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Synthesis and properties of a phosphorus-containing flame retardant epoxy resin based on bis-phenoxy (3-hydroxy) phenyl phosphine oxide

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Abstract

A reactive phosphorus-containing compound, bis-phenoxy (3-hydroxy) phenyl phosphine oxide (BPHPPO) was first successfully synthesized to produce the phosphorus-containing flame retardant epoxy resin (BPHPPO-EP). The chemical structures were characterized from FTIR, MS, NMR spectra and elemental analyses. Thermal degradation behaviors and flame retardant properties of the cured epoxy resins were investigated from the thermogravimetric analysis (TGA) and the limiting oxygen index (LOI) test using 4,4′-diaminodiphenylsulfone (DDS) as curing agent. The high char yields and the high limiting oxygen index values were found to certify the great flame retardancy of this phosphorus-containing epoxy resin.

Keywords: Bis-phenoxy (3-hydroxy) phenyl phosphine oxide; Epoxy resins; Flame retardance; Thermal properties; Mechanical properties

1. Introduction

Epoxy resins have the following excellent characteristics: moisture, solvent, and chemical resistance; toughness; low shrinkage; superior electrical and mechanical properties; and good adhesion to many substrates. The versatility in formulation also made epoxy resins widely applied industrially for surface coating, adhesive, painting materials, pottings, composites, laminates, semiconductor encapsulation, and insulating material for electric devices, etc. [1−4]. The common epoxy resin systems, however, cannot satisfy some applications which require high thermal and flame resistance. Several techniques and approaches for modification of epoxy backbone have been employed in improving the flame retardance of epoxy polymers. A feasible approach for improving flame retardation of epoxy polymers involves the application of fire-retardant epoxy resins and curing agents. Although halogen atoms (e.g. bromine or chlorine) can be used to form some of the most widely applied flame retardant materials, in particular for polymers used in composite organic matrices or in electronic equipment, they have obvious disadvantages, for example, the potentiality of corroding metal components and toxic corrosive fumes of hydrogen halide formed during combustion [5,6]. For this reason, halogen-free flame retardants for polymers have attracted more attention from scientists and engineers in recent years.

Jeng et al. [7] used phenyl phosphonic dichloride to synthesize phosphorus-containing amines as a series of curing agents which provide epoxy polymers with high phosphorus content; Deng and Shi [8] synthesized hyperbranched (3-hydroxyphenyl) phosphate (HHPP) with high functionality as a curing agent of epoxy resins, and the LOI value was much improved; Wang and Lin [9] synthesized 2-(6-oxido-6*H*-dibenz(*c*,*e*)(1,2) oxaphosphorin-6-yl)-1,4-dihydroxy phenylene with 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO), which also revealed excellent flame retardancy and mechanical properties; Shieh and Wang [10] synthesized bis(3-hydroxyphenyl) phenyl phosphate(BHPP), which was used as a curing agent for diglycidyl ether of bisphenol-A (BA-EP). The resulting phosphorous-containing epoxy resin exhibited better flame retardancy and higher thermal stability than the regular bromine containing flame retardant epoxy resin.

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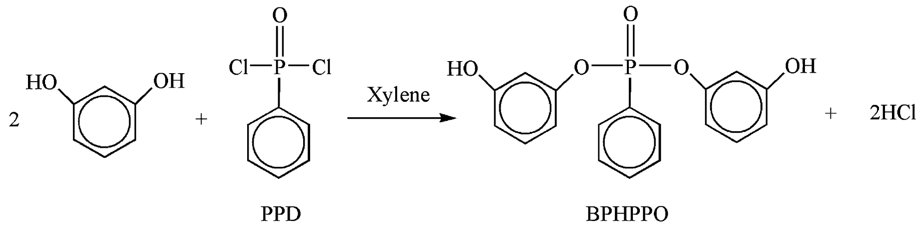


Scheme 1. The synthesis of BPHPPO.

The purpose of this study is to synthesize a novel phosphorus-containing flame retardant epoxy resin. In this work, bisphenoxy (3-hydroxy) phenyl phosphine oxide (BPHPPO) as well as an epoxy resin containing BPHPPO were synthesized as phosphorus-containing compounds, the structures of BPHPPO and the resin have been characterized, and the thermal and mechanical properties of the cured resins have also been investigated. This flame retardant epoxy resin possesses high phosphorus content that exhibits excellent flame retardancy than the conventional bisphenol-A epoxy resin and tetrabromobisphenol A epoxy resin.

2. Experimental

2.1. Materials

All reagents and solvents were reagent grade or were purified by standard methods before use. Phenyl phosphonic dichloride (PPD) was purchased from Acros Co. Resorcinol from Jinlin Reagents Co. China was used to synthesize BPHPPO. Tetrabromobisphenol A epoxy resin (TBBA-EP, epoxide equivalent weight (EEW) ≈ 244, Br% ≈ 8.68%) and bisphenol-A epoxy resin (BA-EP, EEW ≈ 227) were purchased from Huangshan Shanfu Chemicals Ltd., Co. China. Triphenyl phosphine (Ph_3P) from Shanghai Sanwei Co. was used as a curing accelerator. 4,4′-Diaminodiphenysulfone (DDS) obtained from Yinsheng Chemicals Ltd., Co. China was used as a curing agent. Epichlorohydrin (ECH) from Acros Co. was used without further purification. Xylene and toluene from Hangzhou Zhisheng Co. China were used as solvents.

2.2. Synthesize of BPHPPO

To a 500-ml four-necked reaction vessel equipped with thermometer, reflux condenser and mechanical stirrer were added 220 g resorcinol and 200 g xylene. Heat up the mixture to 125 °C slowly, 80 g of phenyl phosphonic dichloride was added continuously in 4 h by syringe pump until the resorcinol was dissolved. The reaction was maintained at 125 °C for 14 h at reflux until no HCl gas could be detected any more. The excess resorcinol was removed by washing with deionized water several times. After distillation, the xylene was removed

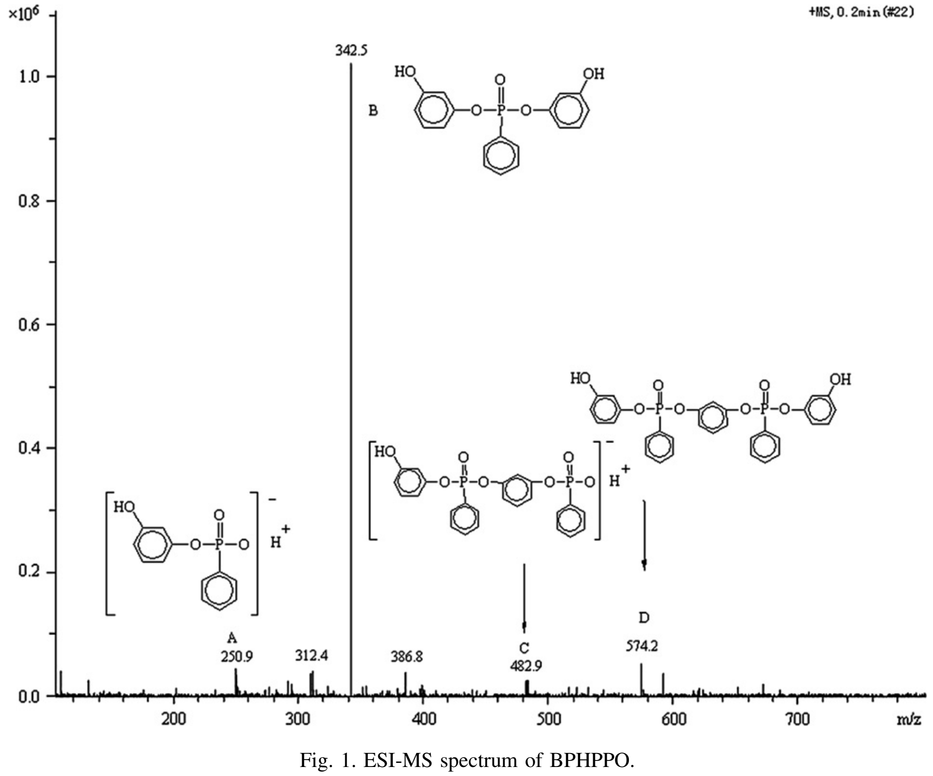


Fig. 1. ESI-MS spectrum of BPHPPO.

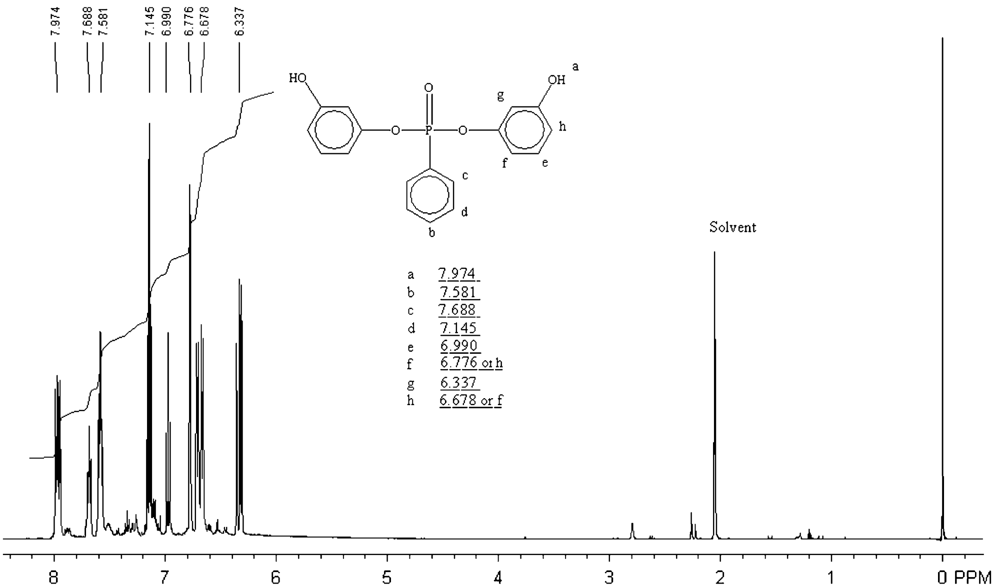


Fig. 2. ^1H NMR spectrum of BPHPPO using CD_3COCD_3 as solvent.

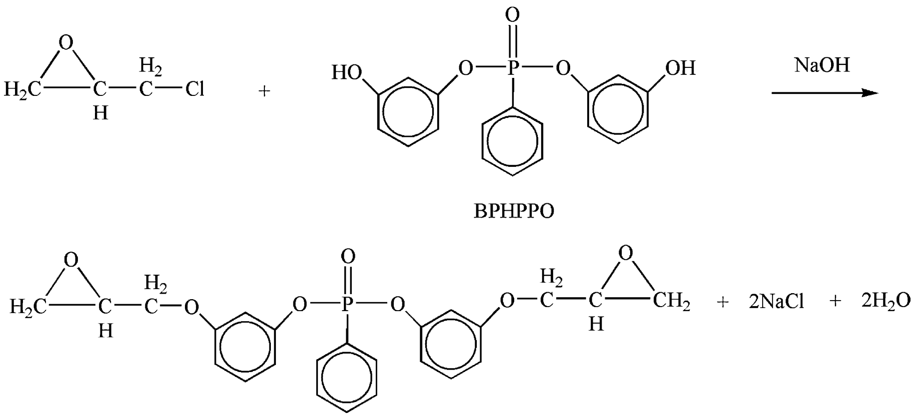
entirely. Purple colored viscous product (101.7 g) was obtained. The reaction equation is shown in Scheme 1. IR (KBr): 3323 cm^{-1} (—OH of phenyl); 1601 cm^{-1}, 1479 cm^{-1} (aromatic C—C); 1275.5 cm^{-1} (P═O); 1234 cm^{-1}, 979 cm^{-1} (P—O—Ph); ESI-MS: $m/z = 342.5$ (see Fig. 1); Elemental analysis: Calc. %: C: 63.16, H: 4.38; found %: C: 63.09, H: 4.50; ^1H NMR (CD_3COCD_3) (ppm): 7.97 (—OH of phenyl), 6.34—7.78 (aromatic proton) (see Fig. 2).

2.3. Synthesize of BPHPPO-containing epoxy resin (BPHPPO-EP)

To a 250-ml four-necked reaction vessel equipped with reflux condenser and mechanical stirrer were added 34 g of BPHPPO and 100 g of ECH. 30 g of 30 wt% aqueous NaOH were added into the vessel over a period of 1.5 h by syringe pump and further reacted at the reflux temperature for 2 h. Hot water (100 g) and toluene (150 g) were added into the separatory funnel. The organic phase was distillated to remove the toluene and the brown colored viscous epoxy resin (epoxide equivalent weight, EEW = 244.1) was obtained. The chemical reaction of the synthesis of the BPHPPO-EP is outlined in Scheme 2. IR (KBr): 1604 cm^{-1}, 1492 cm^{-1} (aromatic C—C); 1289 cm^{-1} (P═O); 1263 cm^{-1}, 995 cm^{-1} (P—C—Ph); 909.1 cm^{-1} (oxirane ring); Elemental analysis: Calc. %: C: 63.44, H: 5.07; found %: C: 63.21, H: 5.16; ^1H NMR (DMSO, d_6) (ppm): 7.50 (m, 1H, aromatic protons), 7.17—7.23 (m, 4H, aromatic protons), 6.3—6.7 (b, 8H, aromatic protons), 4.31 (d, 2H, CH_2 of 1,2-epxoypropyl), 4.02 (b, 2H, CH_2 of 1,2-epxoypropyl), 3.61—3.80 (b, 4H, saturated protons), 3.06 (m, 2H, saturated protons); ^{13}C NMR (DMSO,d_6) δ (ppm): 160.2, 160.0, 126—132, 107.6, 101.9 (phenyl), 69.5, 50.2, 44.3 (oxriane ring).

2.4. Curing procedure of epoxy resins

DDS was used as curing agent for the BPHPPO-EP or TBBA-EP. Ph_3P of 0.2 wt% was mixed as a curing accelerator.



Scheme 2. The synthesis of the BPHPPO-EP.

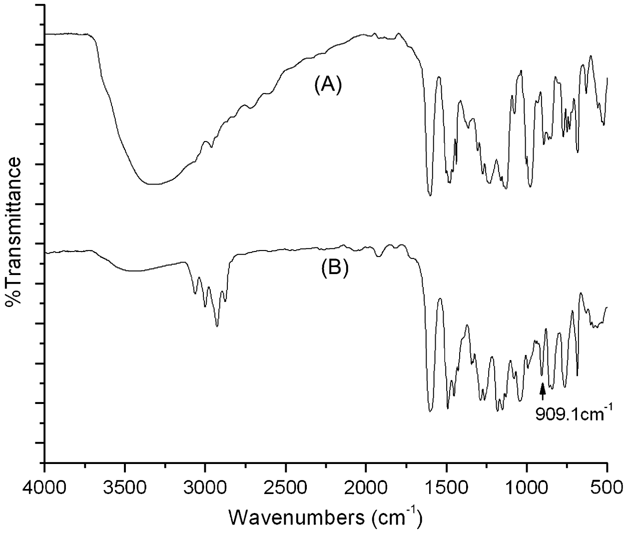


Fig. 3. FTIR spectrum of BPHPPO and BPHPPO-EP.

The blend was cured at 150 °C for 1 h, 200 °C for 2 h and 260 °C for another 1 h.

2.5. Characterization

The electrospray ionization-mass spectrometry (ESI-MS) was carried out on a Bruker Esquire-LC-00075 spectrometer. FTIR spectra were recorded on a Nicolet 5700 FT-IR spectrophotometer. ^{1}H NMR and ^{13}C NMR characterizations were carried out by Bruker Avance DMX 500 NMR spectrometer by using tetramethylsilane (TMS) as internal standard. Elemental analyses were performed by a ThermoFingnigan EA-1112 elemental analyzer. The epoxide equivalent weight (EEW) of epoxy resin was determined by HCl/acetone titration method. Thermogravimetric analysis (TGA) was performed using a Pyris 1 thermogravimetric analyzer (Perkin−Elmer Cetus Instruments, Norwalk, CT) at a heating rate of 10 °C/min under nitrogen and air atmosphere. The LOI is the minimum fraction of oxygen in a mixture of oxygen and nitrogen which could just support flaming combustion. The LOI tests were performed according to the testing procedure of ISO4589-1984 with test specimen bar of 7−15 cm in length, 6.5 ± 0.5 mm in width and 3.0 ± 0.5 mm in thickness. Ten sample bars suspended vertically were ignited by a Bunsen burner. The flame was removed and the timer was started. The concentration of oxygen was raised if the specimen was extinguished before burning 5 cm or 3 min. The oxygen content was adjusted until the limiting concentration was determined. Tensile properties were measured on a Zwick Roell Z202 Universal Material Testing Machine at a testing rate of 1 mm/min, the specimens were dumbbell-shaped with the testing part in the middle (dimension of the cross-section is 6 mm × 4 mm and the length of the testing part is 40 mm). Flexural properties were measured on a Zwick Roell Z202 Universal Material Testing Machine at a testing rate of 0.5 mm/min, with the dimension of the specimens 3 mm × 9 mm × 90 mm.

3. Results and discussion

3.1. Synthesis of BPHPPO

The synthesis of BPHPPO was performed by starting from phenyl phosphonic dichloride and resorcinol in the ratio of 4.5:1, which is presented in Scheme 1. ESI-MS spectrum of BPHPPO is shown in Fig. 1. The peak of mass–charge ratio at 342.5 just substantiated the molecular weight of BPHPPO. The compound A is a fraction of BPHPPO. The compound D is the dimer of BPHPPO. The compound C is the fraction of the dimer. The proportion of the compound D in the residue is very little and it can also participate into the following synthesis to obtain the epoxy resin. The compounds A and C were generated by the attack of the ions in the test. The

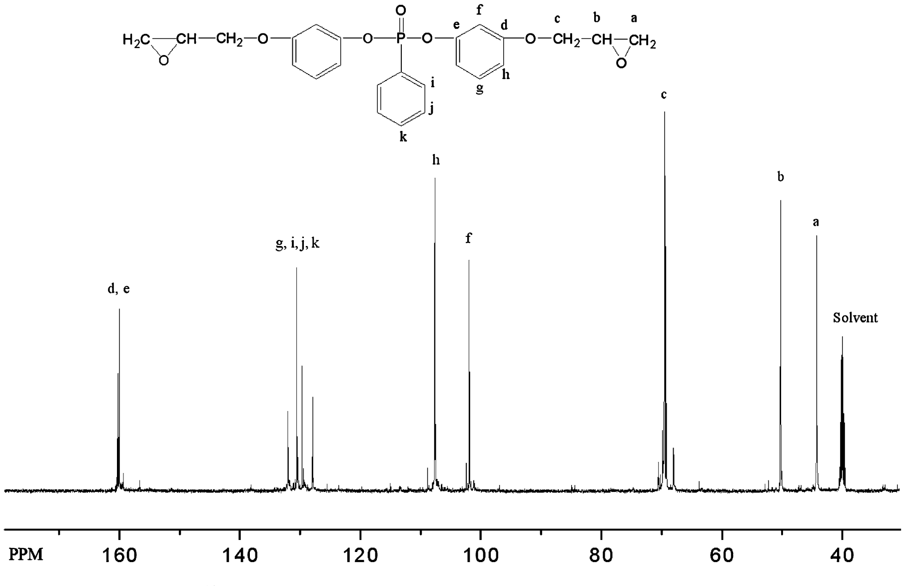


Fig. 4. ^{13}C NMR spectrum of BPHPPO-EP using DMSO, d_6 as solvent.

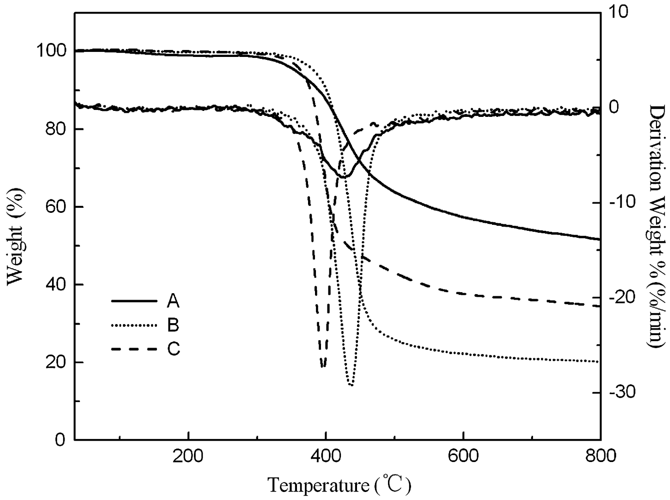


Fig. 5. TGA thermograms of the cured epoxy resins under nitrogen: (A) BPHPPO-EP; (B) BA-EP; (C) TBBA-EP.

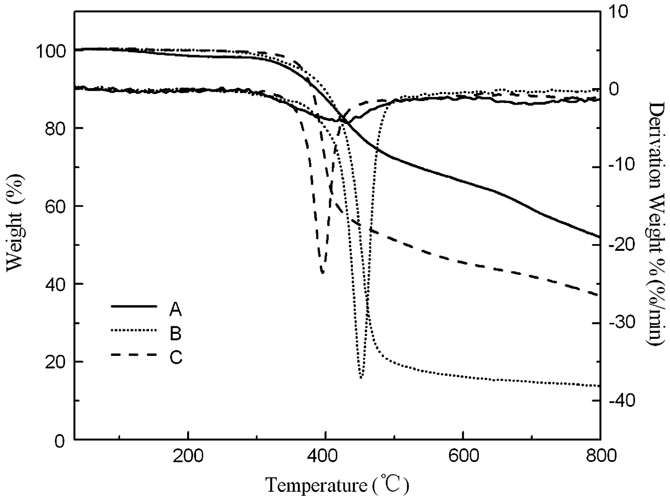


Fig. 6. TGA thermograms of the cured epoxy resins under air: (A) BPHPPO-EP; (B) BA-EP; (C) TBBA-EP.

molecular formulas of these compounds are also shown in Fig. 1. Fig. 2 shows the ^{1}H NMR spectrum of BPHPPO. The chemical shifts between 2 and 3 are attributed to the impurities of the raw materials. The chemical shifts corresponding to every proton on the phenyl rings were marked at $\delta = 6.34 \sim 7.98$ ppm. The FTIR spectrum of BPHPPO is shown in Fig. 3(A). The strong absorption around 1275.5 cm^{-1}corresponded to the vibration with P=O, which is characteristic of phosphate compounds; 1234 cm^{-1} and 979 cm^{-1} are assigned to P−O−C (aromatic) stretching; the absorption around 3300 cm^{-1} is attributed to the vibration of HO−P stretching. Therefore, the proposed structure of BPHPPO could be confirmed by the above characterization definitely.

3.2. Synthesis of BPHPPO-EP

The FTIR spectrum of the BPHPPO-EP is shown in Fig. 3(B). The strong absorption peak of −OH around 3300 cm^{-1} observed in Fig. 3(A) almost disappeared in Fig. 3(B) because of the reaction of the hydroxyl group with epichlorohydrin, and the characteristic absorption peak at 909.1 cm^{-1} for oxirane ring emerged in Fig. 3(B). These characteristic peaks indicated that the epoxy resin contains phosphorous group. ^{13}C NMR spectrum of BPHPPO-EP (Fig. 4) also confirmed the chemical structure of the synthesized resin, the peaks at 69.5 ppm, 50.2 ppm, 44.3 ppm were assigned to the carbons in epoxy group and 160.1 ppm to the aromatic carbons linked with oxygen atom. According to the result of the EEW titration, the EEW of BPHPPO-EP is 246.9 g/eq, which is close to the theoretical EEW of 227 g/eq.

3.3. Thermal properties of the cured epoxy resins

TGA is the most favored technique for rapid evaluation in comparing and ranking the thermal stability of various polymers. The TGA measurements of epoxy resins were carried out under air and nitrogen atmospheres at a heating rate of 10 °C/min from room temperature to 800 °C. Figs. 5 and 6 show the thermal degradation behaviors of the cured epoxy resins, and the test data are summarized in Table 1. It could be noted that the BPHPPO-EP (containing 7.79% of phosphorus) has exhibited higher char yield (51.8% in the N_2 and 52.1% in the air at 800 °C) than that of the BA-EP and TBBA-EP. The cured BA-EP exhibited a 5% weight loss at 384 °C and a 10% weight loss at 401 °C, the rapid weight loss was found at 436 °C in N_2; the cured TBBA-EP represented a 5% weight loss at 365 °C and a 10% weight loss at 377 °C, the rapid weight loss was found at 396 °C; the cured BPHPPO-EP showed a 5% weight loss at 357 °C, a 10% weight loss at 391 °C, the rapid weight loss was found at 427 °C. The rapid weight loss temperature of the BA-EP is higher than that of the BPHPPO-EP, but the BPHPPO-EP exhibited a second stage of comparatively rapid weight loss around the temperature 681 °C. This phenomenon plays an

Table 1
Thermal properties of the cured epoxy resins

Epoxy resin	P (%)	Br (%)	Curing agent	Temperature of weight loss (°C)				Char yields at 800 °C		LOI
				5%		10%				
				Air	N_2	Air	N_2	Air (%)	N_2 (%)	
BA-EP	0	0	DDS	368	384	400	401	13.9	20.2	22.5
BPHPPO-EP	7.79	0	DDS	350	357	388	391	52.1	51.8	34
TBBA-EP	0	8.68	DDS	370	365	380	377	37.1	34.5	27

Table 2
Mechanical properties of the cured epoxy resins

Epoxy resin	Tensile properties			Flexural properties		
	Tensile strength (MPa)	Tensile modulus (MPa)	Strain at break (%)	Flexural strength (MPa)	Flexural modulus (MPa)	Displacement at break (mm)
BA-EP	27.2	2980	1.0	53.5	2730	2.8
BPHPPO-EP	14.6	3480	0.6	48.7	3060	2.4

important role in improving the flame retardancy of the resins. The phosphorus group decomposed around 427 °C and formed a phosphorus rich residue covered over the surface of the resins which prevent further decomposition by raising the second decomposition temperature to 681 °C and generated a higher char yield eventually. The char yields of BA-EP, BPHPPO-EP and TBBA-EP were 20.2%, 51.8% and 34.5%, respectively. The similar phenomena in air could also be observed in the Table 1. These results implied that the BPHPPO-EP had higher char yields than BA-EP and TBBA-EP. which was important to flame-resistant epoxy resins, since high char yields always lead to high flame retardancy of the phosphorated polymers [11−16].

3.4. LOI test of the cured epoxy resins

The flame retardant property of the cured epoxy resins was evaluated by measuring their LOI values. Table 1 shows the LOI of epoxy resin with various phosphorus or bromine contents. It is clear that the flame retardancy of the cured BPHPPO-EP is much better than that of cured BA-EP and TBBA-EP. The cured BPHPPO-EP produced much less fumes than the cured TBBA-EP during combustion. So the flame retardance could be enhanced remarkably by raising the content of phosphorus in the epoxy resins, and when at a similar molar proportion in the compound, the phosphorus element also exhibited much better flame retardancy than the bromine element did [14,17].

3.5. Mechanical properties of the cured epoxy resins

The tensile properties of the cured BPHPPO-EP and BA-EP were characterized by vertical drawing test and flexural properties by three-point bending test. The results are shown in Table 2. The cured BPHPPO-EP resin exhibits higher modulus in both tensile and flexural tests and has similar flexural strength of the cured BA-EP. However, the tensile strength of the BPHPPO-EP is relatively lower, which may restrict the use of the resin in some of the applications.

4. Conclusions

A novel phosphorus-containing compound BPHPPO was synthesized successfully, and the phosphorus-containing epoxy resin was synthesized by making use of the BPHPPO. The flame retardant property of the cured BPHPPO-EP was much better than that of the conventional bisphenol-A epoxy resin and tetrabromobisphenol A epoxy resin. Even more, the fumes generated in the combustion were fewer.

Acknowledgments

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