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ORIGINAL CONTRIBUTION

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A phosphate-based epoxy resin for flame retardance: synthesis, characterization, and cure properties

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Abstract A phosphorus-containing oligomer, bis(3-hydroxyphenyl) phenyl phosphate (BHPP), was synthesized through the reaction of phenyl dichlorophosphate and 1,3-dihydroxybenzene, and characterized by elemental analysis, Fourier transform IR spectroscopy, and ^{1}H NMR and ^{31}P NMR spectroscopy. Consequently, the phosphate-based epoxy resins with a phosphorus content of 1 and 2 wt % were prepared via the reaction of diglycidyl ether of bisphenol-A with BHPP and bisphenol-A, and were confirmed with Fourier transform IR spectroscopy and gel permeation chromatography. Phenolic melamine, Novolak, and dicyanodiamide were used as curing agents to prepare the thermoset resins with the control and the phosphate-based epoxy resins. Thermal properties and thermal degradation behavior of these thermoset resins were investigated by using differential scanning calorimetry and thermogravimetric analysis. The thermoset resins cured with phenolic melamine exhibited higher glass-transition temperatures than the other cured resins owing to the high rigidity of their molecular chain. Thermogravimetric analysis studies demonstrated that the decomposition temperatures of the thermoset resins cured with Novolak were higher than those of the others. A synergistic effect from the combination of the phosphate-based epoxy resin and the nitrogen-containing curing agent can result in a great improvement of the flame retardance for their thermoset resins.

Keywords Phosphate-based epoxy resin · Synthesis · Cure properties · Flame retardance

Introduction

Epoxy resins have been commercially developed for more than half a century, and have many major industrial applications owing to their attractive characteristics of high tensile strength and modulus, low shrinkage on curing, excellent moisture, high adhesion to many substrates, good chemical and corrosion resistance, excellent dimensional stability, and superior electrical properties [1, 2, 3]. Epoxy resins have been widely used in various industrial fields, such as coating, potting, adhesives, laminates, and composites. In the last 2 decades, the rapid development of epoxy resins in electronic applications has been achieved, which include encapsulations for semiconductors, packaging for integrated circuit chips and ball grad access, insulating materials for electric devices such as copper-clad laminates and solder mask resistant ink for printed circuit broads. In most cases, these electronic applications require good flame retardance for epoxy resins [4, 5, 6]. Therefore, imparting flame retardance to epoxy resins has received a great deal of attention. Several techniques have been employed to improve the flame retardance of epoxy resins. The most common approach is to incorporate halogen atoms into the epoxy resins, so that the brominated epoxy resins can achieve the expected flame retardance. The brominated epoxy resins are mostly derived from diglycidyl ether of bisphenol-A (BPA) (DGEBA) and tetrabromo BPA (TBBA) with suitable catalysts [7, 8, 9]. However, flame-retardant epoxy resins containing bromine release hydrogen bromide during combustion, which causes corrosion and toxicity. Considerable environmental effects and health restrictions have been considered in recent years in regard to controlling the inherent flammability of epoxy resins by incorporation of flame-retardant additives. These considerations have led to a reexamination in terms of overall fire hazards of halogen-based epoxy resins and the search for halogen-free and environmentally friendly flame-retardant epoxy resins [10, 11, 12, 13, 14].

Phosphorylation is considered to be one of the most efficient methods of conferring flame retardance on epoxy resins [15, 16]. Organophosphorus compounds exhibit high flame-retardance efficiency for epoxy resins and have also been found to generate less toxic gas and smoke than halogen-containing compounds [17, 18, 19]. Therefore, less destruction to the earth's environment is the noteworthy benefit of replacing halogens with phosphorus in flame-retardant epoxy resins, and the flame retardance of epoxy resins via phosphorylation has been widely studied [20, 21]. Incorporating covalently bonded phosphorus into epoxy resins could be achieved using phosphorus-containing oxirane compounds or curing agents. Several approaches for achieving this aim have been reported [22, 23, 24, 25]. As a reactive-type flame retardant, the oxirane compound with phosphorus in the backbone of epoxy resins exhibits much better flame retardance and overcomes several drawbacks associated with the physical blend of the epoxy resins and the flame retardants. However, the phosphorus content of these compounds was not very high, and the improvement of flame resistance for epoxy resins was not quite satisfied [26, 27]. Some studies indicated that a significant improvement of flame-retardance efficiency was observed when phosphorus and nitrogen elements existed simultaneously in the curing system of epoxy resins. Therefore, the combination for the phosphorus–nitrogen synergistic effect on flame retardance is very interesting [28, 29, 30, 31].

Recently, the European Community proposed restricting the use of brominated diphenyl oxide flame retardants in electric/electronic applications because highly toxic and potentially carcinogenic brominated furans and dioxins may form during combustion [32]. The World Health Organization and the US Environmental Protection Agency also recommend exposure limits and risk assessment of dioxins and similar compounds [33, 34]. It is essential that new environmentally friendly flame-retardance systems are developed to meet the constantly changing demand of new regulations, standards and test methods. In this work, we synthesized phosphate-based epoxy resins through incorporating the phosphorus-containing moieties into the molecular backbone of epoxy resins. The curing systems of these phosphate-based epoxy resins with several curing agents were prepared, and the thermal and the flame-retardance properties were also investigated. The purpose of this study was to develop new environmentally friendly flame-retardant epoxy resins. It also deals with recommending a novel curing system, in which a combination of phosphorus and nitrogen elements can hopefully generate a synergistic effect on flame retardance. These "green" flame-retardant epoxy resins are expected to impart the requirement for environmental protection in electric/electronic applications.

Experimental

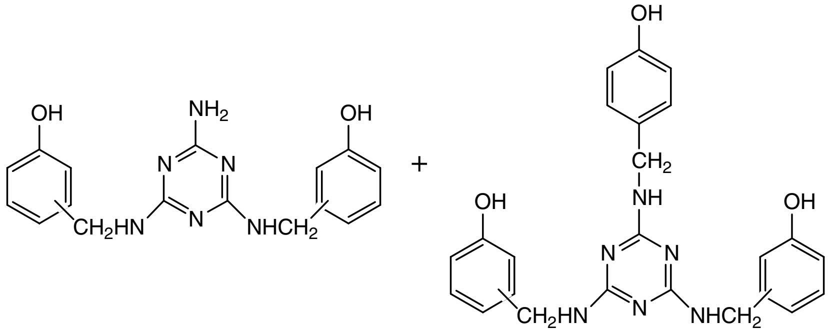
Materials

Phenyl dichlorophosphate was commercially obtained from TCI Co., Japan. 1,3-Dihydroxybenzene, 2-methy imidazole (2MI), triphenyl phosphine (Ph_3P), xylene, methyl cellosolve (MCS), and tetrahydrofuran (THF) were reagent grade and were purchased from Aldrich Chemical Co., USA. Xylene and THF were dried with sodium and distilled at reduced pressure before use. DGEBA (commercial name YD-128) with an epoxide equivalent weight (EEW) of 187 g was supplied by Kuk Do Chemical Co., Korea. The curing agents of dicyanodiamide (DICY) and Novolak with a hydroxyl equivalent weight of 105 g were supplied by Suzhou Special Chemical Co., China. Phenolic melamine as a novel curing agent was kindly supplied by Gun Ei Chemical Industry Co., Japan. Phenolic melamine is a mixture of trimers and tetramers of cresol and melamine, whose chemical structures are shown in Scheme 1. The nitrogen in phenolic melamine makes it nonflammable. Two grades of phenolic melamine, PS-6313 and PS-6333, were employed in our experiment with hydroxyl equivalent weights of 148 and 169 g and nitrogen contents of 20 and 25 wt %, respectively.

Synthesis of bis(3-hydroxyphenyl) phenyl phosphate

1,3-Dihydroxybenzene (110 g, 1 mol) dissolved in dried xylene (180 ml) was introduced into a four-neck, round-bottom 1,000-ml glass flask equipped with a thermometer, a nitrogen inlet, a reflux condenser, and a mechanical stirrer. The mixture was stirred and heated slowly to 70 °C for about 30 min until 1,3-hydroxybenzene had dissolved completely in xylene, and then the

Scheme 1 Chemical structure of phenolic melamine resin



mixture was heated to 90 °C. Phenyl dichlorophosphate (105 g, 0.5 mol) was added continuously to the flask at a constant rate over a period of 2 h under a nitrogen gas atmosphere. The HCl gas was detected immediately. The temperature was maintained at 90 °C during the addition of phenyl dichlorophosphate. The reaction mixture was headed to 125 °C, and then stirred for 2.5 h under a nitrogen gas atmosphere. The reaction was assumed to end when no more HCl evolution was detected with the wet pH test paper. After cooling to room temperature, the precipitant was filtered and recrystallized with THF. A light-yellow crystalline solid was collected by filtration, and dried under reduced pressure. The crude materials gave 152 g bis(3-hydroxyphenyl) phenyl phosphate (BHPP).

Synthesis of the phosphate-based epoxy resins

DGEBA (500 g) was introduced into a four-neck, round-bottom 1,000-ml glass flask, and then heated to 120 °C. It was stirred and vacuumed for 1 h to remove trace water. Successively, the vacuuming was stopped, and nitrogen gas was charged into the flask. When the temperature was increased to 130 °C, BHPP and BPA were added to DGEBA in terms of the designed formulation, in which phosphate-based epoxy resins with a phosphorus content (1 and 2 wt %) and an EEW (455 g Eq^{-1}) were expected to be obtained. Ph_3P or 2MI (0.3 wt % of the amount of the reaction mixture) used as a catalyst was synchronously added. On the basis of the expected phosphorus content and the EEW, the amount of BPA and BHPP could be calculated through the following equations as

$$\frac{100}{E_1} - \left(\frac{W_1}{1/2 \times 358} + \frac{W_2}{1/2 \times 288}\right) = (100 + W_1 + W_2) \times \left(\frac{1}{E_2}\right) \tag{1}$$

and

$$P(\%) = \frac{W_1 \times 0.0956}{100 + W_1 + W_2} \times 100, \tag{2}$$

where W_1 and W_2 are the weights of BHPP and BPA, respectively, while the amount of DGEBA is 100 g; E_1 and E_2 are the EEWs (455 and 187 g Eq^{-1}) of the phosphate-based epoxy resin and DGEBA, respectively; $P(\%)$ is the expected phosphorus content. The reaction mixture was gradually heated to 160 °C and stirred for 4 h under a nitrogen gas atmosphere. The brown phosphate-based epoxy resins with an EEW of about 457 g Eq^{-1} (value obtained by the HCl potentiometric titration method) were obtained after cooling to room temperature.

A phosphorus-free epoxy resin, used as the control resin for comparison of curing properties with the phosphate-based epoxy resins, was also synthesized via the reaction of DGEBA with BPA, BHPP was omitted in accordance with methods described earlier. The EEW (around 456 g Eq^{-1}) of the control resin was obtained through modulating the weight ratio of DGEBA and BPA to 4.3/1.

Curing procedure of epoxy resins

The control resin and the phosphate-based epoxy resins with phosphorus contents of 1 and 2 wt % were cured with DICY, Novolak, and phenolic melamine. The curing agents and curing accelerator 2MI (0.2 wt %) were dissolved in MCS as a solvent and, then, the epoxy resins and the solution of curing agents were mixed homogeneously in an epoxide-to-hydroxyl equivalent ratio of 1/1. The reaction mixtures were kept at 60 °C for 1 h under vacuum to remove the solvent. Then, the reaction mixtures were cured at 150 °C for 1.5 h and postcured at 180 °C for 3.5 h. After curing, all samples were cooled to room temperature to prevent stress-cracking.

Characterization

The melting point and the glass-transition temperature (T_g) were determined using a PerkinElmer Pyrid-1 differential scanning calorimetry (DSC) apparatus. All measurements were made under a nitrogen gas atmosphere at a heating rate of 10 °C min^{-1} on samples weighing about 10 mg. Elemental analysis was carried out with a Heraeus CHN-O rapid elemental analyzer with acetanilide as a standard. ^{1}H NMR and ^{31}P NMR spectra were obtained with a Bruker MC-80 NMR spectrometer with dimethyl sulfoxide-d_6 as a solvent. For the ^{31}P NMR spectrum, phosphoric acid was used as an external standard. Fourier transform (FT) IR spectra were obtained using a Nicolet 205 FTIR spectrometer with a KBr sampling method. Gel permeation chromatography (GPC) measurements were performed using a Waters 515 GPC with THF as the solvent at a flow rate of 1.0 ml min^{-1}. Thermogravimetric analysis (TGA) was performed with a PerkinElmer Pyrid-1 TGA analyzer at heating rate of 10 °C min^{-1} under an air or a nitrogen gas atmosphere from 23 to 800 °C.

Measurement of flame-retardant properties

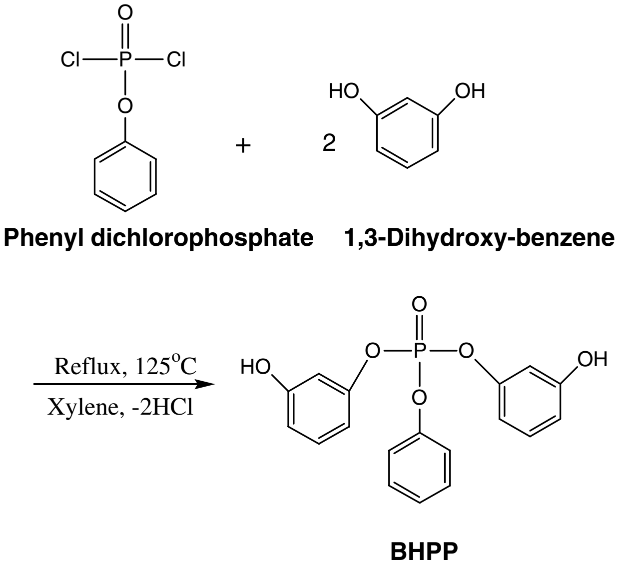
Limiting oxygen index (LOI) measurement was performed using a HD-2 oxygen index apparatus with a magneto-dynamic oxygen analyzer, according to the ASTM D-2863 specification. The mixture of oxygen and nitrogen gas was continuously sent through the combustion chamber at a flow rate of 17 l ml^{-1}. The sample bar (65×3.0×0.5 mm) was clamped vertically in the holder in the center of the combustion column. The top of the sample bar was ignited using a butane gas burner so that the sample bar was well lit and the entire top was burning. The relative flammability of the sample bar was determined by measuring the minimum concentration of oxygen which would just support flaming combustion of the sample bar.

The UL94 vertical test was carried out according to the testing method proposed by Underwriter Laboratory. Five test sample bars (127×12.7×1.6 mm) suspended vertically over surgical cotton were ignited using a butane gas burner. The end of the sample bar was ignited twice, and each ignition was carried out for 10 s. The class of UL94 V-0 is obtained if the burning time of each sample bar after 10-s ignition does not exceed 10 s, and the total burning time for five samples does not exceed 50 s; at the same time, the surgical cotton below the specimen cannot be ignited by the flaming drippings.

Results and discussion

Synthesis of BHPP

BHPP was synthesized through the reaction of phenyl dichlorophosphate and hydroquinone according to Scheme 2. In the process of the synthesis, the nucleophilic-active chlorine in phenyl dichlorophosphate could serve as a reactive site for the electrophilic-active hydrogen in hydroquinone. BHPP is a light-yellow crystalline solid with a melting point of about 216 °C determined by DSC. The chemical structure of BHPP was confirmed by elemental analysis, ^{1}H NMR, ^{31}P NMR, and FTIR spectroscopy. The calculated values of BHPP in terms of the formula ($C_{18}H_{15}O_6P$) are C, 60.34; H, 4.18; O, 26.82; P, 8.66; and the analyzed data show that C, H, O, and P are 60.71, 4.14, 26.87, and 8.28, respectively. It was found that the elemental analysis of the BHPP prepared was in good agreement with the calculated values. The FTIR spectrum of BHPP is shown in Fig. 1. The strong absorption peaks at 1,182.27 and 1,239.52 cm^{-1} indicate the formation of P–O–Ph; however, the distinctive absorption peak at 684 cm^{-1} for the P–Cl stretch in phenyl dichlorophosphate disappears, which demonstrates the reaction of phenyl dichlorophosphate and hydroquinone. The chemical structure of BHPP could be further confirmed by the other absorption peaks, at 973.72, 1,015.8, and 1,032.14 cm^{-1} for P–O–Ph, 3,550–3,200 cm^{-1} for Ph-OH, and 1,264.35 cm^{-1} for P=O. The ^{1}H NMR spectrum of BHPP is shown in Fig. 2. The chemical shifts attributable to two hydroxy protons were observed at $\delta = 9.38$–9.50 ppm (d, 2H). The chemical shifts corresponding to the phenol ring protons were found at $\delta = 6.55$–7.04 ppm (m, 8H), and the chemical shifts corresponding to the phenyl ring protons were found at $\delta = 7.52$–7.95 ppm (m, 5H). Furthermore, the ^{31}P NMR spectrum of BHPP exhibited an intense single peak at $\delta = -15.43$ ppm (as shown in Fig. 3), indicating the presence of a phosphonate unit of BHPP. These characterizations confirmed the chemical structure of BHPP.



Scheme 2 Synthetic scheme of bis(3-hydroxyphenyl) phenyl phosphate (*BHPP*)

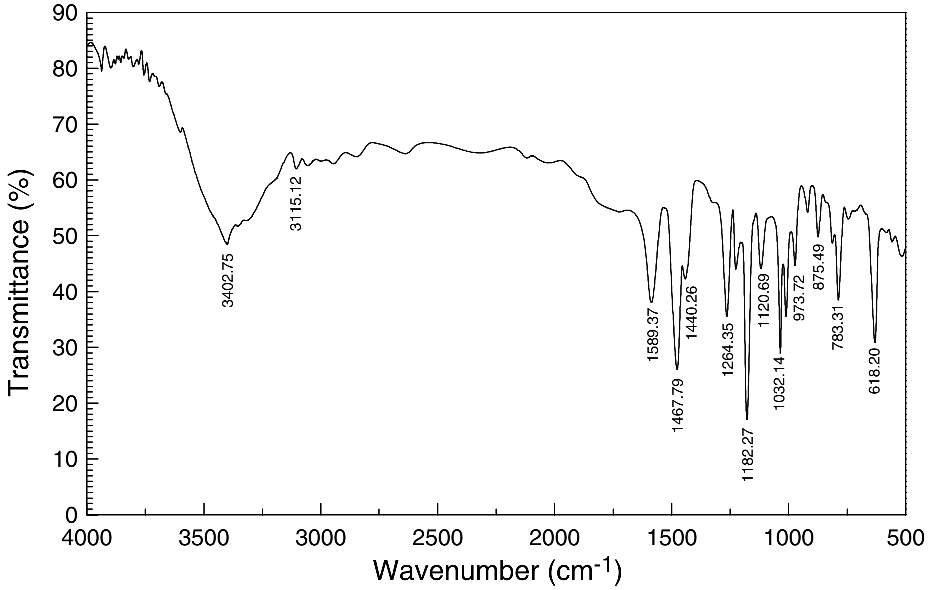


Fig. 1 Fourier transform (*FT*) IR spectrum of bis(3-hydroxy-phenyl) phenyl phosphate (*BHPP*)

Synthesis of phosphate-based epoxy resins

The phosphate-based epoxy resins were synthesized via the reaction of DGEBA with BHPP and BPA, in which BPA was added to adjust the phosphorus content of the epoxy resins. The synthetic scheme is shown in Scheme 3. The catalyst was necessary to facilitate the reaction. The effect of reaction time on the EEWs of the phosphate-based epoxy resins with different catalyzing systems is shown in Fig. 4. The EEWs for the 2MI and Ph_3P catalyzing systems increased rapidly during the first 60 min, but increased gradually after 1 h. They reached constant values after 4 h, which implied the completion of the reaction. Compared with 2MI, Ph_3P exhibited a much better catalytic effect for the reaction. It was also observed that the reaction speed was very slow without the addition of a catalyst.

The phosphate-based epoxy resin was characterized by FTIR spectroscopy, and its IR spectrum is shown in Fig. 5. The characteristic absorption peaks are as follows: 914.86 cm^{-1} (oxirane ring); 1,261.84 cm^{-1} (P = O); 985.79, 1,028.36, 1,176.45, and 1,245.92 cm^{-1} (Ph–O–P); 3,550–3,200 cm^{-1} (Ph–OH), and 1,362.85 cm^{-1} ($-CH_3$). The performance of the reaction was also demonstrated by the GPC diagram as shown in Fig. 6. It could be observed that, for DGEBA, the main distribution peaks at molecular weights of 284, 781, and 1,227 appeared in the diagram with percentages of 81.7, 16.4, and 1.7 wt %, respectively. The molecular weight was also determined by GPC, and DGEBA possessed an M_n of

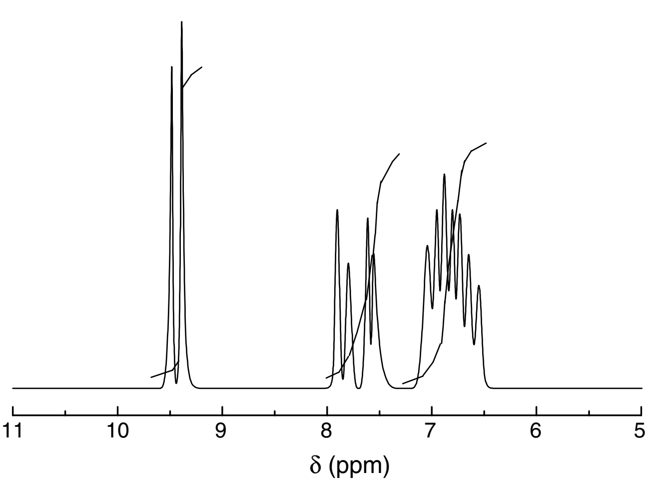


Fig. 2 ^1H NMR spectrum of BHPP

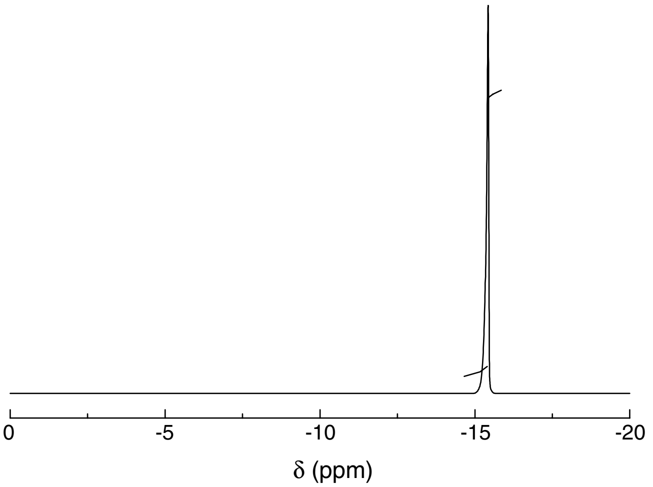
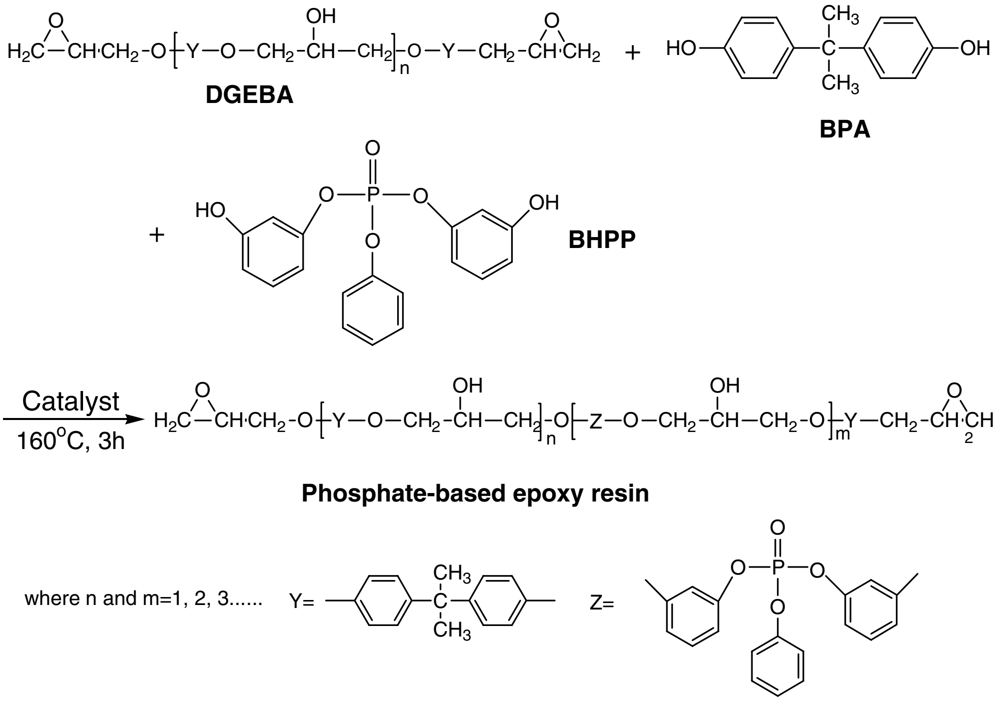


Fig. 3 ^{31}P NMR spectrum of BHPP

Scheme 3 Synthetic scheme of the phosphate-based epoxy resin



431. For the phosphate-based epoxy resins with a phosphorus content of 1 wt % (EP-P1), the distribution peaks at molecular weights of 284 and 781 weaken sharply, and the percentages are both lower than 2 wt %. However, distribution peaks at molecular weights of 1,227, 2,053, and 4,208 appear in the GPC diagram. Over the whole range of the distribution of the molecular weight, the percentage of the molecular weight of 1,227 reached 79 wt %. Almost the same result was seen for the epoxy resins with a phosphorus content of 2 wt % (EP-P2). From the GPC analysis in Fig. 6, it was also found that EP-P1 and EP-P2 possessed an M_n of 1,355 and 1,526, and an M_w of 3,581 and 3,962, respectively. These results verified the completion of the reaction of DGEBA with BHPP and BPA.

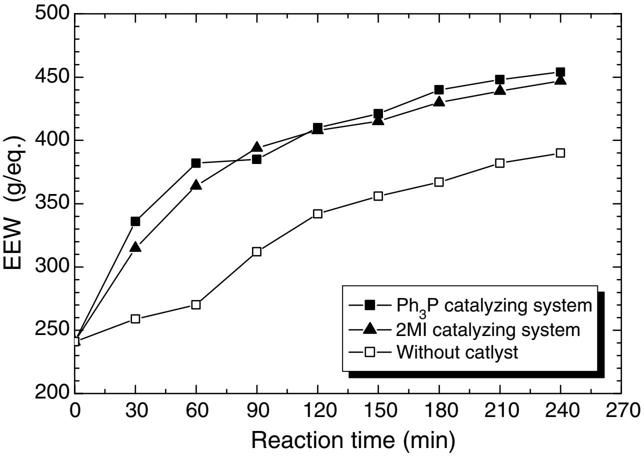
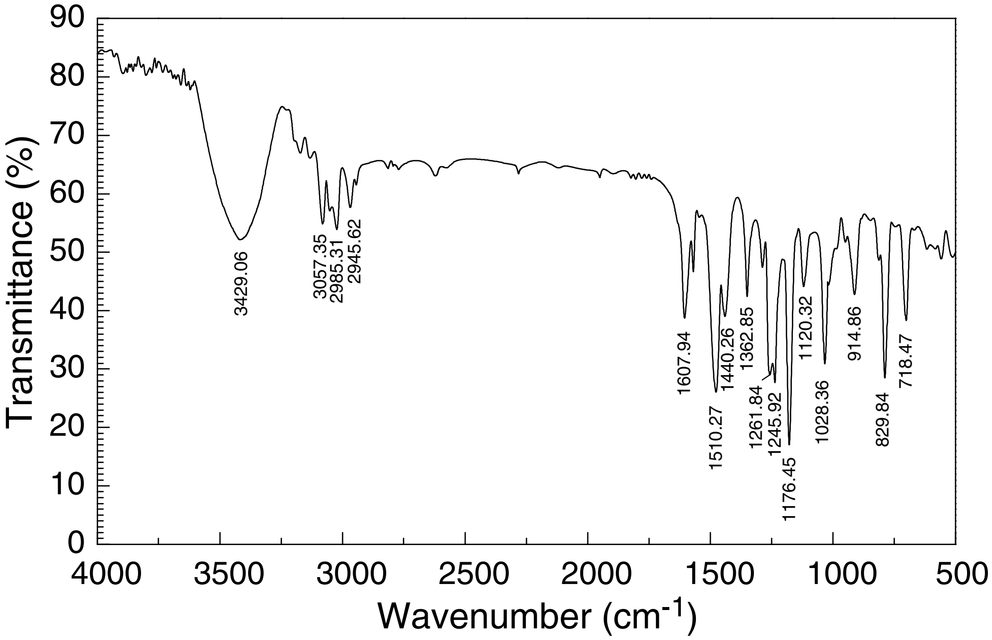


Fig. 4 Reaction time versus the epoxide equivalent weight (*EEW*) of the phosphate-based epoxy resin in different catalyzing systems

Thermal analysis of the cured epoxy resins

T_g is a very important parameter for the thermoset epoxy resins because it established the service environment for the epoxy-based materials. In most cases, the epoxy resins are only used well at a temperature below T_g. Therefore, identification of the mechanisms responsible for T_g changes and prediction of T_g depression are critical for the engineering design and the application of the epoxy resins and their curing systems. T_gs of the control and the phosphate-based epoxy resins cured with various curing agents were obtained by DSC measurements, and the data are listed in Table 1. The T_gs of the phosphate-based epoxy resins cured with the four curing agents were found to be slightly lower than those of the control resin cured with the four curing agents. It has been reported that incorporating a linear phosphorous-containing group into the epoxy main chain will decrease the rotational barrier of the epoxy and, therefore, reduce the T_gs of the polymers [6, 35]. The EP-P1/Novolak thermoset resin shows a lower T_g than the EP-P1/DICY one. It could be explained that the cross-linking density of the EP-P1/DICY thermoset resin was higher than that of the EP-P1/Novolak one. However, the T_g of the EP-P1/DICY thermoset resin was lower than that of

Fig. 5 FTIR spectrum of the phosphate-based epoxy resin



the EP-P1/PS-3313 or the PS-3333 one. This may be attributed to the higher rigidity of phenolic melamine than that of DICY, which compensates somewhat for the loss in cross-linking density, though DICY has a higher hydroxyl equivalent weight than phenolic melamine resins. The same arguments can be derived from the difference of the T_gs of the control resin thermoset resins cured with the four curing agents. On the other hand, the EP-P1/PS-3313 thermoset resin has a higher T_g than the EP-P1/PS-3333 one, owing to the higher EEW of PS-3313 than that of PS-3333. Exactly the same phenomenon was observed for EP-P2 cured with the four curing agents. It was also found that the T_g of the EP-P2 thermoset resin was always lower than that of the EP-P1 one when cured with the same curing agent. It was already mentioned that BHPP is a linear, main chain, and phosphorus-containing oligomer. BHPP has a much more flexible molecular chain than BPA. Therefore, the reduction in the T_g of the EP-P2 thermoset resins should arise from the decrease in the rigidity of the molecular chain. However, it is still noteworthy that both EP-P1 and EP-P2 exhibited high T_gs over 130 °C when cured with the four curing agents mentioned previously. These high T_g values suggest the phosphate-based epoxy resins prepared in this work could potentially be applied for FR-4 type copper-clad laminates [36].

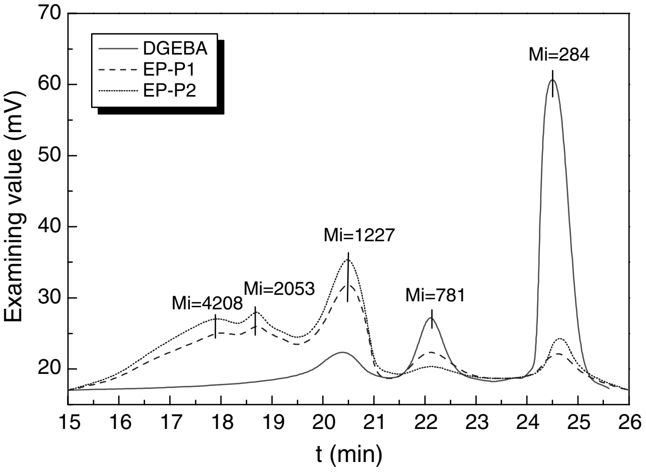


Fig. 6 Gel permeation chromatography (*GPC*) diagrams of diglycidyl ether of bisphenol-A (*DGEBA*) and the phosphate-based epoxy resins

The TGA measurements of the thermoset control and phosphate-based epoxy resins were carried out in air and nitrogen gas atmospheres for all the samples. The thermal degradation behaviors of these thermoset resins are shown in Figs. 7 and 8, and the test data are summarized in Table 1. The thermoset control resins cured with the four curing agents are thermally stabler than the phosphate-based epoxy resins cured with the four curing agents. The relatively poor thermal stability of the thermoset phosphate-based epoxy resins comes from the phosphorous group degrading at relatively low temperature [24, 25, 31]. However, the temperature at the rapid weight loss for the thermoset phosphate-based epoxy resins cured with the four curing agents was found to be much higher than that for the thermoset control resins cured with the four curing agents. This phenomenon has been observed in other phosphorylated polymer systems, and is classified to play an important role in

Table 1 Thermogravimetric analysis data of the control resin and the phosphate-based epoxy resins (EP-P1 and EP-P2) cured with various curing agents

Sample	T_g (°C)	Temperature at the characteristic weight loss (°C)				Temperature at the rapid weight loss (°C)		Char ratios at 700 °C (wt %)
		1 wt %		10 wt %				
		Air	N_2	Air	N_2	Air	N_2	
Control/DICY	135.6	201	212	335	379	417	431	7.6
EP-P1/DICY	134.5	186	194	321	363	411	425	16.3
EP-P2/DICY	133.2	152	149	292	278	427	432	19.4
Control/Novolak	133.7	235	244	396	405	442	449	5.5
EP-P1/Novolak	131.9	226	239	389	394	439	450	6.8
EP-P2/Novolak	130.5	197	185	368	374	433	443	13.1
Control/PS-3313	139.4	187	172	332	354	431	439	6.4
EP-P1/PS-3313	137.1	180	162	324	341	432	435	16.3
EP-P2/PS-3313	135.6	161	158	321	347	426	432	17.6
Control/PS-3333	137.9	213	198	358	366	431	434	7.5
EP-P1/PS-3333	135.4	194	186	355	352	434	435	15.5
EP-P2/PS-3333	133.5	178	229	346	365	428	435	17.8

improvement of the flame retardance of the phosphate-based epoxy resins [15]. It was also observed that the char ratios of the thermoset phosphate-based epoxy resins were much higher than those of the thermoset control resins. On heating, the phosphorous groups of the thermoset resins first decompose to form a phosphorous-rich residue, which prevents further decomposition of the resins by raising the decomposition temperatures and consequently results in a high char yield [37]. This char yield has been correlated to denote the flame retardance and has been widely referenced in studies of the flame properties of polymers [17, 18, 19, 20].

The results in Table 1 also indicate that the EP-P1 or EP-P2/Novolak thermoset resin possessed a much higher decomposition temperature at a weight loss of 1 and 10 wt % than the other three curing systems both in air and in a nitrogen gas atmosphere; but the decomposition temperatures of the DICY/EP-P1 and EP-P2 thermoset resins were the lowest. For phenolic melamine, their thermoset resins were moderate. Compared with PS-3133, the decomposition temperature of the EP-P1 or the EP-P2/PS-3333 thermoset resin was much higher. Sato and Yokoyama [38, 39] reported that polymers with a high aromatic content could possess good thermal stability. Apparently, the molecular chain of Novolak is mainly constituted of regular phenol units. The incorporation of these regular phenol units into the backbone enhanced the thermal stability of the EP-P1 or the EP-P2/Novolak thermoset resin. It could be also noticed that the EP-P1 or the EP-P2/Novolak thermoset resin showed the highest temperature at the rapid weight loss, which was attributable to the same reason. Phenolic melamine also contains a phenol group; however, its aromatic content is relatively lower than that of Novolak; therefore, the thermal stability of its thermoset resin was slightly worse than that of Novolak. DICY does not contain an aromatic group; thus, the thermal stability of its cured resins was the worst. The TGA data also showed that the thermal stability decreased with increasing phosphorus content of the phosphate-based epoxy resins when cured with the same curing agent. These results mean that some chain structure or group in BHPP may have poor thermal stability.

From Table 1, it is also seen that the EP-P2/DICY thermoset resin has a char ratio of 19.4 wt % at 700 °C, which is greater than that of the other thermoset resins. The char ratio (around 17.7 wt %) of EP-P2/PS-3313 or PS-3333 thermoset resin was slightly lower than that of the EP-P2/DICY thermoset resin, and ranked as the second-highest value. The EP-P1/Novolak thermoset resin exhibited the smallest char ratio of 6.8 wt % of all the samples. These results implied that the char ratio is strongly dependent on the phosphorus and nitrogen contents, and the char ratio increases with increasing of phosphorus and nitrogen contents. The higher the phosphorus and nitrogen contents, the higher the char ratio of the thermoset resin cured with the same curing agent. For the curing agents used in these experiments, the nitrogen content of DICY (67 wt %) is much higher than that of phenolic melamine (20–25 wt %), but Novolak does not contain nitrogen. So the char ratios of the thermoset resins cured with the four curing agents increase according in the order DICY > PS-3333 > PS-3313 > Novolak. Usually, the degree of oxidation of the thermoset resins can be reduced with the increase of the phosphorus and nitrogen contents at high temperatures; furthermore, the char ratio has been correlated to denote the flame retardance. The relationship between the char ratio and the flame retardance will be discussed in following section.

Flame-retardance properties

The flame-retardance properties of all the samples were examined by LOI and UL94 vertical measurements, and

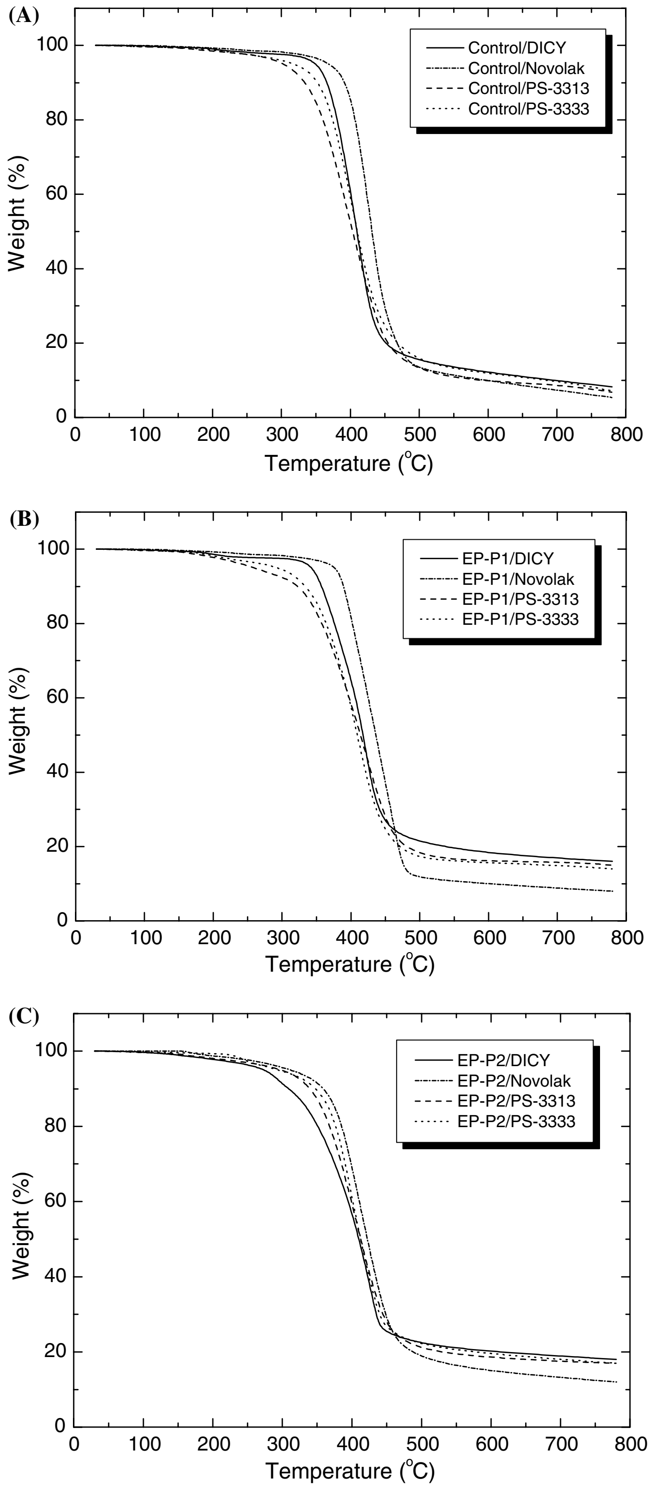


Fig. 7 Themogravimetrc analysis (*TGA*) thermograms of the thermoset resins cured with various curing agents in a nitrogen gas atmosphere: **a** control resin; **b** EP-P1; **c** EP-P2

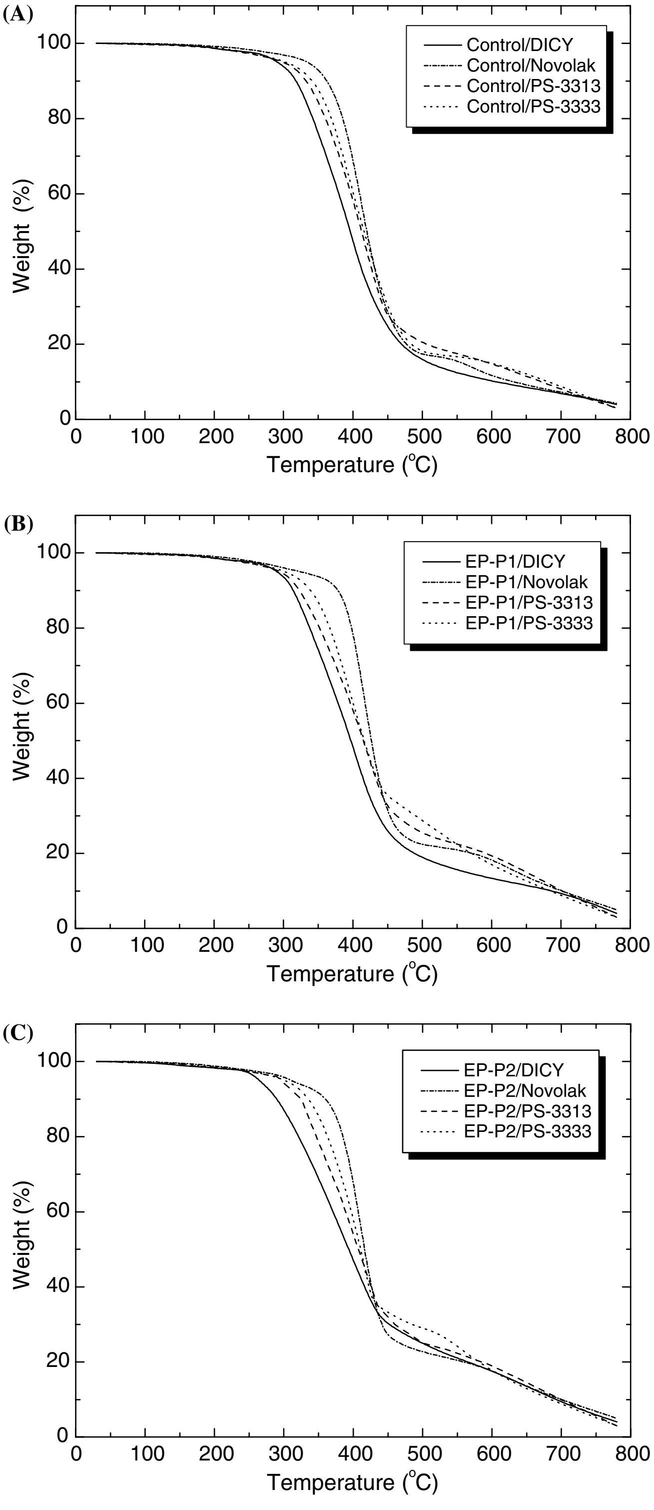


Fig. 8 TGA thermograms of the thermoset resins cured with various curing agents in an air atmosphere: **a** control resin; **b** EP-P1; **c** EP-P2

Table 2 Limiting oxygen index (*LOI*) values and UL94 vertical test results of the control resin and the phosphate-based epoxy resins (EP-P1 and EP-P2) cured with various curing agents

Sample	Phosphorus content (wt %)	Nitrogen content (wt %)	LOI	UL94 grade
Control/DICY	0	2.786	25	Fail
EP-P1/DICY	0.947	2.786	34	V-0
EP-P2/DICY	1.888	2.786	35	V-0
Control/Novolak	0	0	24	Fail
EP-P1/Novolak	0.812	0	28	V-2
EP-P2/Novolak	1.622	0	28	V-2
Control/PS-3313	0	4.697	25	Fail
EP-P1/PS-3313	0.755	4.697	32	V-1
EP-P2/PS-3313	1.511	4.697	34	V-0
Control/PS-3333	0	6.486	25	Fail
EP-P1/PS-3333	0.730	6.486	31	V-1
EP-P2/PS-3333	1.462	6.486	33	V-0

the data are listed in Table 2. The LOI values of these thermoset resins are noteworthy. From these values, it can be seen that the thermoset control resins cured with the four curing agents exhibited poor flame-retardance properties. The control resin/Novolak thermoset resin does not contain any flame-retardant element; therefore it has a low LOI value of 24 and failed in the UL 94 vertical test. However, the thermoset control resins cured with DICY, PS-3133, and PS-3333 could not achieve any significant improvement in the flame retardance through solely incorporating nitrogen; thus, they demonstrated low LOI values and also failed in the UL 94 vertical test.

As shown in Table 2, the EP-P2/DICY thermoset resin exhibited the highest LOI value of 35 of all the samples, and UL94 V-0 grade was achieved. The EP-P1/DICY, EP-P2/PS-3313, and EP-P2/PS-3333 thermoset resins also indicated good flame retardance with the LOI values ranging from 32 to 34, and UL94 V-0 grade was achieved for these three thermoset resins. The LOI values of the EP-1 and EP-2/Novolak thermoset resins were lower than those of the other thermoset resins. The UL94 vertical tests for these two thermoset resins only reached V-2 grade. On the basis of the data, it could be concluded that the LOI values, as an indicator to evaluate the flame retardance, could be improved by increasing both the phosphorus and the nitrogen contents. Generally, a polymer a the phosphorus moiety exhibits good flame retardance through forming the phosphorus char, which acts as an insulation layer of heat transfer to reduce the production of combustible gases during combustion. The higher the phosphorus content, the better is the effect of decreasing the exothermicity of the pyrolysis reaction and decreasing the conductivity of the burning materials. As a result, the flammability can be greatly limited. However, the EP-P2/Novolak thermoset resin still exhibited poor flame retardance, though its phosphorus content was as high as 1.62 wt %. These results indicate that the synergistic effect of phosphorus and nitrogen also plays an important role in the improvement of the flame retardance. This performance may be based on the concept that the nitrogen moiety enhances the formation of the phosphorus char, as well as produces a lot of nitrogen gas to prevent oxygen from the burning materials. Therefore, the highly synergistic flame-retardance efficiency comes from the combination of phosphorus and nitrogen in the backbone of the thermoset resins.

In order to get more details about the synergistic effect of the combination of phosphorus and nitrogen on the flame retardance, the relationship between the ratio of phosphorus-to-nitrogen (P/N) and the LOI is plotted in Fig. 9. It is very important to notice that the LOI value increased with the increase of the ratio of P/N. This result indicates the effective synergism of phosphorus and nitrogen mainly depends on the ratio of P/N. On the other hand, as discussed in the previous paragraph, the char ratio is correlated to denote the flame retardance. From the char ratio listed in Table 1, it was observed that the LOI strongly relied on the char ratio and increased with the increase of the char ratio. Obviously, an increase in char residua can limit the production of combustible carbon-containing gas, and reduce the exothermicity of the pyrolysis reaction and the thermal conductivity of the burning materials, consequently limiting the flammability. Therefore, the higher the char ratio, the higher is the LOI value. These results were in good agreement with a solid-phase mechanism of flame retardance [40, 41].

In summary, a combination of the phosphate-based epoxy resins prepared in this study and a nitrogen-containing curing agent can provide excellent flame retardance (UL94 V-0) as well as good thermal stability.

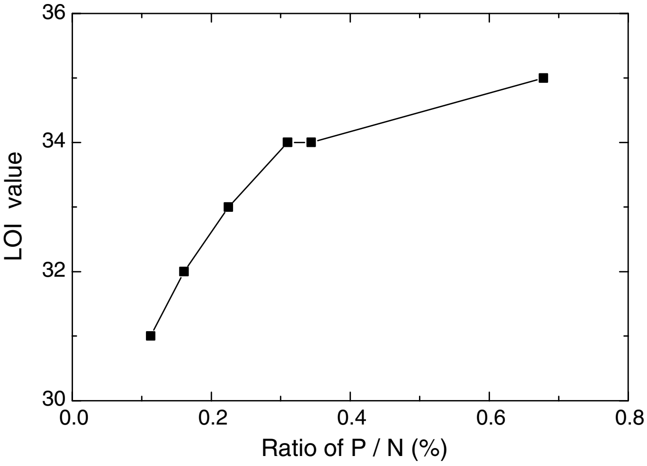


Fig. 9 Limiting oxygen index (*LOI*) value versus the ratio of phosphorous to nitrogen (*P*/*N*) in the thermoset resin

These curing systems of halogen-free epoxy resins will have potential applications in electronic fields with consideration of environmental and health effects.

Conclusion

FTIR, ^{1}H NMR, and ^{31}P NMR spectroscopy, DSC, and elemental analysis characterized a phosphorus-containing oligomer, BHPP, which was synthesized by the reaction of phenyl dichlorophosphate and 1,3-dihydroxybenzene. The novel phosphate-based epoxy resins, EP-P1 and EP-P2, were successfully synthesized via the reaction of DGEBA with BHPP and BPA, and were confirmed with FTIR and NMR spectroscopy and GPC. Phenolic melamine resins, DICY, and Novolak were used as curing agents to prepare the thermoset resins with the control resin, EP-P1 and EP-P2. The TGA demonstrated that the thermoset resins cured with Novolak exhibited better thermal stability than the others. Owing to the high rigidity of the molecular chain, the T_gs of the thermoset resins cured with phenolic melamine were higher than those of the others. The high phosphorus content resulted in a significant increase of the char ratio but a slight decrease of the temperature of decomposition for the thermoset resins. As a function of the synergistic effect of phosphorus and nitrogen, the thermoset resins of EP-P2 cured with DICY and phenolic melamine revealed excellent flame retardance with LOI values above 35 and UL94 V-0 grade. These curing systems may be used potentially as ‘‘green’’ materials in electric/electronic fields.

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