High-efficiency flame retardant behavior of bi-DOPO compound with hydroxyl group on epoxy resin

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ARTICLE INFO

ABSTRACT

To explore the more effective non-halogen flame retardants in epoxy resins, a flame retardant named ABD owning relatively short bridged bonds and a hydroxyl group was synthesized via addition reaction between acrolein and 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO). Then, ABD was applied into flame retardant epoxy resin, diglycidyl ether of bisphenol-A, cured by 4,4′-diamino-diphenylmethane. When the mass fraction of ABD in epoxy resin was only 3 wt%, the thermoset acquired a higher limited oxygen index (LOI) value 36.2% and passed UL94 V-0 rating. ABD also reduced all the values of peak of heat release rate (pk-HRR), total heat release (THR), average effective heat of combustion (av-EHC), total mass loss (TML) and average CO_2 yield, and increased the residue yield. In contrast to DOPO, ABD can impose the higher LOI value, the higher UL94 rating and the lower peak value of HRR to epoxy thermosets. Further, the results from the cone calorimeter test reveal that the better flame retardant performance of ABD was caused by quenching effect from phosphaphenanthrene groups in gas phase and the charring effect from the joint action of phosphaphenanthrene group and hydroxyl group in condensed phase simultaneously. The excellent flame retardant performance of ABD is from its higher phosphorus contents and its special hydroxyl group.

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1. Introduction

Epoxy resins (EP) have excellent electrical insulation, sealing performance, good physical-mechanical and adhesive properties, and are widely applied in various industry fields, such as coating, adhesive, electrical insulation materials and so on. Unfortunately, the flammability of epoxy resin leads to fire disaster ineluctably, which severely limits their wider utilization. Therefore, flame retardant functionalization of epoxy resin is very crucial [1,2].

Nowadays, adding flame retardant to epoxy resin is an effective and shared way to improve its flame retardancy. In the midst of this, the research of phosphaphenanthrene flame retardant epoxy resin has become the focus of attention [3—6]. 9, 10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and its derivatives are widely used in epoxy resins due to their characteristic flame retardant effect [7—11]. They can exert flame retardant effect both in gas phase and condensed phase through releasing free radicals

and charring effect [12—15]. A lot of work has been reported on the molecular design and synthesis of DOPO derivatives [16—18], and the factors affecting the flame retardant efficiency have been investigated. The flame retardant efficiency of DOPO derivatives can be influenced by two ways: 1) the phosphorus content of DOPO derivatives; 2) the other functional groups in DOPO derivatives. The high phosphorus content DOPO derivatives in epoxy resin directly influences the quenching effect in gas phase and the charring effect in condensed phase. For example, 4 wt% DOPO-based triazole compound (DTA, P content: 8.9%) was applied into EP cured with DDM achieved an LOI value of 34.8% and V-0 rating in UL-94 test [19]. 5 wt% melamine-organophosphinic acid salt (MDOP, P content: 8.7%) was applied into EP cured with DDM achieved an LOI value of 35.6% and V-0 rating in UL-94 test [20]. They all have the relative high phosphorus contents and imposed the higher flame retardant efficiency to epoxy thermosets with the lower addition ratios. Meanwhile, the other functional groups, such as phosphazene [21,22] triazine [23,24] triazine-trione [25,26] phosphate [27,28] borate [29,30] siloxane [31,32] or maleimide [33,34] in DOPO derivatives, can respectively jointly worked with phospha-phenanthrene group to generate flame retardant group synergistic

effect, thereby enhancing the flame retardant efficiency in epoxy thermosets. Accordingly, some non-typical functional groups in molecules also can provide positive influence to flame retardant properties. The hydroxyl group is the special group. Due to owning four hydroxyl groups, pentaerythritol usually was used as charring agent in intumescent system. A tri-DOPO compound TGD [35] has better charring flame retardant effect in comparison with another tri-DOPO compound TAD [36], which has similar chemical structure as TGD. The only difference between TGD and TAD is that TGD has more three hydroxyl groups than TAD. Therefore, hydroxyl group is effective charring group in flame retardant molecules. According to the previous researches, it is an effective way to enhance flame retardant efficiency of molecules to design DOPO derivative structures with high phosphorus content and effective flame retardant functional groups [37–40].

In this work, we synthesized a DOPO derivative named ABD (in Fig. 1) based on DOPO and acrolein via addition reaction, which contains two phosphaphenanthrene groups connected by relatively short bridged bonds and a hydroxyl group. Therefore, the better flame retardant efficiency was expected due to its higher phosphorous contents and the charring group-hydroxyl group. Accordingly, the flame retardant behavior and mechanism of ABD in epoxy thermosets was systematically explored.

2. Experimental

2.1. Materials

DOPO was supplied by Jiangyin Hanfeng Chemical Co., Ltd, Jiangsu. Acrolein was purchased from Shenyang Chemical Reagent Factory, Liaoning. The epoxy resin diglycidyl ether of bisphenol-A (DGEBA, commercial name: E−51) was purchased from Blue Star New Chemical Material Co., Ltd, Jiangsu. 4, 4′-Diamino-diphenyl-methane (DDM) and tetrahydrofuran (THF) were bought from J&K Scientific Ltd, Beijing. All the materials were used directly without further purification.

2.2. Synthesis of ABD compound

DOPO (69.12 g, 0.32mol), acrolein (8.4 g, 0.15mol), and 300 ml tetrahydrofuran (THF) were added into a 500 ml three-necked flask equipped with a stirrer. The mixture was cooled to 10 °C in ice-water bath. Then, the mixture was stirred for 3 h to ensure that the double bond and the aldehyde groups of acrolein fully reacted with the P−H bond in DOPO. After the mixture was heated to 80 °C to remove the solvent THF, the product was obtained. Then the heated product ABD was washed three times with 95 °C deionized water. The product ABD was obtained after vacuum drying at 110 °C. Cooled to room temperature, the product ABD was grinded into powder. Yield: 99.0%. The reaction formulation was shown in Fig. 1. FTIR spectrum (KBr, cm^{-1}): 3419 (-OH); 3062 (Ar−H); 2919 (-CH$_2$-); 2851 (C−H); 1634, 1594, 1582, and 1559 (aromatic skeleton); 1430 (P-Ph); 1201 (P=O); 909 (P−O-Ph); 753 (P−C). The ^{1}H nuclear magnetic resonance (^{1}H NMR) data obtained (methanol-d$_6$,

ppm) are δ = 7.0 to 8.3(Ar−H, 16H), δ = 5.9 to 6.2(-OH), δ = 5.2 to 5.6(P−CH$_2$), δ = 4.7 to 4.9 (P−CH), δ = 1.9 to 4.4(CH$_2$). The ^{31}P nuclear magnetic resonance (^{31}P NMR) datum obtained (methanol-d$_6$, ppm) are δ = 34.6 and 34.1. Element data (calculated/experimental): ABD(C$_{27}$H$_{22}$O$_5$P$_2$), C: 66.39/65.31, H: 4.51/4.69.

2.3. Preparation of flame retardant epoxy thermosets with ABD

DGEBA and ABD were heated to 120 °C and stirred till ABD was completely dissolved in DEGBA. Then, DDM was added into the mixture at 110 °C and mixed thoroughly. After the epoxy resin mixture was degassed at 120 °C for 3 min, it was poured into the preheated molds and cured at 120 °C for 2 h and then at 170 °C for 4 h. The samples were respectively labeled as 2%ABD/EP, 3%ABD/EP and 4%ABD/EP based on the mass fraction of ABD in EP thermosets. The control samples, EP and 3%DOPO/EP were also prepared in the same manner but without the addition of ABD. The ratios of DGEBA, DDM, ABD and DOPO in each epoxy thermosets were listed in Table 1.

2.4. Characterization

Fourier transform infrared (FTIR) spectra were characterized on a Nicolet iN10MX-type spectrometer (Thermo Fisher Scientific, USA) using potassium bromide discs with a total of 32 scans.

^{1}H NMR and ^{31}P NMR spectra were detected using a Bruker Advance III HD 700 MHz NMR spectrometer (Bruker, Switzerland). Methanol-D4 was used as the solvent.

Elemental analysis was performed on a Vario EL elemental analyzer (Elementar Analysensysteme GmbH, Germany) with a combustion temperature at 900 °C. The results were the average of the 2 times repeated tests.

Thermogravimetric analysis (TGA) was performed with a PerkinElmer instrument STA8000 thermal gravimetric analyzer (PerkinElmer, USA). The weight of the samples was kept within 5−10 mg and heated from 50 °C to 700 °C at a heating rate of 20 °C/min under 20 ml/min flow of nitrogen atmosphere.

The limited oxygen index (LOI) value was determined using a Dynisco LOI instrument (Fire Testing Technology, UK) according to the standard ASTM D2863-97 (sample dimension: 130.0 mm × 6.5 mm × 3.2 mm).

The UL-94 vertical burning test was obtained using an FTT0082 instrument (Fire Testing Technology, UK) according to ASTM D3801-2010 (sample dimension: 125.0 mm × 12.7 mm × 3.2 mm). In this test, the burning grades of material were classified as V-0, V-1, V-2 or NR (no rating).

Cone calorimeter (Fire Testing Technology, UK) tests were performed according to ISO 5660 at a heat flux of 50 kW/m^2. The equipment is Fire Testing Technology apparatus with a cone radiator and two samples were tested (sample dimension: 100 mm × 100 mm × 3 mm).

The glass transition temperature of sample was measured using a Q20 differential scanning calorimeter (TA Instruments, USA)
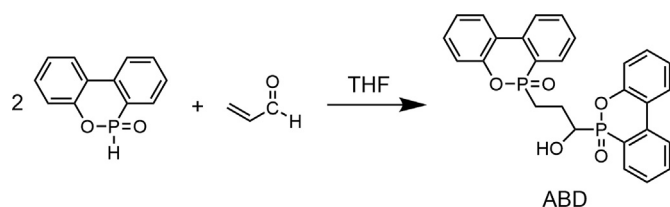

Fig. 1. Synthesis route of ABD.

Table 1
The formulas of the phosphorous-containing epoxy resins cured with DDM.

Samples	DGEBA (g)	DDM (g)	ABD		DOPO (g)	P-content (wt.%)
			(g)	(wt.%)		
EP	100	25.3	−	−	−	0
2%ABD/EP	100	25.3	2.6	2.0	−	0.25%
3%ABD/EP	100	25.3	3.9	3.0	−	0.38%
4%ABD/EP	100	25.3	5.2	4.0	−	0.51%
3%DOPO/EP	100	25.3	−	−	3.9	0.43%

under a nitrogen atmosphere. The heating and cooling procedure proceeded at a rate of 20 °C/min over temperature range of 40–220 °C.

SEM was used to examine the morphology of the char residue obtained from cone calorimeter test and EDX was used to determine the content of the elements contained from UL94 test using a Phenom™ Pro scanning electron microscope (Phenom World, Netherlands) at vacuum conditions with a voltage of 15 kV.

To recognize the pyrolysis ways of ABD, a Perkin Elmer gas chromatography-mass spectrometer (GC-MS) equipped with STA 8000 thermal gravimetric analyzer was employed. The helium (He) was utilized as carrier gas for the volatile products. The injector temperature was 280 °C, the temperature of GC-MS interface was 280 °C and the cracker temperature was 450 °C.

3. Results and discussion

3.1. Characterization of the molecular structure of ABD

For confirming the successful synthesis of ABD, the chemical structure of ABD was detected using FTIR, ^{1}H NMR and ^{31}P NMR, respectively. In Fig. 2, the spectrum of ABD presents the characteristic absorption peak at 3419 cm^{-1}, which correspond to −OH stretching vibration; the absorption bands at 2919 cm^{-1} and 2851 cm^{-1} correspond to CH stretching vibration on the alkyl chain; the absorption bands at 1594 cm^{-1}, 1430 cm^{-1}, 1201 cm^{-1}, 909 cm^{-1} and 753 cm^{-1} attribute to the absorption bands of phosphaphenanthrene group. The two bands of C=C double bond at 1731 cm^{-1} and C=O bond at 1650 cm^{-1} in acrolein disappeared in ABD spectrum, confirming the successful addition reaction between DOPO and acrolein.

The ^{1}H NMR and ^{31}P NMR spectra were also employed to further verify the chemical structure of ABD. As shown in Fig. 3a, the chemical shifts at 7.0−8.3 ppm ascribe to the aromatic H in phosphaphenanthrene group; the chemical shifts at 5.5−6.0 ppm correspond to the signal of −OH; the chemical shifts at 3.8−4.3 ppm are assigned to C−H close to hydroxyl group; the chemical shifts at 1.5−2.1 ppm are from the signal of CH$_2$ farthest to phosphaphenanthrene group; the chemical shifts at 2.1−2.5 ppm are caused by the CH$_2$ group near phosphaphenanthrene group. The integral area ratio of the five kinds of H chemical shifts is about 16: 1: 1: 2: 2, which corresponds to the calculated value of different

H atoms in ABD. In Fig. 3b, the ^{31}P NMR spectrum exhibits two signals at 34.6 ppm and 34.1 ppm, which were caused by P atoms in P−CH$_2$ and P−CH, respectively. The integral area ratio of the two P chemical shifts is 1: 1, which confirmed that the DOPO groups have been equally linked in molecule. The ^{1}H NMR and ^{31}P NMR data all demonstrate that the ratios between different H atoms and between different P atoms in ABD accord with the calculated values of ABD molecule. According to all the analyses above, the target product ABD has been synthesized successfully.

3.2. Thermal analysis of epoxy thermosets

T_g is an important influence factor for application of epoxy resin thermosets. The results are illustrated in Fig. 4. The T_gs of epoxy resins gradually decreased from 166 °C to 156 °C with increasing the ABD contents from 0 to 4 wt%. Typically, the T_g of 3%ABD/EP sample is just decrease 8 °C compared with that of neat EP, meanwhile it has reached the UL94 V-0 rating. Further, in contrast to 3%DOPO/EP, the T_g of 3%ABD/EP was slightly raised 3 °C, which should be resulted by that ABD did not react with epoxy group and increased the crosslinking density.

The TGA curves of EP composites under nitrogen in Fig. 5 showed their thermal decomposition behavior, and some typical data were listed in Table 2. Compared with neat EP, the onset degradation temperature ($T_{d,1\%}$) decreased from 369 °C to 344 °C and the char yield increased from 15.7% to 19.8% in the 3%ABD/EP sample. Meanwhile, the pyrolysis behavior of 3%ABD/EP was similar to that of 3%DOPO/EP. It revealed that ABD can generate condensed phase flame retardant effect like DOPO [12] due to their phosphaphenanthrene structure.

3.3. LOI and UL94 tests

The flame retardant properties of the EP thermosets were measured by LOI and UL94 vertical burning tests, and the tested results were shown in Table 3. It can be seen that the neat EP sample only achieved a 24.7% LOI value and no rating (NR). After the addition of different amounts ABD, the LOI values of the samples obviously increased with increasing the mass fraction of ABD in the thermosets, and the highest LOI value was 39.1% with the addition of 4 wt% ABD in epoxy composites. Meanwhile the samples with only 3 wt% ABD and 4 wt% ABD all passed the UL94 V-0 rating, and the 2%ABD/EP sample also passed UL94 V-1 rating.

The control sample, 3%DOPO/EP showed a LOI value of 35.5% and no UL94 rating. Compared with 3%DOPO/EP, 3%ABD/EP acquired better flame retardant performance in UL94 test and maintained a high LOI value. This comparison disclosed that the phosphaphenanthrene compound ABD possessed the more positive flame retardant effect in epoxy composites than DOPO did.

3.4. FTIR analysis of the char residue from UL94

To explore the difference of UL94 test results between 3%ABD/EP and 3%DOPO/EP, the char residue from UL94 test were analyzed by FTIR. The char residue from 3%ABD/EP self-extinguishment after UL94 test was detected (ignited twice, 10 s at a time), while the char residue from 3%DOPO/EP was blow out after ignited once because it burned to the clap.

In Fig. 6, both of the curves of the two samples present a strongest characteristic absorption peak at 3420 cm^{-1}, which attributes to amino structure from curing agent left mostly in residue. Therefore, the characteristic peak at 3420 cm^{-1} is used as a reference for comparing with the changes of other absorption peaks because the addition amounts of curing agent in two samples are same. The absorption bands of 3%ABD/EP at 1609 cm^{-1}, 1508 cm^{-1}

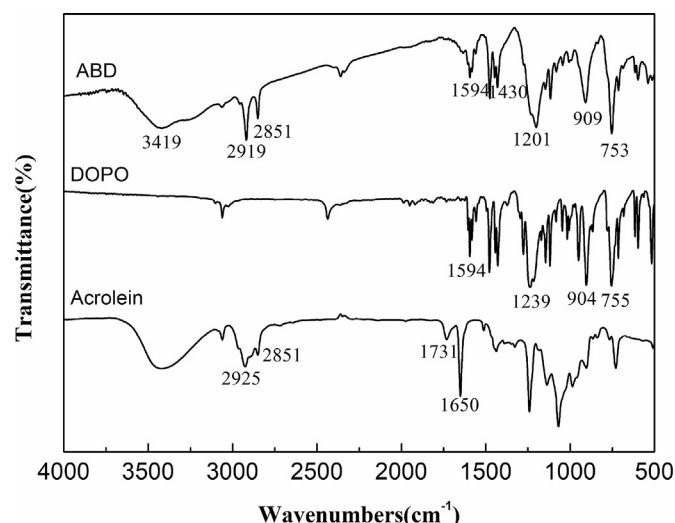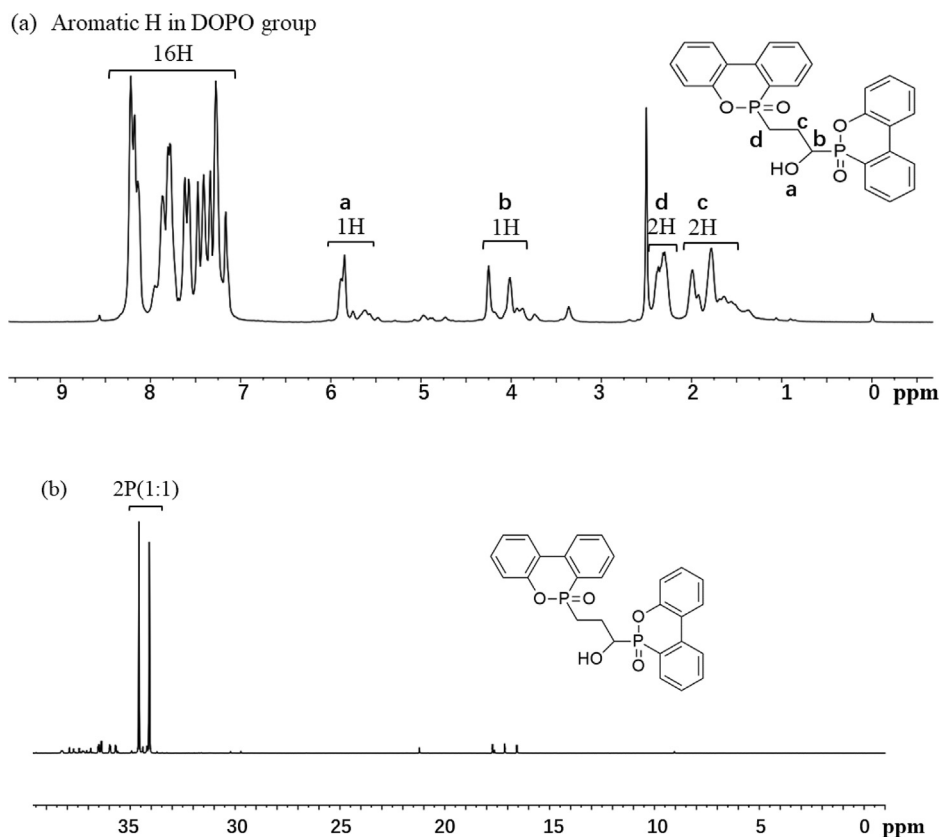**Fig. 2.** FTIR spectra of ABD, DOPO and acrolein.

Fig. 3. (a) ^{1}H NMR and (b) ^{31}P NMR spectra of ABD.

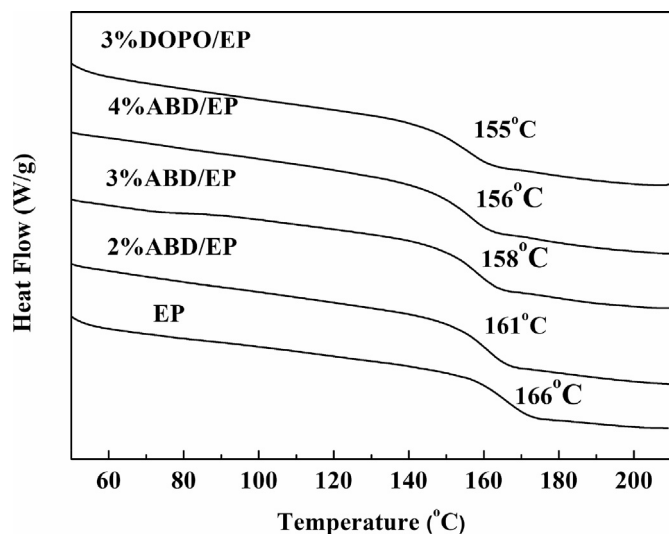Fig. 4. DSC curves of epoxy thermosets.

Fig. 5. TGA curves of epoxy thermosets under nitrogen.

and 826 cm^{-1} from bisphenol A structure are stronger than those of 3%DOPO/EP, and the absorption bands of 3%ABD/EP at 2960 cm^{-1} and 2922 cm^{-1} corresponding to CH stretching vibration on the alkyl chain are also stronger than those of 3%DOPO/EP. The results imply more matrix were remained in the residue of 3%ABD/EP. The absorption bands of 3%ABD/EP at 1233 cm^{-1}, 1175 cm^{-1}, 1113 cm^{-1} and 1031 cm^{-1} are assigned to the absorption bands of phospha-phenanthrene group, which are also stronger than those of 3% DOPO/EP obviously, further proving that ABD exerted a better
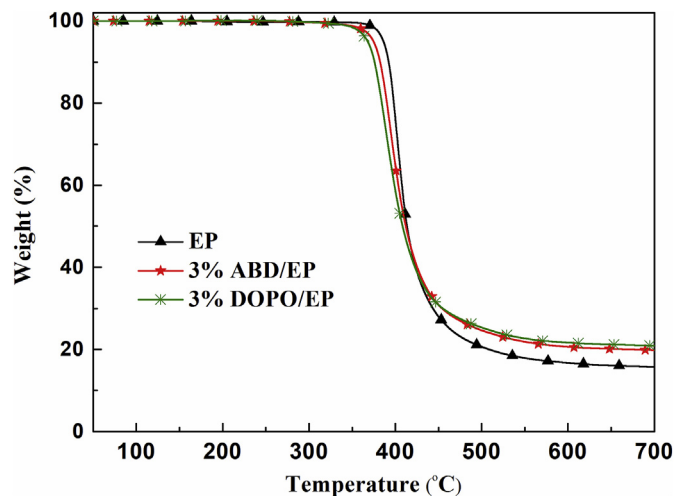
Table 2
The typical TGA data of epoxy thermosets.

Samples	$T_{d,1\%}$ (°C)	Char yields at 700 °C (wt.%)
EP	369	15.7
3%ABD/EP	344	19.8
3%DOPO/EP	340	20.9

action in the formation of char residue in condensed phase during combustion. The absorption bands of 3%ABD/EP at 3320 cm^{-1}

Table 3
LOI value and UL94 rating of epoxy composites.

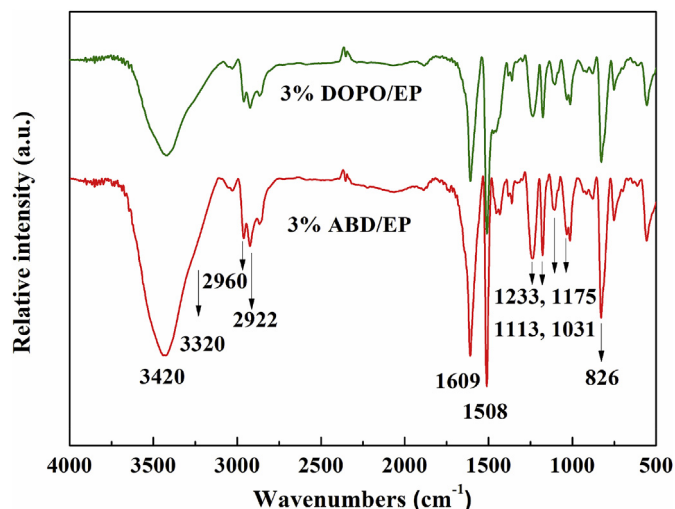| Samples	LOI (%)	UL94 (3.2 mm)			
		av-t_1(s)	av-t_2(s)	Dripping	Rating
EP	24.7	50.8	—	No	NR
2%ABD/EP	32.3	7.4	5.8	No	V-1
3%ABD/EP	36.2	1.7	4.6	No	V-0
4%ABD/EP	39.1	1.4	3.2	No	V-0
3%DOPO/EP	35.5	46.4	—	No	NR

Fig. 6. FTIR spectra of the char residue from UL94 test.

should attribute to organic polyphosphate structure [41], which is stronger than that of 3%DOPO/EP. The result revealed that the hydroxyl group in ABD probably assisted phosphaphenanthrene to generate more phosphorus acid, and then producing polyphosphate. The more polyphosphate facilitated to form more char residue and generate the barrier effect in condensed phase.

3.5. Cone calorimeter test

The cone calorimeter test was adopted to investigate the combustion behaviors of the flame retardant epoxy composites with ABD. The curves of heat release rate (HRR) of ABD/EP were shown in Fig. 7. Table 4 listed the direct burning characteristic parameters ABD/EP, such as time to ignition (TTI), peak of heat release rate (pk-
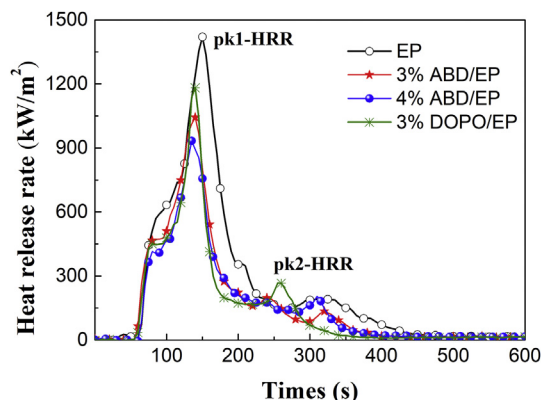

Fig. 7. HRR curves of EP composites.

HRR), total heat release (THR), total mass loss (TML), average of effective heat of combustion (av-EHC), and also listed the secondary burning parameters such as total smoke release (TSR), average CO yield (av-COY) and average CO_2 yield (av-CO_2Y). The different peaks in HRR curves were also marked in Fig. 7, named as pk1-HRR and pk2-HRR respectively.

As shown in Fig. 7 and Table 4, in contrast to neat EP, the pk1-HRR value of 3%ABD/EP was 1043 kW/m^2, which decreased by 26.6%; the pk1-HRR value of 4%ABD/EP was 933 kW/m^2, which decreased by 34.3%; the pk1-HRR value of 3%DOPO/EP was 1182 kW/m^2, which decreased by 16.8%. It proved that ABD can more effectively inhibit the combustion intensity of EP thermosets compared with DOPO. In the curve of 3%DOPO/EP, the pk2-HRR can be seen after 250s, but the pk2-HRR value in 3%ABD/EP and 4%ABD/EP curves cannot be observed obviously. The results indicated there was a different working result on EP composites between ABD and DOPO. The char layer from 3%DOPO/EP generated the fracture during further combustion, thereby causing the release of fuels and forming second burning process; differently, the char layer from ABD/EP samples should be the more compact and thicker and did not break during further burning process. The results disclosed that ABD imposed the char layer with better barrier effect to EP composites, which should be generated not only by phosphaphenanthrene groups but also by the hydroxyl group because hydroxyl group is also an important factor for crosslinking charring in flame retardant chemical structures.

The TTI values of 3%ABD/EP and 4%ABD/EP decreased compared with that of neat EP and it was similar as that of 3%DOPO/EP. The results implied that ABD still promoted the thermal decomposition of EP matrix, exerting flame retardant effect in advance. Further, the decomposition promotion effect from ABD was similar as that from DOPO. Therefore, the promotion effect was just caused by the phosphaphenanthrene group.

TML is also one of important parameters in cone calorimeter test. The final residue yield can be calculated from it and indicate the charring effect during combustion in cone calorimeter test. In contrast to neat EP sample, the TML values of 3%ABD/EP and 4% ABD/EP decreased slightly, indicating that ABD worked and reserved more final residue in condensed phase than EP sample did. Further, the TML value of 3%ABD/EP was also lower than that of 3%DOPO/EP, which confirmed that ABD has the better charring effect than DOPO in epoxy thermosets. The results should be caused by that the hydroxyl group in ABD assisted the phosphaphenanthrene group to generate more final residue. Thus, ABD exhibited better charring flame retardant effect in condensed phase than DOPO. The more final residue implied not only excellent barrier and protective effect but also reduced the fuels to gas phase.

Av-EHC value exposes the burning degree of volatiles in gas phase during combustion. The av-EHC of 3%ABD/EP was 22.6 MJ/kg, which reduced by 24.4% compared with 29.9 MJ/kg of neat EP; the av-EHC of 4%ABD/EP was 21.4 MJ/kg, which reduced by 28.4%. It implied that ABD performed excellent quenching effect in gas phase and accordingly increased the incomplete combustion reaction. But the av-EHC of 3%ABD/EP slightly raised in contrast to that of 3%DOPO/EP, which implied that the quenching ability in ABD was weaker than that of DOPO. The phenomenon should be resulted by the less phosphaphenanthrene group in ABD in comparison with DOPO itself, which led to less phosphorus-containing free radicals in the combustion process and further weakened the quenching effect in gas phase. Therefore, the quenching ability in ABD should correspond with the quantity of phosphaphenanthrene group.

Compared with the neat EP sample, the THR value of 3%ABD/EP thermoset decreased by 29.3% and the THR value of 4%ABD/EP thermoset decreased by 34.3%, implying ABD inhibited the total

Table 4
Cone calorimeter data of epoxy composites.

Samples	TTI (s)	THR (MJ/m^2)	pk1-HRR (kW/m^2)	TML (wt.%)	av-EHC (MJ/kg)	av-COY (kg/kg)	av-CO$_2$Y (kg/kg)	TSR (m^2/m^2)
EP	56	143.6	1420	92.2	29.9	0.13	2.51	5912
3%ABD/EP	51	101.5	1043	87.7	22.6	0.12	1.78	5709
4%ABD/EP	51	94.3	933	87.1	21.4	0.13	1.68	5618
3%DOPO/EP	52	91.9	1182	88.7	21.5	0.14	1.62	6003
Error range	±1	±2	±45	±0.5	±0.5	±0.01	±0.03	±64

burning behavior. But it reduced less than 3%DOPO/EP did. The results were inferred that ABD released less free radicals and produced the weaker flame retardant effect than DOPO in gas phase. Although the more char residue in ABD/EP samples were reserved and accordingly the less fuels were released, the reduced effect on THR in condensed phase can't offset the more heat release from more complete combustion in gas phase.

The reduction in EHC can also explain the changes both in COY and CO$_2$Y. As shown in Table 4, compared with neat EP thermosets, the av-CO$_2$Y values of 3%ABD/EP and 4%ABD/EP thermosets decreased, which implies that the complete burning reaction were weakened. The av-COY increased little if anything, while the av-CO$_2$Y decreased obviously. The results are another evidence of inhibition effect of ABD on volatiles during combustion due to the enhanced ratio of incomplete combustion products (CO). The results also corresponded to the av-EHC data.

Meanwhile the TSR values of ABD/EP samples were lower than that of neat EP, and were also lower than that of 3%DOPO/EP. The results further proved ABD has the better charring effect than DOPO in epoxy thermosets. The decrease of TSR value was caused by that more decomposed fragments from epoxy thermoset matrix were reserved in final residue and more compact char layer was formed through the hydroxyl group and phosphaphenanthrene groups in ABD jointly worked. Therefore, the charring and smoke inhibition effects of ABD are better than that of DOPO.

According to all the results, the better flame retardant performance of ABD was resulted by the quenching effect from phosphaphenanthrene groups in gas phase [39] and the charring effect from the joint action of phosphaphenanthrene group and hydroxyl group in condensed phase simultaneously.

3.6. Morphologies of the cone calorimeter residue

The macroscopic digital images and microscopic SEM photos of the 3%ABD/EP cone calorimeter residue are shown in Fig. 8. Compared with thin and broken char residue of the neat EP (Fig. 8, c1), 3%ABD/EP produced more and thicker char residue. The results disclosed ABD had better charring ability, which accordingly inhibited the combustion of matrix and reduced the combustion intensity. Further, the expansion ratios of 3%ABD/EP char residue (Fig. 8, a1) were elevated with the incorporation of ABD in thermosets and it was similar as that of 3%DOPO/EP (Fig. 8, b1). From macroscopic photos, no obvious differences can be observed between 3%ABD/EP and 3%DOPO/EP, but the microscopic photos disclosed some particular traces of ABD charring effect.

The SEM photos of 3%ABD/EP (Fig. 8, a2) showed a relatively complete char layer and some closed cracks on the surface of char layer. In contrast to several open holes and closed cracks in the cone calorimeter residue of 3%DOPO/EP (Fig. 8, b2), only less closed cracks were observed in that of 3%ABD/EP, indicating that ABD had better barrier effect in condensed phase than DOPO. The better charring effect should contribute to the higher rating in UL94 test.

3.7. Pyrolysis behavior of ABD

To further explore the pyrolysis behavior and flame retardant mechanism of ABD, the GC-MS was adopted with a pyrolysis temperature at 450 °C in TGA, when ABD decomposition mass loss is 50 wt%. The GC spectrum of the decomposed ABD fragments was shown in Fig. 9. In Fig. 9, the cracked fragments of ABD were divided into five groups mainly and they were located at 5.7min, 10.3min (6−12min), 13.1min and 14.2min, respectively.

At 5.7 min, the mainly pyrolytic fragment is phenol (C$_6$H$_6$O, m/z = 94), and then it will continue to be degraded to alkene cyclopentadiene (C$_5$H$_6$, m/z = 66). During 6−12 min, the results at 10.3 min were chosen as the representative of the fragment group. They mainly include two groups of fragments: one group are composed of phosphaphenanthrene fragments, such as DOPO-CH$_3$ (m/z = 230), DOPO (m/z = 216), DOPO free radical (m/z = 215); another group are composed of aliphatic free radicals containing PO$_2$, such as the free radicals with the m/z values at 134, 119, 91, 77, 63. The retention times at 13.1min and 14.2min have similar fragments. At 13.1 min, a typical phosphorus oxybenzone structure (m/z = 170) from DOPO can be observed. Then, it continued to decomposed to two aromatic fragments (m/z = 141, m/z = 115). At 2.3 min and 3.6 min, the fragments were analyzed and confirmed that they are the little pieces from chromatographic column and not from sample ABD.

Combined with the MS results in Fig. 10 and the molecular structure formula of ABD in Fig. 1, the pyrolysis route of ABD can be inferred finally, as shown in Fig. 11. All the fragments from ABD can be divided to three parts: 1) phenol and phenoxyl free radicals; 2) aliphatic free radicals containing PO$_2$; 3) aromatic fragments.

3.8. Flame retardant modes of ABD

According to all the discussion, the flame retardant modes of ABD in EP thermosets was illustrated as follows.

ABD has three kinds of fragments after pyrolysis: 1)The phenol and phenoxyl free radicals, which have quenching effect in gas phase during combustion; 2) aliphatic free radicals containing PO$_2$, which can combine with epoxy resin matrix to char and form carbonaceous layer containing phosphorus, thereby generating better barrier effect on fire and heat; 3) aromatic fragments, which can be captured or quenched to form final residue.

ABD can degrade into three kinds of main fragments with flame retardant effect in burning reaction: one hand, phenol and phosphorus-containing free radicals can quench the hydrocarbon free radicals from the decomposed matrix, terminate the chain reaction of combustion and inhibit the combustion chain reaction in gas phase [26,30]; On the other hand, aliphatic free radicals containing PO$_2$ can combine with epoxy resin matrix to char and form carbonaceous layer containing phosphorus, thereby generating better barrier effect on fire and heat. The aromatic fragments also can be easily captured or quenched to form final residue. Further, the hydroxyl group in ABD was observed to form carbonyl with PO$_2$, which facilitate to react with the hydroxyl and phenol group from matrix, thereby producing more phosphorus-
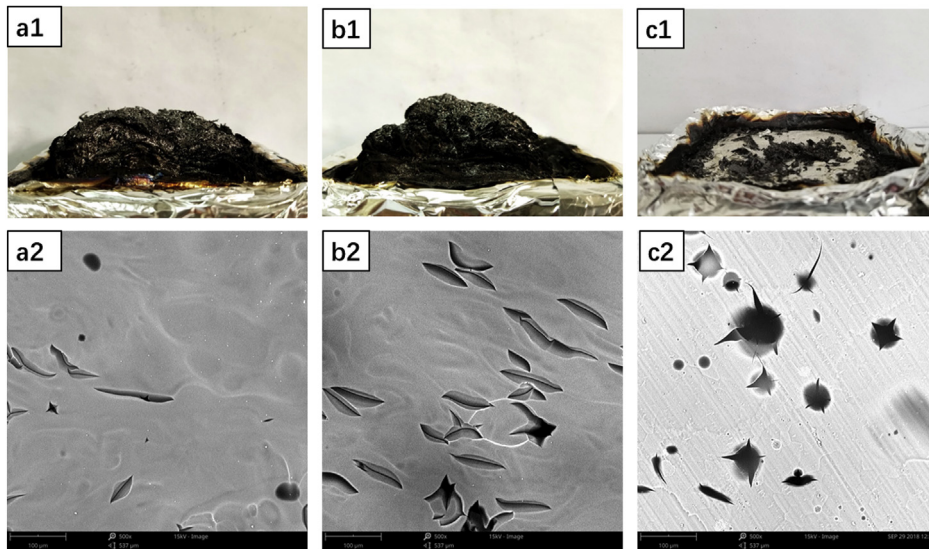
Fig. 8. Digital photos and SEM photos of the cone calorimeter residue. a1, a2: 3%ABD/EP; b1, b2: 3%DOPO/EP; c1, c2: EP.
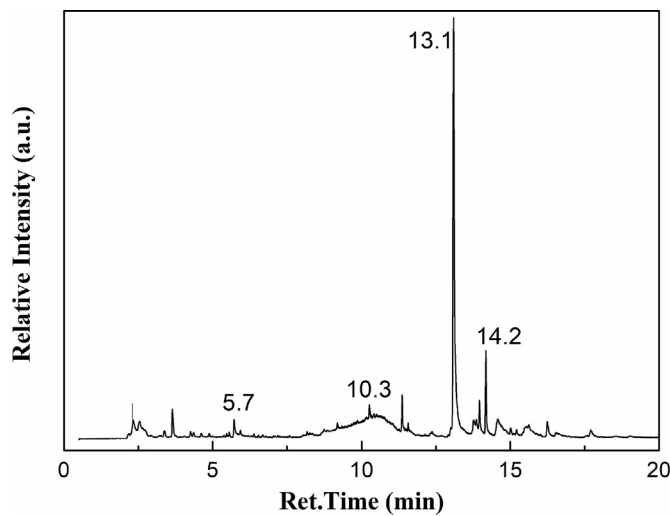

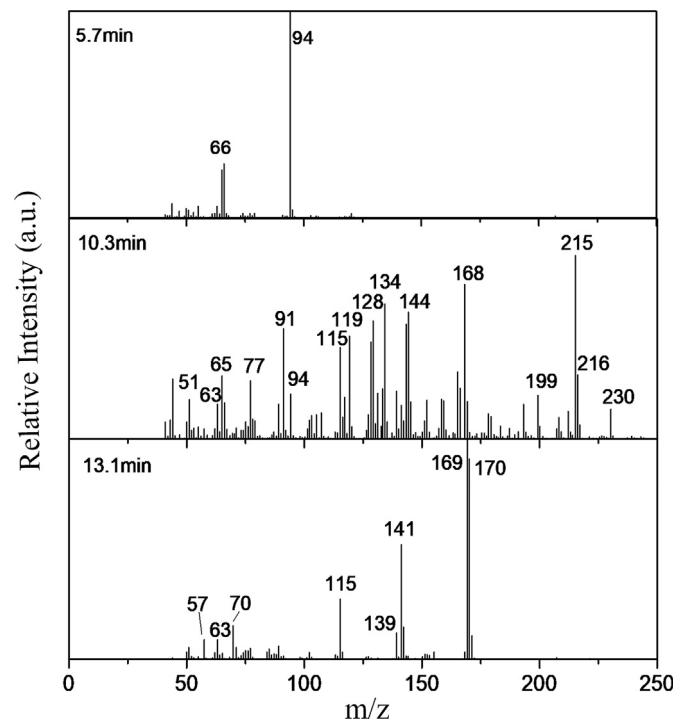**Fig. 9.** GC spectrum of the pyrolysis products of ABD.

Fig. 10. MS spectra of main fragments of the pyrolyzed ABD at 450 °C.

containing residue in condensed phase. These flame retardant effects from phosphaphenanthrene groups and the joint actions of phosphaphenanthrene group and hydroxyl group in condensed phase simultaneously improved the LOI value, the level of UL94, HRR, EHC and other parameters of the combustion performance.

Therefore, the better flame retardant performance of ABD in contrast to DOPO is resulted by two reasons: the quenching effect from phosphaphenanthrene groups in gas phase and the charring effect from the joint action of phosphaphenanthrene group and hydroxyl group in condensed phase simultaneously. Compared with the samples with addition of DOPO, ABD/EP thermosets possessed better flame retardant properties, which caused by ABD structures with higher phosphorus content and the hydroxyl group.

4. Conclusion

A flame retardant ABD, containing two phosphaphenanthrene groups connected by relatively short bridged bonds with a hydroxyl group, was synthesized and characterized. Its flame retardant effect on EP were investigated. The epoxy thermoset with only 3 wt% ABD

obtained a higher LOI value of 36.2% and passed UL94 V-0 rating. ABD also reduced all the values of pk-HRR, THR, av-EHC, TML and av-CO$_2$Y, and increased the char yields. In contrast to DOPO, ABD can impose higher LOI value, higher UL94 rating and lower peak value of HRR to epoxy thermosets. The better flame retardant performance from ABD should be caused by the quenching effect from phosphaphenanthrene group in gas phase and the charring effect from the joint action of phosphaphenanthrene group and hydroxyl group in condensed phase simultaneously. The special structure of ABD with higher phosphorus content and hydroxyl group is the main reason that ABD can impose better flame retardant performance to epoxy thermosets.
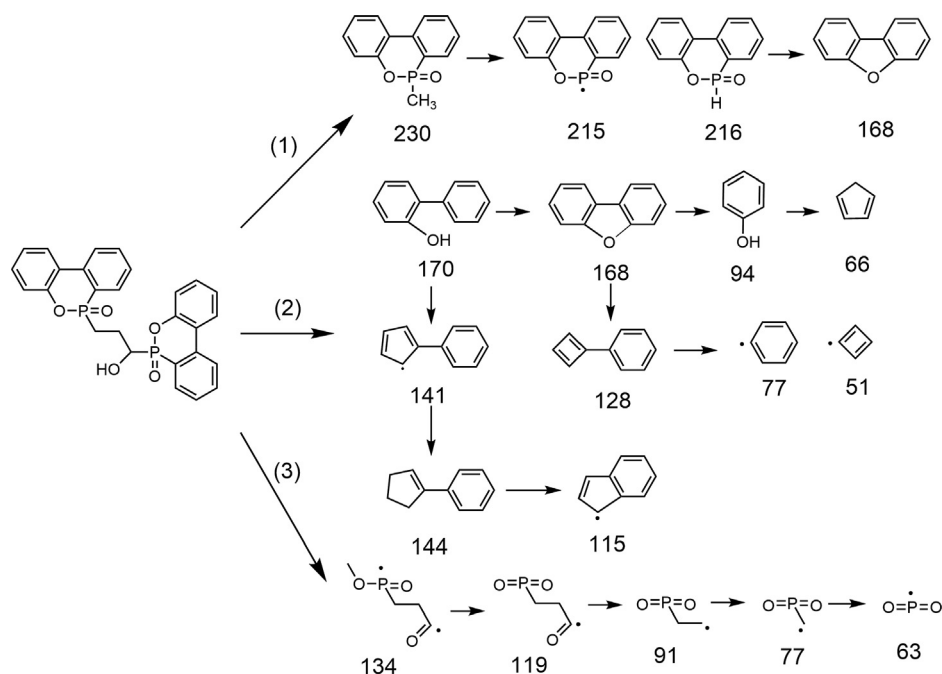
Fig. 11. The deduced pyrolysis route of ABD.

Acknowledgment

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