

Halogen-Free Flame Retardant Epoxy Resins from Hybrids of Phosphorus- or Silicon-Containing Epoxies with an Amine Resin

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ABSTRACT: Epoxy–melamine hybrid resins were obtained from *in situ* polymerization of siliconized (SE500) and phosphorylated (PE690) epoxy resins with hexakis(methoxymethyl)melamine (HMMM). The hybrid resins having HMMM contents less than 15 wt % exhibited high transparency and homogeneity. The compatibilities between SE500 and melamine as well as that between PE690 and melamine were poor than the compatibility between general bisphenol-A epoxy and melamine. Incorporation of HMMM

altered the degradation mechanisms and enhanced the thermal stability of the epoxy resins, especially for PE690 based resins. Excellent flame retardant property was observed with the hybrid resins because of the Si–N and P–N synergisms of flame retardation. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1071–1077, 2006

Key words: epoxy; melamine; synergism; flame retardant

INTRODUCTION

Halogen-free flame retardant epoxy resins are desired in the developments of “green” printed circuit boards and semiconductor devices for modern microelectronics. To remove halogenated flame retardants from the epoxy formulations, some alternatives containing phosphorus, silicon, and nitrogen groups are reported.^{1–12} In addition, synergistic systems from combination of more than two flame retardation mechanisms or flame retardant elements are also studied to enhance the efficiency of flame retardants.^{13–18} Some workable examples are phosphorus/silicon and phosphorus/imide synergisms. The enhancement of thermal stability from incorporation of silicon and imide groups to epoxy resins is also noteworthy, as high thermal stability is very attractive for epoxy resins practically utilized in modern lead-free microelectronics.

Melamine resins are cheap plastics and are used earlier in adhesives, laminating resins, molding compounds, and coatings.^{19–22} The nitrogen-rich melamine group is expected to impart flame retardancy to polymers, since melamine groups form polymeric products of melam and melem via a de-ammonia re-

action under heat.^{23,24} Both melam and melem are highly heat-insulating and thermally stable, therefore, to perform a flame retardant effect to polymers in condensed phase. In addition, ammonia gas evolved from thermal degradation of melamine is incombustible to play a significant effect of flame retardancy in gas phase. In the previous work,²⁵ we prepared epoxy/melamine hybrid resins through *in situ* polymerization of hexakis(methoxymethyl)melamines (HMMM) and diglycidylether of bisphenol-A (DGEBA). Incorporation of melamine structure into epoxy resin compositions enhanced their thermal stability and flame retardancy. In this work, siliconized and phosphorylated epoxy compounds are used to replace DGEBA in formation of epoxy–melamine hybrid resins to further promote the performance of epoxy–melamine hybrid resins and to examine the silicon–nitrogen and phosphorus–nitrogen synergisms on flame retardancy and thermal properties of epoxy resins.

EXPERIMENTAL

Materials

Hexakis(methoxymethyl)melamine (HMMM) was from Monsanto Chemical Company. *p*-Toluenesulfonic acid (*p*-TSA), tetrahydrofuran (THF), 4,4'-diaminodiphenylmethane (DDM), and (3-glycidoxypropyl)trimethoxysilane (GPTMS) were obtained from Aldrich Chemical Company and were used as received. Siliconized (SE500) and phosphorylated (PE690) ep-

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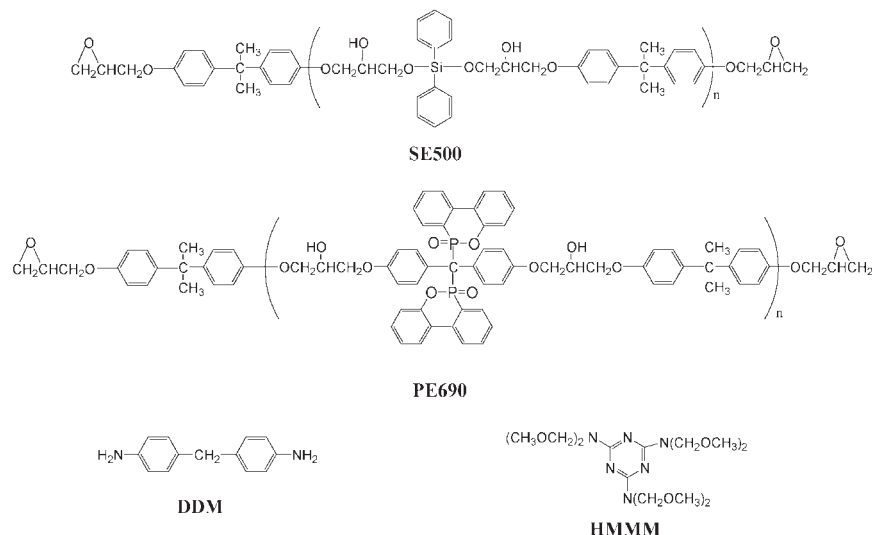


Figure 1 Chemical structures of used epoxy compounds, melamine compound, and curing agent.

oxy compounds, having epoxy equivalent weights of 500 and 690, respectively, were prepared in the laboratory according to the reported method.^{7,15} The chemical structure of HMMM, SE500, and PE690 are shown in Figure 1.

Equipment

The morphology of the fracture surface of the cured hybrid resins was observed with a scanning electronic microscope (SEM, Hitachi S-3000N Hi-SEM, Japan). Energy dispersive X-ray (EDX) measurements were conducted with a Horiba ES-320 EDX micro analyzer equipped in the SEM. DSC thermograms were recorded with a Thermal Analysis DSC-Q10 differential scanning calorimeter at a heating rate of 10°C/min under a nitrogen gas flow of 40 mL/min. Thermogravimetric analysis (TGA) was performed by a Thermal Analysis TGA-2050 thermogravimetric analyzer at a heating rate of 10°C/min under nitrogen or air atmosphere. The gas flow rate was 100 mL/min. Limited oxygen index (LOI) values were measured on a Stanton Redcraft flame meter. The percentage of oxygen in the O₂-N₂ mixture, deemed sufficient to sustain the flame, was taken as the LOI.

Preparation of epoxy-melamine hybrid resins

Epoxy-HMMM hybrid resins with various HMMM contents were prepared through *in situ* epoxy polymerization and HMMM sol-gel reaction.²⁵ The preparation of SEHM-10 (siliconized epoxy hybrid material containing 10 wt % of HMMM) was described below as an example. A solution of HMMM (0.34 g) in THF (20 g) was added with H₂O (0.02 g) and *p*-TSA (0.01 g). The solution was stirred at room temperature for 1 h

to give Solution A. SE500 (3.0 g) and DDM (0.3 g) were dissolved in 20 g of THF. After adding 0.06 g of GPTMS, this solution was stirred at room temperature for 10 min to give Solution B. Solution A and B were then poured together and stirred at 60°C for 30 min and the solvent was evaporated out. The residual was then cured with heat at 120°C (1 h), 160°C (1h), and 190°C (2 h). A clear and transparent resin was obtained.

RESULTS AND DISCUSSION

Preparation of epoxy-melamine hybrid resins

Epoxy-melamine hybrid resins based on SE500 (SEHM) and PE690 (PEHM) were prepared. Various amounts of HMMM were loaded in the preparation compositions as shown in Table I. The elemental contents of the cured epoxy resins were calculated from the curing compositions. Transparent samples of both types of hybrid resins were obtained with HMMM amount less than 15 wt % (Fig. 2). Further, increasing the HMMM amount in resin composition resulted in opaque products because of phase separation. In the previous work, a DGEBA-melamine hybrid resin containing 40% HMMM did not exhibit phase separation behavior. The upper amounts limiting for HMMM in SEHM and PEHM resins are much smaller than the amount for DGEBA-melamine hybrid resins. This result directly indicates the relatively poor compatibilities between SE500 and melamine as well as that between PE690 and melamine, while being compared with the compatibility between DGEBA/melamine. The morphology and homogeneity of the transparent SEHM and PEHM samples were observed with an SEM and an SEM-EDX, respectively. Figure 3 shows

TABLE I
Compositions of Prepared Epoxy–Melamine Hybrid Resins

Hybrid resins	Epoxy type	Amounts of HMMM (wt %)	N contents (wt %)	Si contents (wt %)	P contents (wt %)	Total (N + Si + P) contents (wt %)	T_g (°C)
SEHM-0	SE500	0	1.3	2.6	0	3.9	111
SEHM-5	SE500	5	2.6	2.5	0	5.1	110
SEHM-10	SE500	10	3.9	2.3	0	6.2	105
SEHM-15	SE500	15	5.7	2.2	0	7.9	99
PEHM-0	PE690	0	0.9	0	2.1	3.0	161
PEHM-5	PE690	5	2.3	0	2.0	4.3	154
PEHM-10	PE690	10	3.6	0	1.9	5.5	154
PEHM-15	PE690	15	4.9	0	1.7	6.6	136

the SEM micrographs of fracture surfaces of SEHM-15 and PEHM-15. Separated epoxy and melamine domains were not observed to demonstrate the homogeneity of the hybrid resins. On the other hand, some distinct domains can be seen in nanoscale viewpoint. Therefore, the melamine resin formed nano-sized domains distributing in epoxy resin matrix. The formation of epoxy–melamine hybrid resins is demonstrated. Figure 4 shows the SEM-EDX element mapping micrographs of SEHM-15 and PEHM-15. Silicon and nitrogen elements in SEHM-15 and phosphorus and nitrogen in PEHM-15 were observed. All of the detected elements showed homogeneous distributions in the samples with an observation area of $60 \times 60 \mu\text{m}^2$. The relatively weak signals of nitrogen mapping could be understood with the small nitrogen amounts of the samples. The results from SEM-EDX measurements also give sufficient support to the formation of epoxy–melamine hybrid resins, i.e., the mixing of epoxy and melamine resins is in nanoscale.

Thermal properties of epoxy–melamine hybrid resins

The prepared epoxy–melamine hybrid resins were first examined with DSC (Fig. 5). An obvious baseline shift corresponding to glass-transition behavior (T_g)

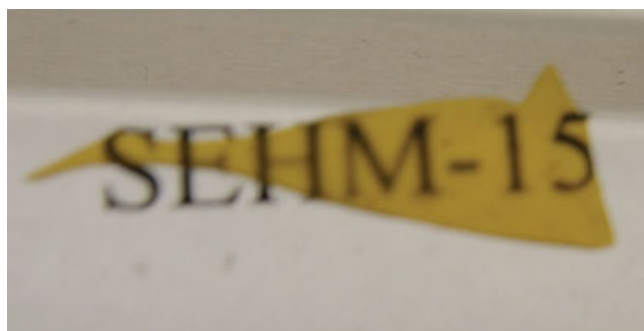
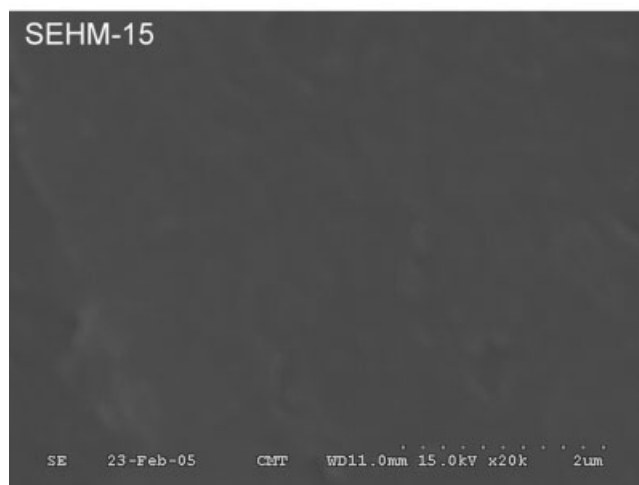


Figure 2 Photograph of SEHM-15: a highly transparent sample. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

was observed for all samples. Since the curing reaction of epoxy resin is exothermic and the gel reaction of hydrolyzed HMMM is endothermic,²⁵ the disappearance of exothermic and endothermic peaks at high



(a)



(b)

Figure 3 SEM micrographs of fracture surfaces of SEHM-15 and PEHM-15.

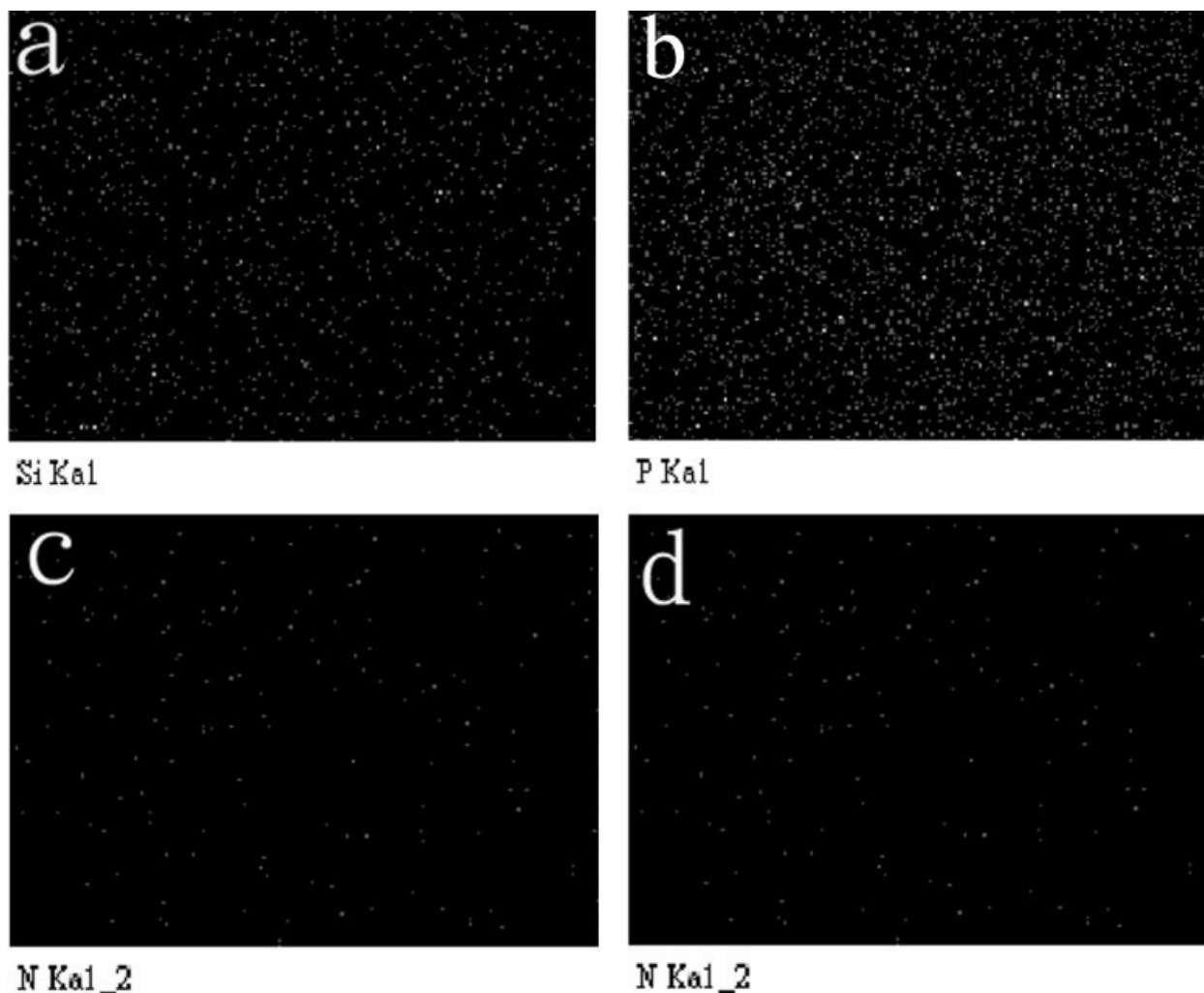


Figure 4 SEM-EDX element mapping on the fracture surfaces: (a) SEHM-15 Si-mapping, (b) SEHM-15N-mapping, (c) PEHM-15 P-mapping, and (d) PEHM-15N-mapping.

temperature region in the thermograms indicates the high conversions of curing reaction for the hybrid resins. Formation of an interpenetrated network (IPN) and an enhancement of glass-transition temperature are expected for the resulting resins from *in situ* curing epoxy and HMMM. However, it is regretful to see that adding HMMM into the epoxy resin compositions resulted in a T_g shift toward low temperatures. The degree of shift also increased with increasing the added amounts of HMMM (Table I). The relatively low glass-transition temperatures of the hybrid resins might be due to the small amounts of the added HMMM, which was not as much as enough to form a complete HMMM network in the hybrid resins. The HMMM domains thus serve like a plasticizer for epoxy resin networks to lower the T_g 's of the hybrid resins. However, an enhancement of T_g was indeed observed with DGEBA/melamine hybrid resin possessing a high HMMM content of 40 wt %.²⁵ Because of the poor compatibility between SE500 and HMMM

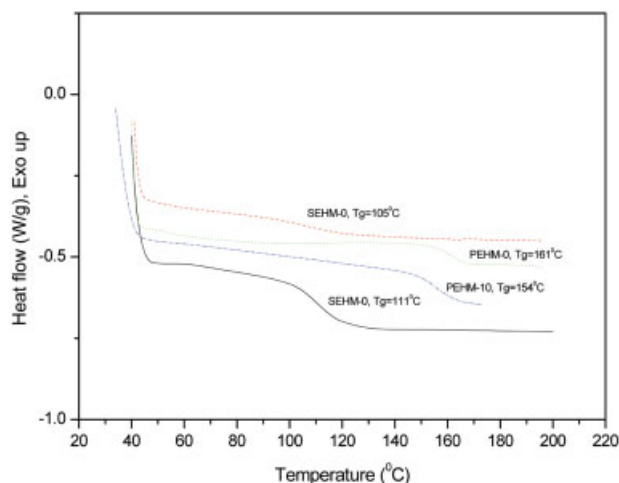


Figure 5 DSC thermograms of some epoxy-melamine hybrid resins: determination of their glass-transition temperatures. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

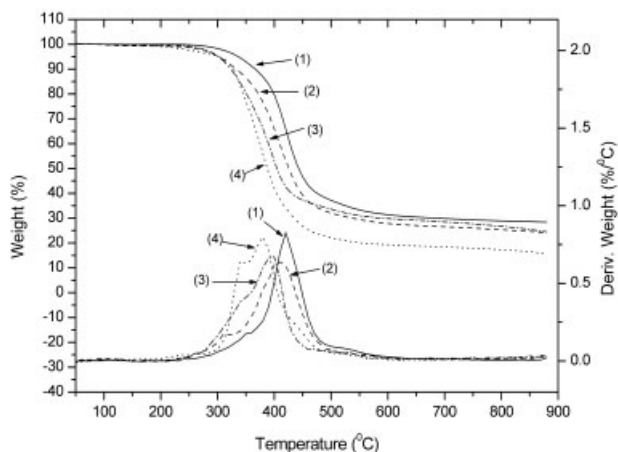


Figure 6 TGA and DTG thermograms of SEHM-0 (Curve 1), SEHM-15 (Curve 2), PEHM-0 (Curve 3), and PEHM-15 (Curve 4) in nitrogen.

as well as that between PE690 and melamine, hybrid resins possess high HMMM contents could not be obtained in this work.

The thermal stability and degradation behavior of the hybrid resins were measured with TGA (Figs. 6 and 7). Some analytical data read from TGA thermograms are collected in Table II. Incorporation of HMMM into epoxy compositions decreased the thermal stability of the resulting resins. While heating in nitrogen, the temperature of onset weight loss (T_d) shifted from 340 to 300°C and from 318 to 302°C for SE500 and PE690 based resins, respectively. The relatively poor thermal stability of HMMM hybrid resins arose from the degradation of HMMM part at low temperature region, since pure HMMM cured resin degraded at around 240°C.²⁵ TGA thermograms presents the temperature-dependent weight loss behavior of the resins. While heating in nitrogen, all of the four

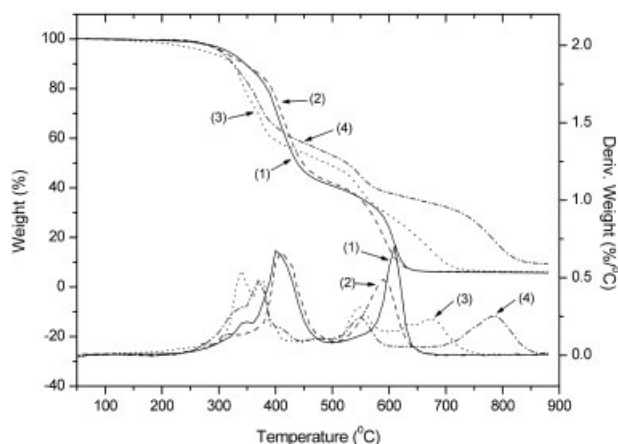


Figure 7 TGA and DTG thermograms of SEHM-0 (Curve 1), SEHM-15 (Curve 2), PEHM-0 (Curve 3), and PEHM-15 (Curve 4) in air.

TABLE II
Thermal Analysis Data of Epoxy and Epoxy/Melamine Hybrid Resins

Sample	T_d (°C)		Char at 700°C (%)		T_{max} (°C)	
	In N ₂	In air	In N ₂	In air	In N ₂	In air
SEHM-0	340	318	31.2	6.0	421	403
SEHM-15	300	300	27.6	6.2	415	408
PEHM-0	318	305	18.7	9.6	380	375
PEHM-15	302	298	29.5	32.3	396	372

samples presented in Figure 6 exhibited similar thermal-degradation patterns. The big shoulders at around 340°C in the differential thermogravimetric (DTG) curves for PE690 based resins were due to the degradation of phosphorous groups. On the other hand, addition of HMMM exhibited different effects on SE500 and PE690 based resins. With HMMM hybridization, the temperature at maximum weight loss rate (T_{max}), which is assigned at the peak position of DTG thermograms, of SE500 based resins decreased from 421 (SEHM-0) to 415°C (SEHM-15). The decrease of T_{max} is reasonable with the low degradation temperature of HMMM. However, an increase of T_{max} was observed with PE690 based resins from 380°C (PEHM-0) to 396°C (PEHM-15). Addition of HMMM showed a significant retardation to the weight loss rate of PE690 resin. At the temperature region of 300–350°C, HMMM domain degraded first and SE500 domain lost weights later. Both TGA and DTG results of SEHM-0 and SEHM-15 suggest that addition of HMMM do not alter the degradation reactions of SEHM resins. For PEHM-15, HMMM and phosphorus groups of PE690 degraded in similar temperature region. The interactions between the degradation products of HMMM and phosphorus groups formed a thermally stable residue attributing to retarding further weight loss.¹⁵ The highly thermally stable residue also resulted in the high char yield of PEHM-15 at high temperatures. The alternation of HMMM on the degradation patterns of PE690 resin is much significant for samples heating in air (Fig. 7). PEHM-0 and PEHM-15 showed similar weight loss behavior and a reduced weight loss rate was observed with PEHM-15 in the temperature range of 300–400°C, as being observed with samples heating in nitrogen. The rapid weight loss arising from oxidative degradation was observed in the temperature region of 550–700°C for PHEM-0. With addition of HMMM, this weight loss shifted to around 700–800°C. The high antioxidative thermal stability of PEHM-15 degradation residue increased the char yield to 32.3 wt % at 700°C. Moreover, the similar weight loss patterns of SEHM-0 and SEHM-15 in air further suggests that addition of HMMM in SE500 does not significantly alter the degradation reactions of the resins.

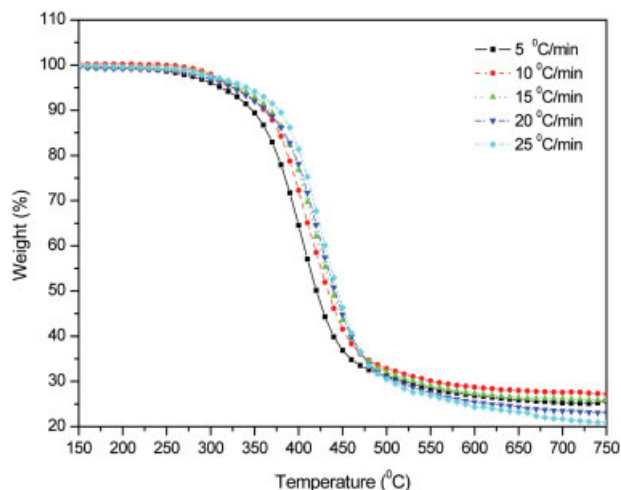


Figure 8 TGA thermograms of SEHM-10 at various heating rates from 5 to 25°C/min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The kinetic studies on the thermal degradation of the hybrid resins were performed with thermogravimetric analysis. The TGA thermograms of SEHM-15 at various heating rates were collected in Figure 8. From the TGA thermograms, it can be seen that the thermal degradation of the hybrid resins was a complex process with multiple stages. Moreover, the degradation processes of the polymer did not vary with heating rates, indicating the calculation method proposed by Ozawa²⁶ for determination of activation energies was suitable for the studied polymers. Ozawa's method could provide activation energy data at all points of the TGA curves and was considered to give reliable data for complicated degradation processes.²⁷ Figure 9 shows the examples of the plots for determination of the activation energies of degradation reactions. The calculated data are collected in Figure 10 to express the relationship between the activation energies varying with degradation reaction conversions. Incorporation of melamine resin increased the activation energies of the hybrid resins in degradation. This enhancement of activation energy should be understood with the thermal resistance of melamine that increased the energy demand for thermal degradation. The high activation energies observed with degradation of SEHM samples are also reasonable, since degradation of silicon groups results in thermally stable silica residuals.

Flame retardant property

According to the condense-phase mechanism of flame retardation, formation of thermally stable char contributes to reduce flammability of a polymeric material through heat resistance and barrier to combustible

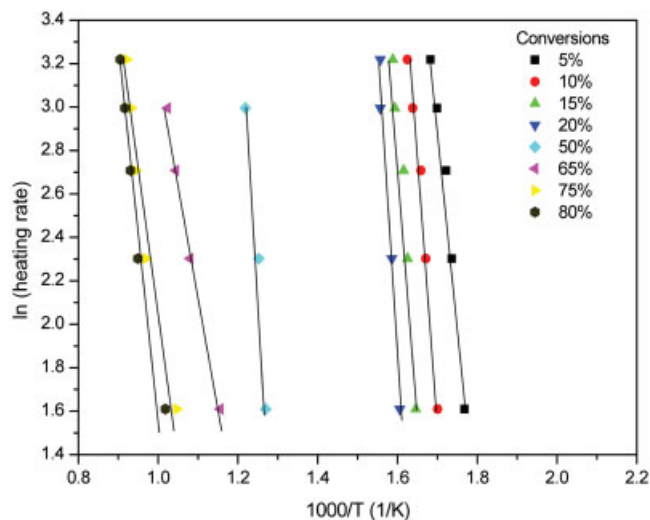


Figure 9 The plots for determining activation energies of the degradation reactions of hybrid resins according to the Ozawa method for PEHM-15 in air. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

gases of the char. In addition, high char yields also correspond to small amount of volatile and combustible parts generated and involved from the thermal degradation of polymeric materials in fire. From this viewpoint, Krevelen²⁸ established a quantitative relationship between char yield and flame retardancy for polymeric materials. Moreover, Liu et al.²⁹ also reported that the integral procedural degradation temperature (IPDT)^{30,31} calculated from the TGA thermogram of a polymer could be applied to an indicator for the amount of volatile part of a polymer in degradation and for its flame retardancy. Table III collects the

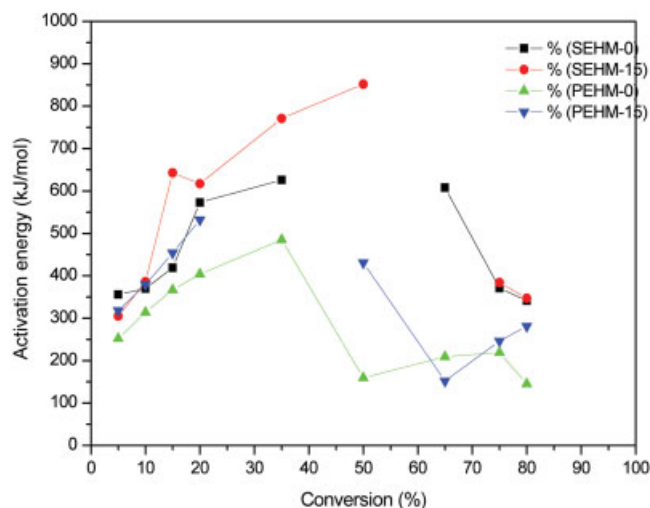


Figure 10 The plots of activation energy against reaction conversions of degradation reactions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE III
Analytical Parameters in Evaluating the Flame Retardancy of the Hybrid Resins

Hybrid resins	Char Yield at 700 °C in air (wt %)	IPDT in air (°C)	LOI
SEHM-0	6.0	385	23.0
SEHM-5	5.4	376	27.0
SEHM-10	5.6	381	27.5
SEHM-15	6.2	385	28.0
PEHM-0	9.6	389	29.0
PEHM-5	32.2	452	30.0
PEHM-10	32.4	428	33.0
PEHM-15	32.3	438	34.0

char yields at 700°C, calculated IPDT values, and measured LOI values of all samples prepared in this work. Addition of HMMM to SE500 did not show significant improvements on the char yields and LOI values of the resulting resins. On the other hand, high char yields and IPDT values were observed with the resins from PE690 and HMMM. The results indicate that addition of HMMM into PE690 altered the degradation mechanisms of the resins and formed highly thermally stable residues in degradation. The high char yields and high LOI values of PEHM resins also indicate their high flame retardancy. The high LOI value of PEHM-15 (34.0) is noteworthy, as in the previous work the DGEBA-HMMM hybrid resin possessing 40 wt % of HMMM only exhibited a LOI value of 32.0.²⁵ It is concluded that addition of HMMM showed effective improvements on the flame retardancy for both SE500 and PE690 resins. The Si—N and P—N synergisms on flame retardancy of epoxy resins are observed and demonstrated.

CONCLUSIONS

The preparation and characterization of epoxy/melamine hybrid resins based on siliconized and phosphorylated epoxy compounds and HMMM were performed. The hybrid resins having HMMM contents less than 15 wt % exhibited high transparency and homogeneity. The compatibilities between SE500 and melamine as well as that between PE690 and melamine were poor than the compatibility between gen-

eral bisphenol-A epoxy and melamine. High LOI values were observed with the hybrid epoxy resins to demonstrate the synergistic effects of Si—N and P—N on the flame retardancy of epoxy resins.

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