Preparation of Silicon-/Phosphorous-Containing Epoxy Resins from the Fusion Process to Bring a Synergistic Effect on Improving the Resins' Thermal Stability and Flame Retardancy

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ABSTRACT: Epoxy resins containing both phosphorous and silicon were prepared via the fusion process of reacting a phosphorous diol and a silicon diol with a bisphenol-A-type epoxy. With various feeding ratios of the reactants, epoxy resins with different phosphorous and silicon contents were obtained. Through curing the epoxies with diaminodiphenylmethane, the cured epoxy resins exhibit tailored glass transition temperatures (159–77°C), good thermal stability (>320°C), and high char yields at 700°C under air atmosphere. The high char yield was demonstrated to come from the synergistic effect of phosphorous and silicon, where phosphorous enriches char formation and silicon protects the char from thermal degradation. Moreover, high flame retardancy of the epoxy resins was found by the high LOI value of 42.5. The relationship of the char yields at 700°C under air atmosphere (ρ) and the LOI values of the epoxy resins could be expressed as LOI = $0.62\rho + 19.2$. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 87: 404–411, 2003

Key words: flame retardance; resin; thermogravimetric analysis

INTRODUCTION

Epoxy resins are widely used as matrix materials for the fabrication of advanced composites in the electrical/electronic industry, owing to their high tensile strength and modulus, good adhesive properties, good chemical and corrosion resistance, low shrinkage in cure, and excellent dimensional stability.[1–4] However, as most of the organic polymers, flammability is one of the main drawbacks of the epoxy resins. Therefore, adding some additional substances into epoxy resins is necessary to reduce their flammability.[5,6] In recent years, with the consideration of avoiding the generation of toxic, corrosive, and halogenated gases as well as releasing the endocrine disrupting chemicals in combustion, the trend is toward using halogen-free flame retardant in polymeric materials.[7–9] Organophosphorous compounds, which generate little toxic gas and smoke under combustion, are among the most studied halogen-free flame retardants.[10–13] By introducing phosphorous into epoxy resins, both phosphorous-containing oxirane compounds and curing agents were prepared.[14–18] On the other hand, the added flame retardants usually bring some negative effects on the physical, mechanical, as well as electrical properties of the polymer matrix. It would be advantageous for polymers if a highly efficient flame retardant was developed to reduce the required amount of additive. Since the flame retardancy of the epoxy resins was found to be highly dependent on the resins' phosphorous contents,[19–21] increasing the flame retardants' phosphorous contents was one of the ways to enhance the flame retardants' efficiency. However, a compound's phosphorous content is limited by the chemical structure of the compound and the synthetic route used to prepare it. On the other hand, the polymeric materials for electronics are asked to have advanced thermal and mechanical properties for the new electronics' processing and packaging techniques. To meet the requirements on thermal properties, most of the phosphorous compounds prepared for epoxy resins' flame retardants are based on aromatic derivatives.[14–20] The structural requirements of the compound limit the phosphorous content the structure can contain and make improving the flame retardancy difficult. However, it would be useful to develop a new epoxy resin system that combines high flame

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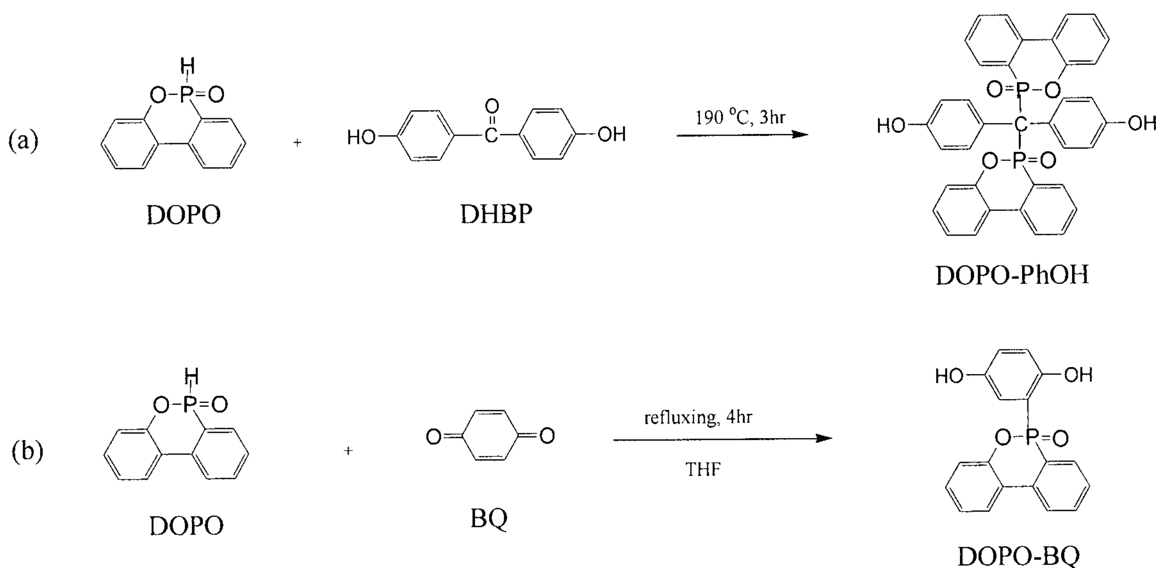


Scheme 1 Synthesis of phosphorous-containing diols.

retardancy with high thermal stability. In previous work,[22,23] phosphorous and silicon playing a synergistic effect on flame retardancy was demonstrated. Incorporating silicon into a phosphorous flame retardant system could significantly level up its flame retardancy. In the present work, phosphorous and silicon were brought together into the epoxies via the fusion process.[24,25] From this process, the contents of phosphorous and silicon of the resulted epoxy resins were also easily altered. The thermal properties and flame retardancy of the cured epoxy resins were investigated. A new phosphorous–silicon-based synergistic flame retardant system for epoxy resins was established.

EXPERIMENTAL

Materials

Diphenylsilanediol (DPSD, from TCI, Tokyo, Japan) was used as received. The A1 catalyst (Chang Chun Plastics Co., Taiwan) was an ethyltriphenylphosphonium acetate/acetic acid complex,[26] which was used as a catalyst for fusion reaction. Triphenylphosphine (TPP, Aldrich) was also used as a fusion reaction catalyst. Bisphenol-A-type epoxy (BE188, epoxy equivalent weight, EEW = 188) was acquired from Chang Chun Plastics Co., Taiwan. 4,4′-Diaminodiphenylmethane (DDM) from TCI (Tokyo, Japan) was used as a curing agent for epoxy resins. The phosphorous compound DOPO-BQ (Scheme 1) was synthesized in our laboratory according to the literature.[26,27] The other phosphorous diol DOPO-PhOH (Scheme 1) was prepared by using the following procedure.[28]

Synthesis of DOPO-PhOH

9,10-Dihydro-oxa-10-phosphaphenanthrene-10-oxide (DOPO, 32 g, 0.15 mol) and 4,4′-dihydroxybenzophenone (DHBP, 5.35 g, 0.025 mol) were mixed together in a 250-mL round-bottomed flask. The mixture was heated to 190°C and stirred for 3 h. The reaction mixture then became thick. After being cooled to 100°C, toluene (150 mL) was added to the flask. The precipitate was filtered and washed with toluene. The obtained solid was then recrystallized from tetrahydrofuran to obtain a white powder product [DOPO-PhOH, yield 75%; meeting point (mp), 324–325°C].

IR (KBr, cm^{-1}): 1181 and 935 (P—O—Ph), 1210 (P═O), 1584 (P—Ph), 3226 (—OH). ^{1}H-NMR [300 MHz, dimethylsulfoxide-d_6 (DMSO-d_6), ppm]: 5.99 (s, 1H); 6.15–6.22 (m, 3H); 6.85–7.13 (m, 7H); 7.25–7.30 (m, 3H); 7.51–7.57 (m, 2H); 7.67–7.78 (m, 4H); 7.91–7.93 (m, 2H); 8.17 (s, 1H); 8.63 (s, 1H); 9.35–9.40 (d, 2H). ^{31}P-NMR (300 MHz, DMSO-d_6, ppm): 29.81 and 31.61. Elemental analysis on $C_{37}H_{26}O_6P_2$: Calcd (%): C, 70.70; H, 4.14; P, 9.87. Found (%): C, 70.70; H, 4.21; P, 9.73.

Preparation of the epoxy through the fusion process

The bisphenol-A-type epoxy BE188 was reacted with the diol compounds (DPSD, DOPO-BQ, and DOPO-PhOH) at 170°C for 60 min with 500 ppm A-1 catalyst or at 190°C for 3 h with 500 ppm TPP catalyst. The reaction compositions (shown in Table I) were calculated based on the 2.0 : 1.0 equival ratio of epoxy group to hydroxyl group. DPSD and DOPO derivatives (DOPO-PhOH or DOPO-BQ, Scheme 1) were charged into the reaction systems with various feeding

TABLE I
Epoxy Resins from The Fusion Process

Epoxy samples	Reaction compositions[a]				Catalyst	Characterization		
	DOPO-PhOH	DOPO-BQ	DPSD	BE188		EEW calc.	EEW meas.	Softening point (°C)
SBE	0	0	1	2	$SnCl_2$	484	505	55
PSE-10	1	0	0	2	TPP	690	721	158
PSE-21	1	0	0.5	3	TPP	638	649	137
PSE-11	1	0	1	4	TPP	612	605	85
PSE-12	1	0	2	6	TPP	585	573	65
PSE-13	1	0	3	8	TPP	572	556	39
SQB-10	0	1	0	2	A-1	538	554	126
SQB-21	0	1	0.5	3	A-1	536	520	80
SQB-11	0	1	1	4	A-1	536	515	60
SQB-12	0	1	2	6	A-1	535	529	52
SQB-13	0	1	3	8	A-1	534	518	45

[a] In equivalent mole ratios.

ratios to result in epoxies with different phosphorous and silicon contents.

Curing procedure for epoxy resins with DDM

The epoxy from the fusion process was mixed with DDM and then cured at 170°C for 1.5 h and postcured at 210°C for 2 h in an oven. The curing compositions were taken on the basis of the equivalent ratio of epoxy group to amine hydrogen of 1 : 0.85.

Determination of the epoxy equivalent weights

The EEW of the epoxy compounds were determined with titration. An amount of 3.00 g of epoxy compound was put into a 250-mL round-bottomed flask, and then 25 mL of 0.2 N HCl/pyridine solution was added. The mixture was then heated to 40°C. While the epoxy compound dissolving in the HCl/pyridine solution, the solution was heated to reflux for 20 min, cooled to room temperature and 6 mL water was added and 0.2 mL of phenolphthalein solution (0.1 wt % in methanol) was added as an indicator. The solution was then titrated with a NaOH solution (0.1*N* in methanol). The EEW value of the epoxy compound was determined with $EEW = (10000W)/[f(B - S)]$, where W is the weight of epoxy compound (g), B is the used amount of 0.1*N* NaOH solution for blank test (mL), S is the used amount of 0.1*N* NaOH solution for sample titration (mL), and f is the calibration factor for NaOH solution's concentration.

Measurements

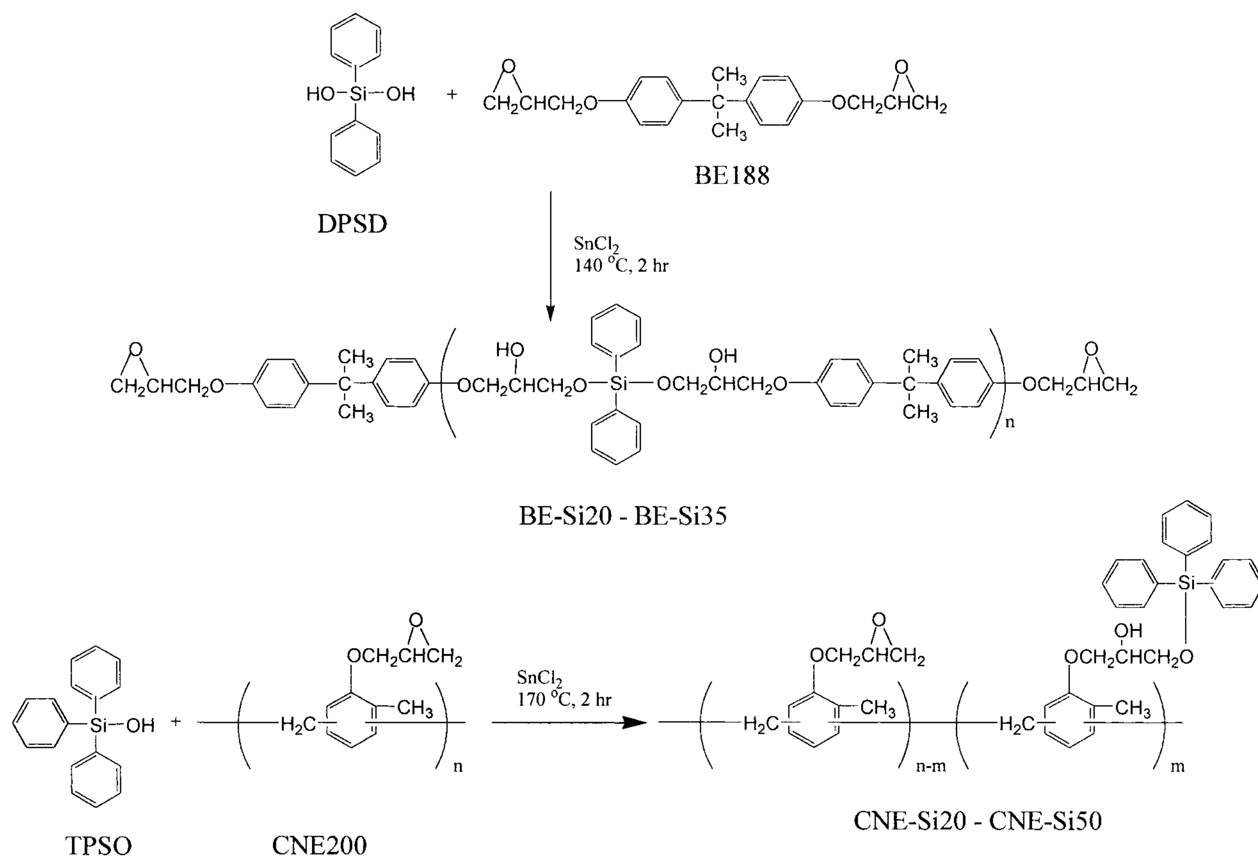
Differential scanning calorimetry (DSC) thermograms were recorded with a Perkin–Elmer DSC 7 at a heating rate of 10°C/min under nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed with a Perkin–Elmer TGA 7 thermogravimetric analyzer at a heating rate of 10°C/min under nitrogen or air atmosphere. Limited oxygen index (LOI) values were measured on a Stanton Redcraft flame meter. The percentage in the O_2–N_2 mixture, deemed sufficient to sustain the flame, was taken as the LOI.

RESULTS AND DISCUSSION

Preparation of the epoxy compounds

The fusion process, being widely used for epoxy chain extension[19,20] and chemical modification,[26–28] performed the coextension reactions of DPSD/DOPO-BQ and BE188 with A1 complex (ethyltriphenylphosphonium acetate/acetic acid complex) as a catalyst (Scheme 2). Transparent products with good conversions were obtained to imply no DPSO remaining in the resulted epoxy compounds. However, although using DOPO-PhOH instead of DOPO-BQ in the fusion reactions, the A1 catalyst was too active to result in gel products. Therefore, TPP was utilized for the coextension reactions of DOPO-PhOH/DPSD and BE188 (Scheme 2). The previous study[29] reported that A1 and TPP were not active enough to promote the addition reaction between oxirane and silanol group. Therefore, the reactivity of silanol group on the oxirane ring might be enhanced by the existence of the phenol derivatives, DOPO-BQ and DOPO-PhOH.

With various reaction compositions, both phosphorous and silicon were successfully incorporated into the resulting epoxy compounds with different phosphorous and silicon contents. The EEW values of the epoxy compounds from titration showed good coincidence with those calculated from the feeding compositions (Table I), to give more evidence to the good conversions of the fusion reactions. Moreover, introducing DPSD into epoxy structure lowers the epoxy compounds' softening points (Table II). This result is reasonable because the silanoxy linkage (from DPSD)



Scheme 2 Preparation of epoxies via the fusion process.

is relatively soft compared with the alkanoxy linkage (from bisphenol-A (BPA)). On the other hand, introducing the DOPO-containing compounds (DOPO-BQ and DOPO-PhOH) into the epoxy compounds' structures increased the compounds' softening points. The elevation on the epoxy compounds' softening points should come from the contributions of the bulk and hard DOPO groups and the large molecular sizes (high EEW values).

Thermal properties of the cured epoxy resins

The glass transition temperatures (T_g) of the cured epoxy resins were measured with DSC and the results

TABLE II
Thermal Analysis of Epoxy Resins Cured with DDM

Epoxy resins	Phosphorous content (wt %)	Silicon content (wt %)	T_g (°C)	TGA analysis data: T_d at 5 wt % loss (°C) N_2	T_d at 5 wt % loss (°C) Air	Char yield at 700°C (wt %) N_2	Char yield at 700°C (wt %) Air	LOI
SBE-D	0.00	2.15	97	376	387	31.5	13.8	22.5
PSE-D-10	4.41	0.00	159	345	338	20.4	27.2	35
PSE-D-21	3.24	0.73	140	332	325	25.2	35.8	42.5
PSE-D-11	2.57	1.16	120	336	320	24.1	23.2	33.5
PSE-D-12	1.81	1.64	98	325	312	23.4	21.8	31
PSE-D-13	1.40	1.90	85	325	315	22.3	17.1	29.5
SQB-D-10	2.12	0.00	140	345	341	22.5	14.2	28
SQB-D-21	1.95	0.89	129	345	319	22.1	10.7	26
SQB-D-11	1.50	1.35	106	322	315	22.3	10.1	26
SQB-D-12	1.01	1.83	85	311	302	22.3	8.1	25
SQB-D-13	0.77	2.08	77	302	293	22.0	7.4	23.5
BPA-490-D	0.00	0.00	111	372	375	15.1	0.0	22

are listed in Table II. Incorporation of the soft silanoxy linkage decreased the cured epoxy resins' T_g, and incorporation of the hard DOPO group increased the T_g of the resins. The PSE-D epoxy resins showed higher T_g's than did the SQB-D epoxy resins, owing to PSE-D epoxies containing twice the amount of DOPO group. With various epoxy compounds from the fusion reactions, the cured epoxy resins T_g were easily tailored within a range of 77 to 159°C.

The thermal stability of the cured epoxy resins was estimated with the onset decomposition temperatures at a 5% weight loss (T_d) in the TGA. Incorporating DPSD groups into epoxies did not alter epoxy resins' thermal stability, as SBE-D and BPA-490-D exhibiting similar T_d (376 and 372°C). However, the T_d of SBE-D was much higher than that of other triglycidyloxyphenyl-based epoxy resin (T_d = 215°C).[30,31] Because the oxydiphenylsilane group (—O—$SiPh_2$—O—) was reported to exhibit a high thermal stability over 400°C,[32–34] it was reasonable that replacing triglycidyloxyphenyl silane group with oxydiphenylsilane group (—O—$SiPh_2$—O—) significantly improved the silicon-containing epoxy resins' thermal stability.

Although phosphorous-containing diols (DOPO-PhOH and DOPO-BQ) were incorporated into the silicon-based epoxies, the thermal stability of the cured resins was lowered, owing to that phosphorous groups decomposed at relatively low temperature regions.[10–19] However, the degradation temperatures (>320°C) of the phosphorous-/silicon-containing epoxy resins were still higher than other phosphorylated epoxy resins.[16–18] The good thermal stability implied that the resins have application potential for advanced electronic/electrical materials. On the other hand, it was noteworthy that the thermal stability of the PSE-D and SQB-D series cured resins decreased with increasing the resins' silicon contents. This phenomenon was unusual and needed more examination.

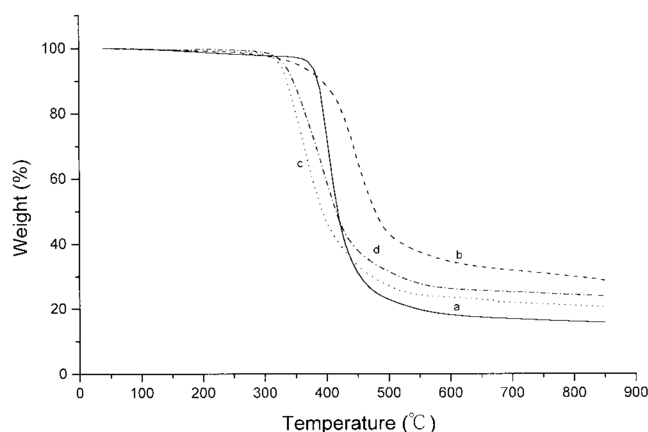


Figure 1 TGA thermograms of cured epoxy resins under nitrogen atmosphere: (a) BPA-490-D; (b) SBE-D; (c) PSE-D-10; (d) PSE-D-21.

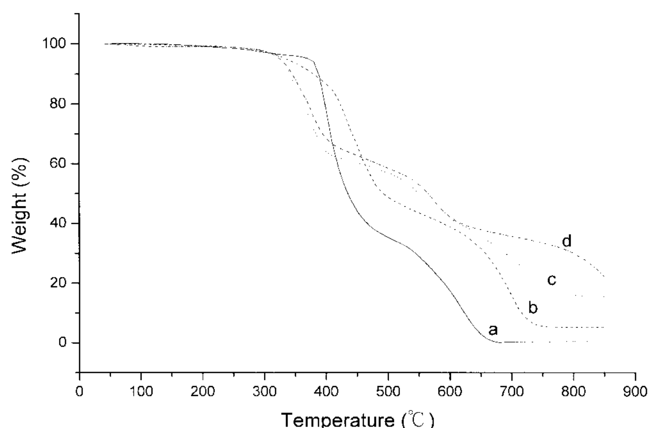


Figure 2 TGA thermograms of cured epoxy resins under air atmosphere: (a) BPA-490-D; (b) SBE-D; (c) PSE-D-10; (d) PSE-D-21.

Thermal degradation of the epoxy resins evaluated with TGA

Figure 1 shows some TGA thermograms of the cured epoxy resins under nitrogen atmosphere. Ordinarily, silicon-[31] or phosphorous-containing[10–13] polymers show a two-stage degradation behavior during the heating process under nitrogen atmosphere. However, the two-stage degradation behavior was not observed for the epoxy resins in this study, owing to the high thermal stability of diphenylsilanoxy and DOPO groups to result in the degradation of the Si-/P-containing groups and the epoxy resin matrix overlapping at the temperature range of 320–450°C. Moreover, the degradation of Si-/P-containing groups generated heat-resistant residues to result in high char yields at 850°C. While heated under air (Fig. 2), the resins exhibited similar weight loss behavior as they did under nitrogen atmosphere at temperatures < 400°C. However, owing to oxidation reaction,[14–18] a rapid weight loss was observed at temperatures > 500°C for the phosphorous-free epoxy resins (BPA-490-D and SBE-D). The oxidation on char resulted in less residues left at temperatures > 700°C. As silicon-containing epoxy resin was reported to exhibit significant char formation under heating with air,[31] SBE-D's less char residue was unusual and could be due to its low silicon content (2.15 wt %). Although the phosphorus group was incorporated into the epoxy resins (Fig. 2, curve c), the weight loss at the high temperature region was significantly retarded.[10–19] The retardation effect on weight loss was further enhanced for epoxy resins containing both silicon and phosphorus groups (Fig. 2, curve d). The abovementioned behaviors could be understood with a synergistic effect of silicon and phosphorous on reserving the residues from oxidation weight loss. With dehydration and carbonization, the phosphorous group acted as a promoter to form heat-resistant char. The char might be

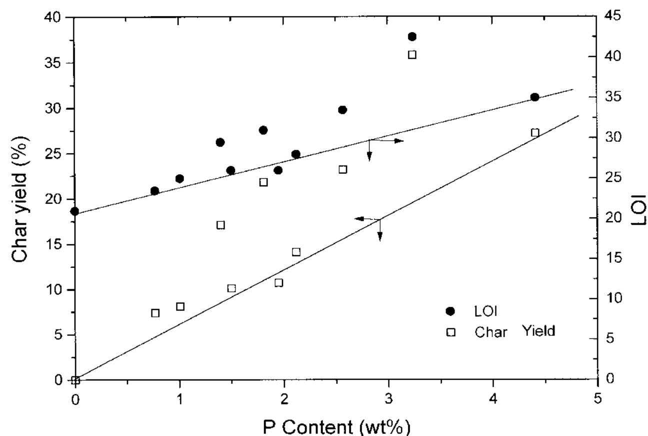


Figure 3 The plots of char ratios of epoxy resins at 700°C under air atmosphere and the epoxy resins' LOI values versus the resins' phosphorous contents.

oxidized to lost weight at temperatures > 650°C. If silicon was also incorporated into the epoxy resins, a protecting layer of silica with high thermal stability might form to protect char from oxidation degradation. The abovementioned action of silica was referred to the low surface potential energy of silicon[35,36] and the highly thermal resistance of silica.[31,36]

Char formation and flame retardancy

From the above discussion, introducing phosphorous and silica into epoxy resins would significantly enhance the resins' char formation at high temperature regions through the mechanisms of dehydration/carbonization and heat-resistant protection from phosphorous and silica, respectively. Because char yield was correlated to be a representation of polymers' flame retardance,[37] these prepared epoxy resins were expected to exhibit good flame-retardant property. The LOI, representing the lowest environment's oxygen volume content for sustaining the flame, was used for quantifying the epoxy resins' flame retardance. The ambient atmosphere's oxygen volume content is about 21%. Therefore, a material exhibiting its LOI above 21 might show flame-retardant property. Generally, materials with LOI values higher than 26 would show self-extinguishing behavior and were considered to be highly flame retardant. Figure 3 showed the relationship of resins' phosphorus contents to their char yields and LOI values. The oblique lines, plotted from the data of the phosphorus-containing/silicon-free samples, showed that char ratios linearly increased with increasing the resins' phosphorous contents.[20] The PSE-D series resins showed their positions above the oblique line, to demonstrate the silicon's enhancement on char formation and LOI values for phosphorus-containing epoxy resins. The above results conform to the epoxy resins' char formation mechanism, where phosphorous enhances char yields and silicon reserves the formed char from oxidation.

As the literature reported,[20] epoxy resins' LOI values showed a linear relationship with the resins' phosphorous contents. Because silicon would significantly alter the char ratios and LOI values of the phosphorus-containing epoxy resins, the abovementioned linear relationship was invalid for the phosphorous-/silicon-containing resins (Fig. 3). Therefore, another correlation was established for estimating the resins' char yields and LOI values, by plotting resins' char yields (LOI values) versus their total contents of phosphorous and silicon (Fig. 4). Both the char ratios and the LOI values were found to linearly increase by increasing the values of the resins' total contents of phosphorous plus silicon. Moreover, the slope of the oblique line in Figure 4 (slope = 20.97 and 18.34) was higher than that in Figure 3 (slope = 6.16 and 3.17), to further demonstrate the phosphorous-silicon's synergistic effect on char enrichment and LOI enhancement.

Krevelen[37] has proposed the relationship of polymer's char yield (ρ, at 700°C under air) and its LOI value as

$$\mathrm{LOI} = 0.40\rho + 17.5 \quad (1)$$

However, Krevelen's equation is not valid for the phosphorus-/silicon-containing epoxy resins. Taking PSE-D-21 as an example, the LOI value calculated from Krevelen's equation is 31.82, which is very different from the measured value of 42.5. By compensating the abovementioned insufficiency, a modified form of Krevelen's equation could be obtained from plotting the epoxy resins' LOI values versus their char yields (Fig. 5), to give the straight line represented as

$$\mathrm{LOI} = 0.62\rho + 19.2 \quad (2)$$

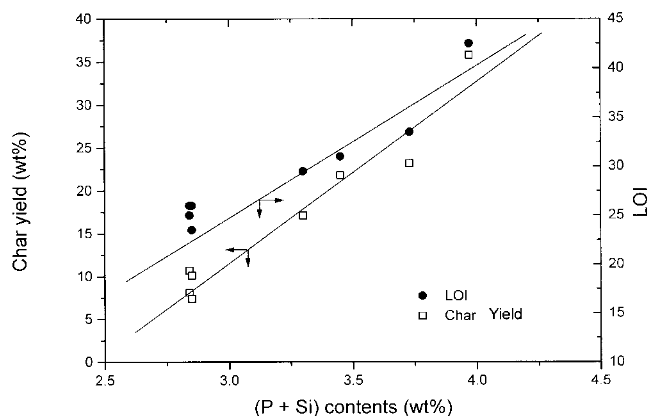


Figure 4 The plots of char ratios of epoxy resins at 700°C under air atmosphere and the epoxy resins' LOI values versus the resins' total contents of phosphorous plus silicon.

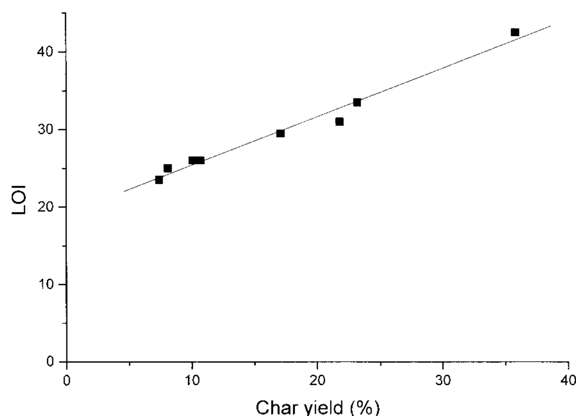


Figure 5 The plot of epoxy resins' LOI values versus char ratios of epoxy resins at 700°C under air atmosphere for the epoxy resins containing both phosphorous and silicon.

because Krevelen's equation is valid only for polymers not containing phosphorous and silicon. Equation (2), therefore, could be a useful expression for estimating epoxy resins' LOI values from their char yields, while both phosphorous and silicon were incorporated into the epoxy resins for LOI enhancement.

Moreover, the difference in the slopes and intercepts of eqs. (1) and (2) might be correlated to the alternation on the epoxy resins' degradation behaviors. The slope represents the changing rate of LOI values with change of char yields. According to the condensed-phase mechanism,[14–21] the formed char improved the polymers' flame retardance through decreasing amounts of released combustible gases and served as a barrier to heat transfer. For silicon-free polymeric materials, weight loss from the formed char was still observed, owing to oxidation at temperatures > 750–800°C. However, the char oxidation was inhibited with silicon incorporation. Therefore, for phosphorous-/silicon-containing epoxy resins, the formed char exhibited extremely thermal stability and antioxidant properties, refusing oxidation and the release of small molecular combustible chemicals and remaining efficiently heat-resistant, especially in a high temperature region. That is to say, the phosphorous-/silicon-containing char would show relatively high efficiency on improving polymers' flame retardance. Because the slopes of eqs. (1) and (2) could be read as the char's efficiency on LOI enhancement, thus, eq. (2), exhibiting a larger slope than eq. (1), was reasonable from the abovementioned thermal behavior. On the other hand, the intercepts of eqs. (1) and (2) were read as the LOI value of a material having no char residue at 700°C heated under air. For this case, all of the material degraded into small molecules and released out. However, such a case would not be observed for the phosphorus-/silicon-containing epoxy resins, unless at much higher temperatures. Therefore, the relatively large intercept of eq. (2) might be from the inorganic ingredients (phosphorous and silicon), which would not be released out as combustible chemicals under fire.

CONCLUSIONS

Epoxy resins containing both phosphorous and silicon were successfully obtained via a fusion process of reacting a phosphorous diol and a silicon diol with a bisphenol-A-type epoxy resin. The resulting epoxy resins' phosphorous/silicon contents and T_g's can be tailored with various feeding ratios of the reactants in the fusion processes. Moreover, a synergistic effect of phosphorous with silicon on enriching epoxy resins' char formation and on enhancing the resins' LOI values was observed. Therefore, a novel epoxy resin system with extremely high flame retardancy, good thermal stability, and high T_g's was successfully prepared in this study. The epoxy resins have the potential to be used in the application of advanced electronic and electrical products.

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