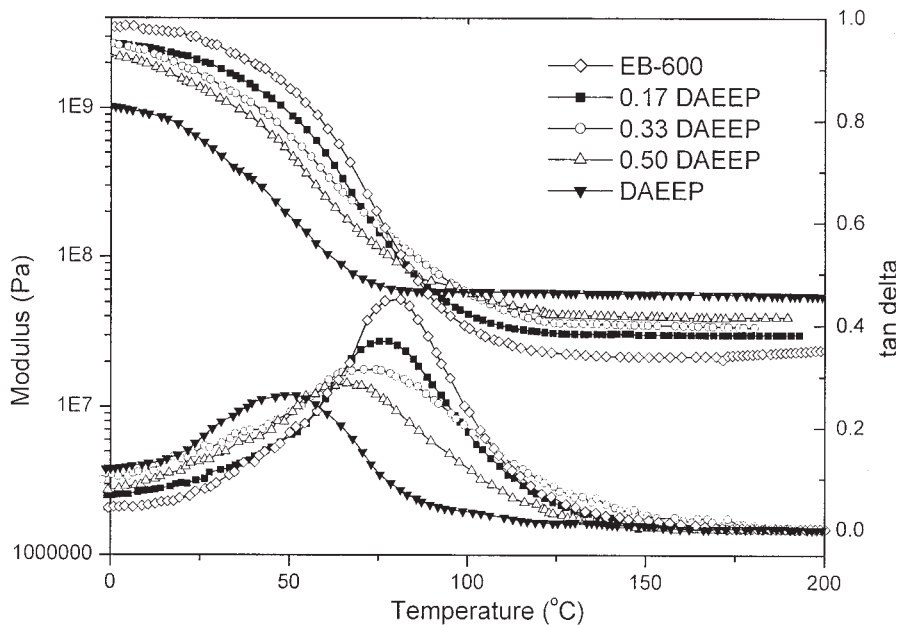


Figure 8 DMTA curves of the EB600 resins with the addition of DAEEP.

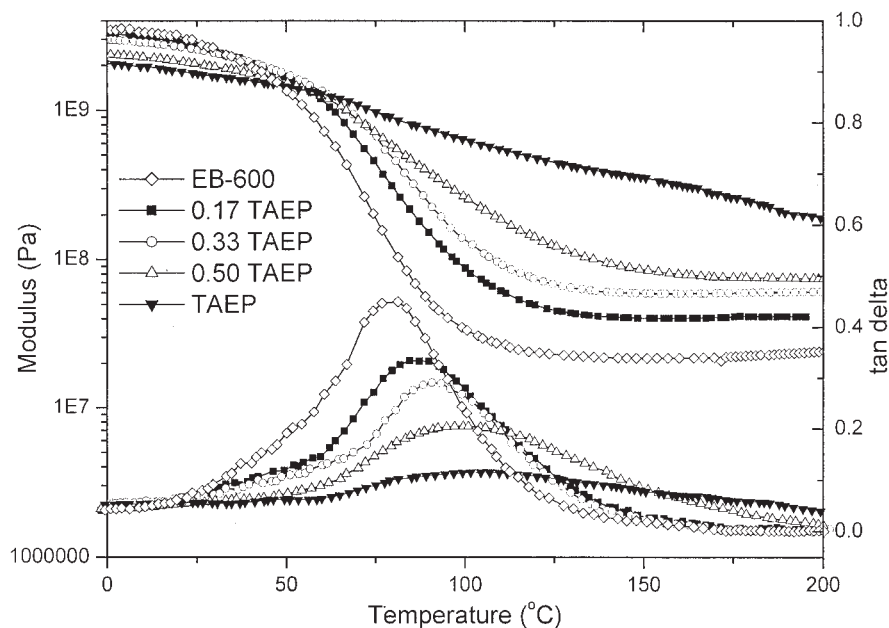


Figure 9 DMTA curves of the UV-cured EB600 resins with the addition of TAEP.

curve. The T_s/T_g ratio expresses the width of the $\tan \delta$ peak; it is a rule that a higher T_s/T_g ratio leads to a narrower $\tan \delta$ peak.¹⁷ V_e (i.e., the molar number of elastically effective network chains per cubic centimeter of a sample) was calculated with the following formula: $V_e = E'/3RT$, where R is the gas constant and T is the temperature (K).¹⁸

The DMTA results for the UV-cured films are also listed in Table V. V_e increased with an increasing concentration of DAEEP or TAEP in EB600. Moreover, V_e of EB600 with TAEP was higher than that of EB600 with DAEEP. These were also investigated with photo-DSC, as discussed previously. A higher V_e values made the chain more restricted and made chain motion possible at higher temperatures. However, the incorporated phosphate units, which greatly reduced the rigidity of the polymer chains, made chain motion possible at lower temperatures.⁹ As listed in Table V,

both T_g and T_s of the UV-cured films decreased with increasing DAEEP concentration, whereas they increased with increasing TAEP concentration. This was because the incorporation of phosphate units was the main factor as the DAEEP concentration increased, and this resulted in the reduction of T_g and T_s for the UV-cured films. However, V_e was the main factor as the TAEP concentration increased, and this made T_g and T_s shift to high temperatures. Moreover, Figures 6 and 7 show that the peak of $\tan \delta$ became flatter for the samples with more DAEEP or TAEP. This was also due to V_e increasing as the DAEEP or TAEP concentration increased. The higher V_e values also made the length of the elastically effective network chains of the samples more inhomogeneous and the $\tan \delta$ peak broad. As a result, the T_s/T_g values decreased with more DAEEP or TAEP, as shown in Table V. Moreover, the T_s/T_g values decreased insignificantly as the DAEEP or TAEP concentration increased; this implied good miscibility between the oligomers and monomers.

TABLE V
DMTA Results of the UV-Cured Resins of DAEEP and TAEP Blends with EB600

Resin	T_e (°C)	T_g (°C)	T_e/T_g	V_e (mmol/ml)
EB600	50	79	0.92	2.19
EB600-0.17 DAEEP	43	77	0.90	3.04
EB600-0.33 DAEEP	34	72	0.89	3.57
EB600-0.50 DAEEP	29	66	0.89	4.08
DAEEP	24	50	0.92	6.75
EB600-0.17 TAEP	54	86	0.91	4.01
EB600-0.33 TAEP	57	92	0.90	5.87
EB600-0.50 TAEP	59	101	0.89	7.21
TAEP	61	105	0.88	17.32

CONCLUSIONS

The addition of DAEEP or TAEP to EB600 and EB270 can greatly reduce the viscosity and promote the photopolymerization rates of the resins. The thermal stability of the UV-cured resins can be improved by the loading of DAEEP or TAEP. In comparison with EB270, the thermal stability of EB600 with the addition of DAEEP or TAEP is more significant because the interaction between the decomposition products for UV-cured EB600 and the monomer is more effective. Moreover, the flame retardancy of the cured films

can be improved with the addition of DAEEP and TAEP.

Good miscibility between the oligomers and monomers was observed with DMTA. T_g decreased as the DAEEP concentration increased because of the reduction in the rigidity of the cured films. However, T_g increased along with an increasing TAEP concentration because of the higher V_e values of the cured films.

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