

Synthesis and Properties of a Novel Phosphorous-Containing Flame-Retardant Hardener for Epoxy Resin

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ABSTRACT: An aryl phosphinate dianhydride 1,4-bis(phthalic anhydride-4-carbonyl)-2-(6-oxido-6H-dibenz[c,e][1,2]-oxaphosphorin-6-yl)-phenylene ester (BPAODOPE) was synthesized and its structure was identified by FTIR and ¹H-NMR. BPAODOPE was used as hardener and flame retardant for preparing halogen-free flame-retarded epoxy resins when coupled with another curing agent. Thermal stability, morphologies of char layer, flame resistance and mechanical properties of flame-retarded epoxy resins were investigated by thermogravimetric analysis, SEM, limiting oxygen index (LOI), UL-94 test, tensile, and charpy impact test. The results showed that the novel BPAODOPE had a better flame resistance, the flame resistance and char yield of flame-retarded epoxy resins increased with an increase of phosphorus content, tensile strength and impact strength of samples gradually decreased with the addition of BPAODOPE. The flame-retarded sample with phosphorus contents of 1.75% showed best combination properties, LOI value was 29.3, and the vertical burning test reached UL-94 V-0 level, tensile strength and impact strength were 30.78 MPa and 3.53 kJ/m², respectively. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: flame retardance; resins; thermosets

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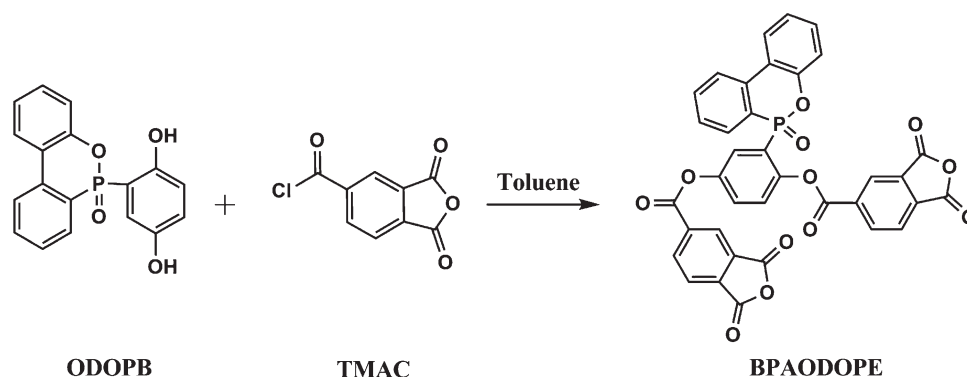
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INTRODUCTION

Epoxy resins are widely used in the fields of electronic/electrical industry and transportation because of their excellent electrical and mechanical properties.¹ However, the flammability of the resin is a major limitation in the application of requiring high heat resistance and flame resistance. Generally, halogen flame retardants were used to prepare the flame-retarded epoxy resins. Recently, in consideration of the numerous toxic substance were generated when the halogen flame retardant were burning, and harmful to natural environment and human health,^{2,3} the advanced flame-retarded epoxy resins are developing toward a tendency of halogen free. As known to all, the mechanical properties of epoxy resin will significantly decrease when using additive flame retardant, while the reactive flame retardant will overcome these defects.⁴ Comparing with the preparation of intrinsic flame-retarded epoxy resin, the chemical synthetic method for preparing the special hardner containing flame-retardant reactive group has many advantages such as simple, easy controllable, it becomes a development tendency to prepare flame-retarded epoxy resins with excellent properties. The research on the reactive curing agents containing phosphorus has been reported more and more in recent years. Many amines

curing agents containing phosphorus were synthesized by Liu and Döring et al.,^{5,6} and succeeded in application in the flame-retarded epoxy resin, the level of flame resistance reached UL94 V-1 and V-0 level, and the Limit Oxygen Index reached 30–48 when the content of phosphorus was between 2% and 4%. Comparing with the amine curing agents, acid anhydride curing agent has many advantages such as lower volatility, low toxicity, longer usage period, and the cured resin has a excellent electrical property and smaller volumetric shrinkage. Recently, a new environment-friendly flame retardant of cyclic phosphorous compound 9,10-dihydro-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and its derivatives have been reported by many researchers,^{7–12} and those DOPO-containing epoxy resins exhibit better thermal stability and excellent flame resistance even in a relatively low phosphorus content. Acid anhydride curing agents was the second largest usage amount hardener for epoxy resin; however, the studies on the acid anhydride curing agents containing phosphorus were rarely reported.^{13–15}

In this study, a novel curing agent containing phosphorus of DOPO-based aryl phosphinate dianhydride (BPAODOPE) was synthesized, and series of flame-retarded epoxy resins were prepared by filling BPAODOPE with different phosphorous



Scheme 1. Synthesis route of BPAODOPE.

contents, the flame resistance, thermal properties and mechanical properties of the flame-retarded epoxy resins were investigated in detail.

EXPERIMENTAL

Materials

2-(6-oxid-6H-dibenz<c,e><1,2>oxaphosphorin-6-yl)-1,4-benzenediol(ODOPB), its trade name was DOPO-BQ, obtained from Shandong Mingshan Chemical Industry Company; Trimellitic anhydride acid chloride(TMAC) was reagent grade and used without further purification, supplied by Jiangxi Sanjiang Fine Chemicals Company; Toluene and pyridine were purchased from Sinopharm Chemical Reagent, toluene was dried with sodium and distilled prior to use, and pyridine used as received. DGEBA (trade name was E-51, epoxy equivalent = 180–196 g/eq) was a kind of epoxy resins and supplied by Wuxi Resin Factory; Methylhexahydrophthalic anhydride (MeHHPA, hardener) was purchased from Puyang Huicheng Chemicals; N-Benzyl dimethylamine (BDMA) was used as an accelerator and purchased from Sinopharm Chemical Reagent; The other reagents were used as received from commercial sources or purified by standard methods.

Synthesis of BPAODOPE

A 250-mL four-necked round bottom flask was equipped with a thermometer, mechanical stirrer, nitrogen-inlet and reflux condenser with exhaust pipe. The flask was charged with ODOPB (3.309 g, 0.01 mol), TMAC (6.381 g, 0.03 mol), pyridine (1 mL), and dried toluene (120 mL). The reaction mixture was stirred at room temperature for 1 h, then heated to 110°C, and refluxed for about 6 h in nitrogen atmosphere, the chemical reaction process was shown in Scheme 1. After the product was cooled to room temperature of 25°C, the precipitant was filtered and washed with chloroform and ethyl acetate. The crude product was recrystallized from acetic anhydride and dried in a vacuum oven at 100°C for 6 h, white powders of BPAODOPE were obtained with 93.1% yield, m.p.: 298.8–300.8°C.

Preparation of Test Samples

Besides the synthesized novel hardener Aryl phosphinate dianhydride (BPAODOPE), methylhexahydrophthalic anhydride (MeHHPA) was used as a cohardener, and the mole ratio of anhydride and epoxy groups was 1: 1. To compare the results, the curing process of epoxy resin kept in the same conditions in all

cases. As shown in Table I, the hardeners of BPAODOPE and MeHHPA were put into the epoxy resin (DGEBA) with different mass ratios and mixed uniformly at the temperature of 60°C, and then 0.1 phr BDMA accelerator was added. The mixture was continuously stirred and put it into an oven at the temperature of 80°C for 20 min, then poured the mixtures into some teflon molds at 80°C. The samples were cured at 120°C for 4 h, and followed by postcuring at 150°C for 6 h.

INSTRUMENTAL ANALYSIS AND MEASUREMENTS

Structure Analysis

FTIR spectra were recorded on a Thermo NEXUS-470 Fourier transform infrared spectrometer using KBr pellet. ¹H-NMR spectra was measured on a Bruker Advance-600 (600 MHz) spectrometer with DMSO-d₆ as a solvent. Melting point of BPAODOPE was measured on a BUCHI B-540 Melting Point Apparatus.

Thermo Analysis

The thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on a NETZSCH STA449C/41G thermal analyzer at a heating rate of 10 K/min under N₂ atmosphere. The weights of samples were tested about 10 mg.

Flame Resistance Tests

The vertical burning tests (UL-94) were measured on a CZF-3 instrument (Jiangning Analytical Instrument Factory, Nanjing) according to ASTM D3801 testing procedure, with sample

Table I. DGEBA Samples Recipes with Different Ratio of BPAODOPE/MeHHPA

Samples	P% ^a	DGEBA(g)	BPAODOPE (g)	MeHHPA (g)
EP-1	0	100	0	84
EP-2	1.00	100	44.9	63.3
EP-3	1.50	100	71.5	48.1
EP-4	1.75	100	86.4	41.7
EP-5	2.00	100	102.3	32.9
EP-6	2.25	100	119.0	24.4

^aCalculated by formula: 'P%' = (weight of BPAODOPE/total weight of the system) × 4.61 wt % × 100%.

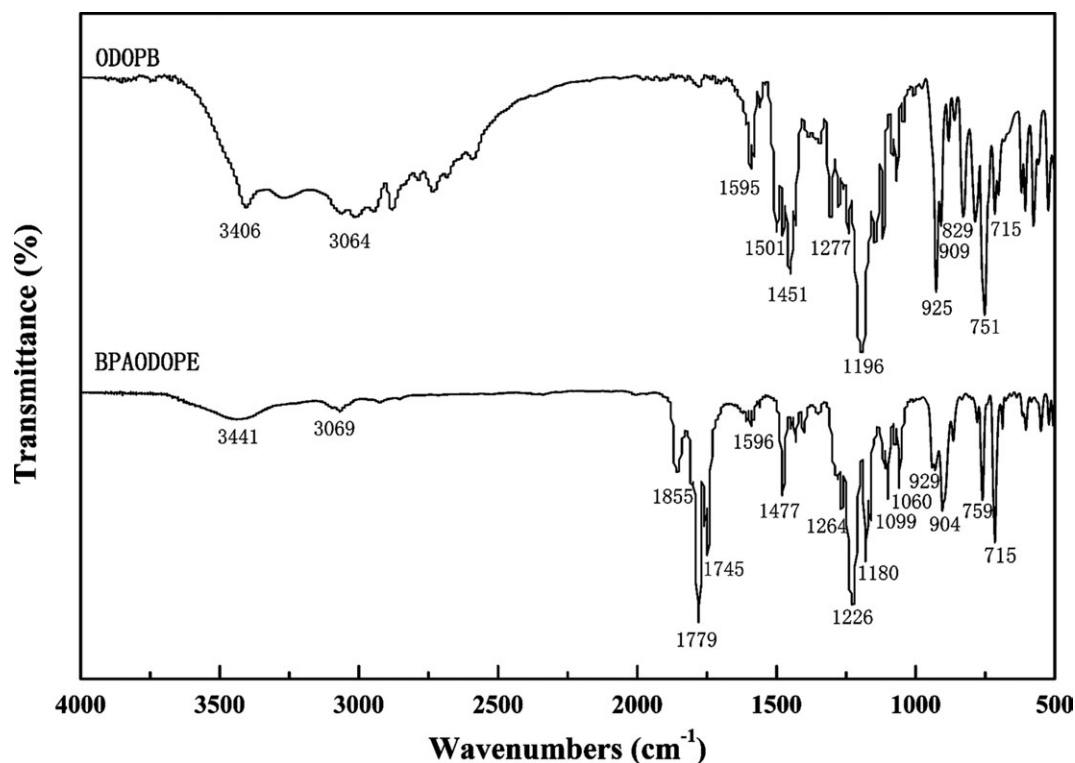


Figure 1. FTIR spectrum of ODOPB and BPAODOPE.

dimensions of $130 \times 13.0 \times 3.0 \text{ mm}^3$. The limiting oxygen index (LOI) was measured on a JF-3 limiting oxygen index chamber (the same factory with CZF-3) according to ASTM D 2863, with sample dimensions of $130 \times 6.5 \times 3.0 \text{ mm}^3$. The percentage of O_2 in the O_2/N_2 mixture was taken as the LOI which was just sufficient to sustain the flame.

Micro-Structure Analysis

Scanning electron microscopy (JSM-6360LV, JEOL) was used to investigate the residues surface of neat EP and flame-retarded EP. The residues for SEM were the combustion residues of burned samples in vertical burning tests.

Mechanical Property Tests

According to ISO 527-2, tensile strength tests of 4.0 mm thick samples were tested with TCS-2000 Electric Tensile Tester (Taiwan, China) with a speed of 10 mm/s at room temperature. Charpy impact tests were performed by GT-7045-MDL Charpy Impact Tester (Taiwan, China) according to ISO 179-1. All the listed results were the mean of five samples.

RESULTS AND DISCUSSION

Synthesis and Characterization

Aryl phosphinate dianhydride BPAODOPE was synthesized by the reaction of trimellitic anhydride acid chloride and ODOPB (Scheme 1) with toluene as solvent and pyridine as acid acceptor. The product was purified by recrystallization from acetic anhydride. The FTIR spectrum of ODOPB and BPAODOPE are shown in Figure 1, the characteristic peak at $3000\text{--}3500 \text{ cm}^{-1}$ (Ar-OH) existed in the crude ODOPB, while it disappeared in BPAODOPE production, and the appearance of characteristic

absorption peaks at 1855 and 1779 cm^{-1} were assigned to C=O of anhydride groups, and the peak at 1745 cm^{-1} was assigned to the C=O stretching vibration of ester groups. Absorption peaks at 929 and 1180 cm^{-1} were associated with the P—O—Ar groups, and the peak at 1477 cm^{-1} was for the P—Ar groups, the peak at 1264 cm^{-1} was for the P=O groups. Aromatic C—C bond was found at 1596 cm^{-1} , and aromatic C—H absorption was found at 3069 cm^{-1} .

The $^1\text{H-NMR}$ spectrum of BPAODOPE was shown in Figure 2, $^1\text{H NMR}$ (DMSO- d_6 , ppm): $\delta = 8.69$ (s, 2H); 8.30 (d, $J = 7.8\text{ Hz}$, 1H); 8.23 (dd, $J = 14.4 \text{ Hz}$, $J = 2.4 \text{ Hz}$, 1H); $7.87\text{--}7.97$ (m, 4H); 7.82 (d, $J = 7.8 \text{ Hz}$, 1H); $7.65\text{--}7.69$ (m, 3H); $7.56\text{--}7.57$ (m, 2H); 7.36 (t, $J = 7.2 \text{ Hz}$, 1H); 7.22 (d, $J = 7.8 \text{ Hz}$, 1H); 7.08 (t, $J = 7.2 \text{ Hz}$, 1H). The spectra were in good agreement with the proposed molecular structure. The structure of BPAODOPE was confirmed by FTIR and $^1\text{H-NMR}$ spectroscopy. Those results confirmed that the target product was synthesized successfully.

Thermal Properties

TGA curves and DTG curves of cured epoxy composites under nitrogen are shown in Figure 3, and the characteristic values obtained from these curves were listed in Table II. As shown in Figure 3 and Table II, the onset degradation and maximum decomposition temperatures for phosphorus-containing epoxy systems are slightly lower than neat epoxy, the weight loss of the phosphorus-containing epoxy resins were significantly higher than the neat epoxy at $200\text{--}300^\circ\text{C}$, which shows the phosphorus-containing epoxy resin composites have a lower decomposition temperature, the major reason was the

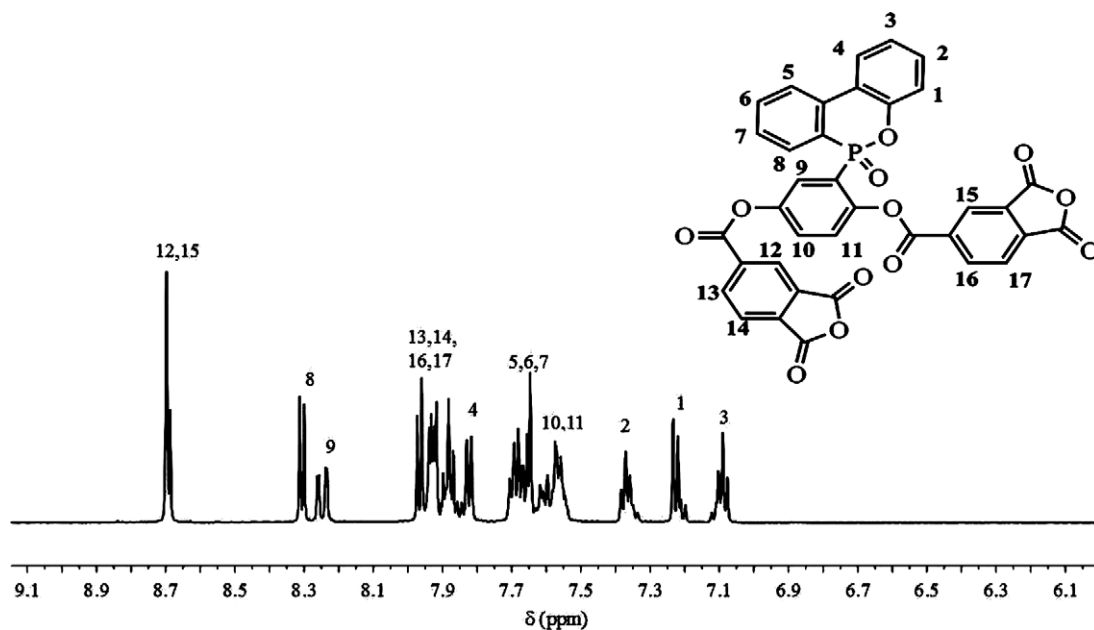


Figure 2. $^1\text{H-NMR}$ spectrum of BPAODOPE(600MHz, DMSO-d_6).

phosphorus group degrading at a relatively low temperature(200–280°C), the network's backbone of cured epoxy containing the phosphorus functional groups caused the poorer thermal stability for the weak P—O—C bond decomposition at low temperature,⁵ this phenomenon was also observed for other phosphorus-containing epoxy resins.^{16–18} From the Table II, the amount of residual char increased remarkably with an increase of phosphorus content. The residues of neat epoxy resin was 7.53% at 800°C, while the residues of flame-retarded epoxy resin with phosphorous content of 2.25% was 27.20% in the same conditions. The increase of residual char restricts the production of combustible gases, decreases the heat release of the pyrolysis reaction, and reduces the thermal conductivity of the burning materials, consequently, restricts the materials burning further. The thermal

stability of epoxy resins was especially affected by the structure of epoxy resin, the type of curing agent, and the curing schedule.¹⁹ The higher char residues of the phosphorus-containing epoxy resin were just caused by phosphorus groups transforming into phosphoric anhydrides and related acid which act as dehydrating agents, and thus promoted char formation.^{13,20} The results indicated that BPAODOPE played an important role in improving the amount of residual char of flame-retarded epoxy resins. DSC was used to measure the glass transition temperature (T_g) of cured epoxy resins, the glass transition corresponds to the major value of T_g of the cured epoxy resin, above which temperature significant chain motion takes place. The T_g values of cured samples were listed in Table II, the value of T_g of the neat epoxy was 148.7°C, and those of the cured systems with different BPAODOPE contents ranged

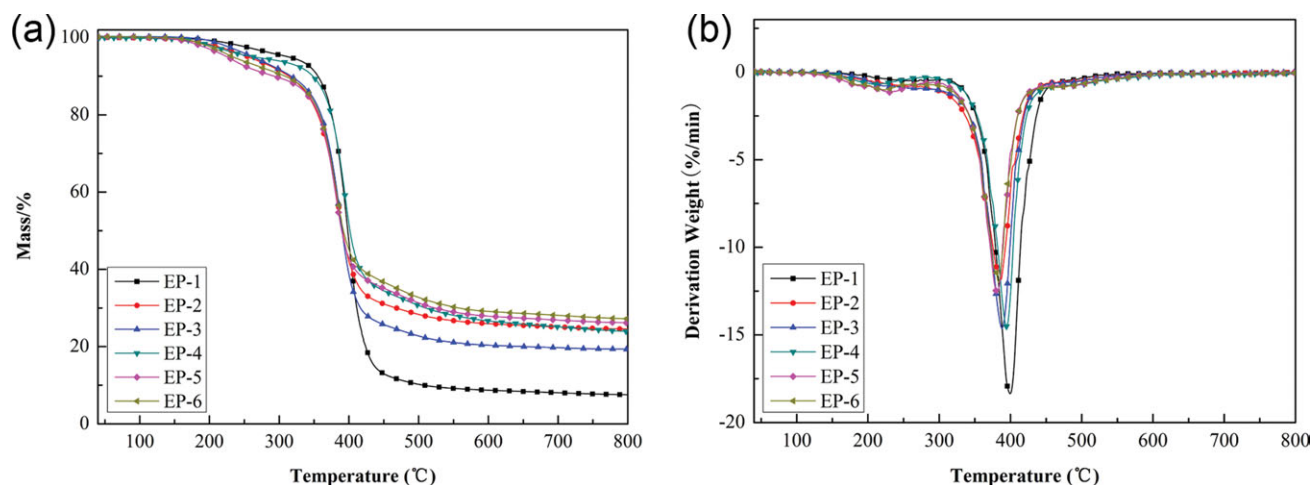


Figure 3. TG (a) and DTG (b) curves of the epoxy resin composites with different phosphorus contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Thermogravimetric Properties of Cured Epoxy Resins with Different Phosphorus Contents

Samples	P%	T_g (°C)	Temperature of weight loss (°C)			Residue at 800°C
			5%	10%	T_{max}	
EP-1	0	148.7	313.0	355.6	399.5	7.53%
EP-2	1.00	144.9	255.5	313.8	386.8	24.50%
EP-3	1.50	141.2	262.0	317.1	388.2	19.31%
EP-4	1.75	134.0	263.0	348.2	394.6	23.91%
EP-5	2.00	128.6	225.3	293.0	381.4	26.16%
EP-6	2.25	125.4	233.7	308.6	383.3	27.20%

from 144.9 to 125.4°C. Compared with the neat epoxy resins, the T_g values of epoxy resins containing BPAODOPE decreased significantly, and the more BPAODOPE introduced, the more decrease T_g obtained. This decrease probably came from the remarkable fall of crosslink density, which was in a great part resulting from the opening oxirane reaction that offset the benefit on T_g from the rigid BPAODOPE structure.

Flame Resistance

The limiting oxygen index (LOI) can be used as an indicator to evaluate the flame resistance of polymer, the LOI values denote the minimum oxygen concentration required to support downward

Table III. Mechanical and Flame-Retardant Properties of the Epoxy Resins with Various Phosphorus Contents

Samples	P%	Tensile strength (MPa)	Impact strength (KJ/m ²)	UL-94	LOI
EP-2	1.00	34.89	4.03	Failed	25.4
EP-3	1.50	32.44	3.76	V-1	27.6
EP-4	1.75	30.78	3.53	V-0	29.3
EP-5	2.00	28.90	3.25	V-0	29.9
EP-6	2.25	27.86	2.85	V-0	30.6

flame combustion. The LOI values of all samples were listed in Table III. It can be seen that the LOI values significantly increase from 19.8 to 30.6 with the phosphorus content increasing from 0 to 2.25 wt %, which indicates that the phosphorus-containing BPAODOPE is very effective in improving the flame retardation of epoxy resins. The vertical burning test (UL-94) determines the upward burning characteristics of polymer. It is clear that the flame retardation of cured epoxy resins increases with an increase of phosphorus content, and UL-94 V-0 rating can be obtained at phosphorus content of 1.75 wt %. The results showed that the flame-retarded epoxy resin can be prepared by incorporating BPAODOPE with minimum phosphorus content of 1.75%.

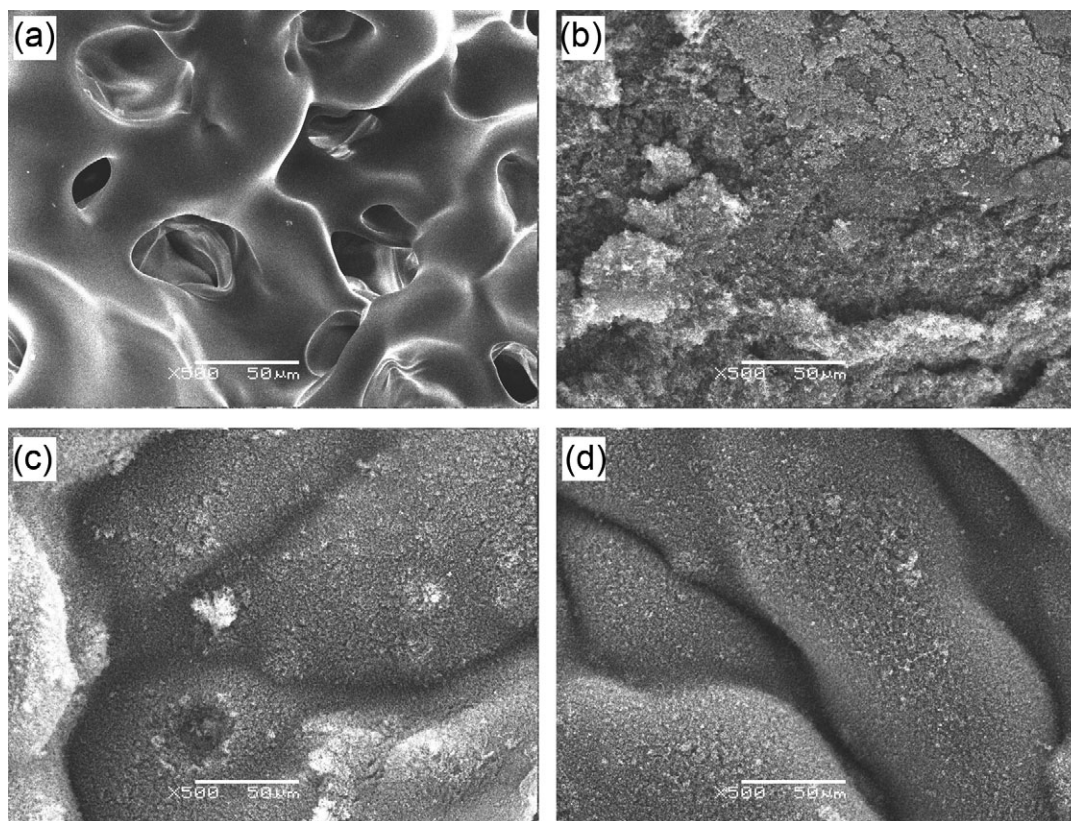


Figure 4. SEM morphology of the residues of samples, (a) EP-1, (b) EP-2, (c) EP-4, (d) EP-6.

Morphology of Residue

The morphologies of four char residues have been observed by SEM, as shown in Figure 4. After the neat epoxy (named EP-1) burned, as shown in Figure 4(a), there are numerous pores, and the pores acted as the channels through which oxygen and the fuel flowing and interacting, thus contributing to combustion, and there are no flame retardation char layers existing in the surface of residue. However, the compact char layers can be observed on the residues surface of the flame-retarded epoxy resins, which was shown in Figure 4(b–d), the char layers effectively protect the internal structures of samples, inhibit the heat transmission and reduce the fuel gases in the combustion process. Incompact char layers were observed in the residue surface with phosphorus content of 1.00% in Figure 4(b); when the phosphorus content increased to 1.75% and 2.25%, as shown in Figure 4(c,d), the compact intact char layers formed on the residue surface, which prevented the combustion of epoxy resins effectively. Therefore, the flame-retarded epoxy systems containing BPAODOPE showed a good flame resistance. Those results were in accordance with the results of TGA, LOI, and UL-94 testing. The formation of char layer demonstrated that phosphorus of BPAODOPE played an important role. During combustion, phosphorus in polymers converted to phosphoric acid, and the further thermal decomposition led to the formation of polyphosphoric acid. The polyphosphoric acid esterified and dehydrated the pyrolyzing polymers, and formed phosphorus-rich char layers simultaneously, which inhibited the pyrolysis reactions further. The protective layers restricted the heat transmission and provided a good flame shield for the underlying material during combustion.²¹

Mechanical Properties

The mechanical properties of the cured epoxy resins were characterized by vertical drawing test and Charpy impact test. The results were shown in Table III. The flame-retarded epoxy resins exhibited lower tensile and impact strengths than neat epoxy resin. Compared with neat epoxy resin, mechanical properties of flame-retarded samples gradually decreased with an increase of BPAODOPE. Tensile strength and impact strength of neat epoxy resin were 37.90 MPa and 5.19 kJ/m²; however, the corresponding strength values of flame-retarded sample dropped to 27.86 MPa and 2.85 kJ/m² when filling BPAODOPE with phosphorous content of 2.25%, the tensile strength dropped 26.5%, and impact strength dropped 45.1% than the neat epoxy resin respectively. The mainly reason for the mechanical strength decreasing was just for the excessive filling of BPAODOPE, meanwhile, BPAODOPE has a lower phosphorous content and a rigid molecular structure, the steric hindrance effect caused by the rigid structure will decrease cross-linking density of epoxy resins, which deteriorate the mechanical properties of flame-retarded epoxy resins. The conclusion can be drawn that the reactive flame retardant BPAODOPE improved the flame resistance of epoxy resin obviously, while the mechanical properties had a certain decline. Considering the combination properties of flame-retarded epoxy resin, the sample of EP-4 with phosphorous content of 1.75% has the best performance, tensile strength, and impact strength were 30.78 MPa and 3.53 kJ/m²,

LOI value was 29.3, and the vertical burning test reached UL-94 V-0 level.

CONCLUSIONS

In this article, a novel aryl phosphinate dianhydride BPAODOPE was synthesized successfully, and used as hardener and flame retardant for preparing halogen-free flame-retarded epoxy resins when coupled with another curing agent. The epoxy resin composites filling with BPAODOPE had excellent flame resistance and higher char yield, and the flame resistance and char yields of the flame-retarded epoxy resins increased with an increase of phosphorus content. The epoxy resins with the phosphorus contents of 1.75% showed excellent combination properties. The results also show that BPAODOPE has some shortcomings, it has a lower phosphorous content, when the phosphorous content is 2.25%, the mechanical properties of epoxy resin will decrease obviously, tensile strength and impact strength of sample were 73.5% and 54.95% for their values of neat epoxy resin respectively. So the further study will focus on the synthesis of some novel reactive flame retardants, which should have a higher phosphorous content of unit mass, and improve the combination properties of flame-retarded epoxy resins.

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