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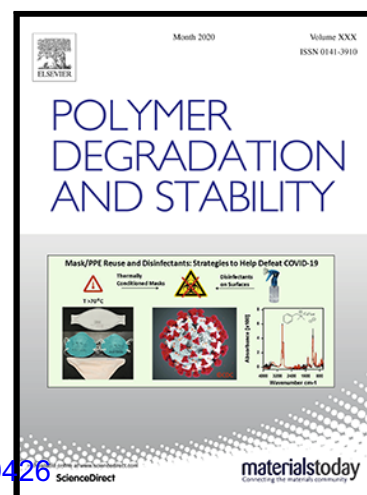
A novel DOPO-based flame retardant containing benzimidazolone structure with high charring ability towards low flammability and smoke epoxy resins

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Highlights

- A phosphaphenanthrene/benzimidazolone-containing flame retardant (POBDBI) was synthesized successfully.
- POBDBI imparted excellent flame retardancy and smoke suppression to EP.
- POBDBI exerted flame-retardant effect both in condensed phase and gaseous phase.

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A novel DOPO-based flame retardant containing benzimidazolone structure with high charring ability towards low flammability and smoke epoxy resins

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Abstract

A novel flame retardant POBDBI was generated by the reaction of p-dibenzaldehyde, 5-amino-2-benzimidazolinone and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), and employed to epoxy resin. The structure of POBDBI was measured by FT-IR and NMR tests. Then flame-retardant EP was fabricated by using POBDBI as a flame-retardant. The

thermal stability, flame-retardant performance and fire behavior were investigated by a series of comprehensive instruments. Combustion tests show the flame-retardant performance of composite materials has been significantly improved. For example, the EP/POBDBI-1.0 with the phosphorus content of 1.0% accorded a V-0 rating and its limiting oxygen index (LOI) value increased to 36.5%. Besides, total smoke production (TSP), peak heat release rate (PHRR) and total heat release (THR) of EP/POBDBI-1.0 dropped significantly, and the corresponding values were decreased by 48.4%, 48.9% and 8.7%, respectively. At the same time, the composition, morphology of chars and gaseous products of POBDBI were studied by X-ray photoelectron spectroscopy (XPS), FT-IR, scanning electron microscope (SEM) and Py-GC/MS. These results presented that POBDBI could not only exerted free radical capture effect, but also enhanced the density of char residue.

Keywords: Epoxy resin; flame retardancy; smoke suppression; flame-retardant mechanism.

1. Introduction

Due to its many good characteristics and properties, such as excellent adhesion properties, good mechanical properties, outstanding chemical solvent resistance and superior electrical insulation properties, EP has been applied in various fields including paints, coatings, laminates, adhesives, industrial tools and electronic equipment, etc. [1-4]. However EP is inherently flammable like most polymer materials, which has limited its in-depth application in more fields, such as

transportation, construction, and aerospace [5]. Utilizing appropriate methods and strategies to cut down its combustible performance has been more crucial [6]. Researchers have conducted various explorations, such as flame retardant monomers [7-10], curing agents [11-13] and additives [14-18], among which the additive method is most suitable for large-scale industrialization. The earliest developed halogen-containing flame retardants have been applied on a large scale due to their good general adaptability, processability and high efficiency. However, recent studies have shown that halogen-containing flame retardants generate toxic gases during the combustion process, which poses a serious threat to the ecological equilibrium [19,20].

So far, more and more researchers are devoted themselves to developing powerful halogen-free flame retardants for EP [21]. As a result of non-toxic, low-smoke and high-efficiency properties, phosphorus type flame retardants are widely concerned [22-25]. Among them, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) derivatives have been widely used as reactive or additive flame retardants owing to good thermal stability and effective gaseous-phase flame extinguishing effect [26-29]. Although DOPO derivatives bring satisfactory flame retardant performance, many studies have shown the smoke suppression performance is not improved [30-32]. For example, Xu [33] synthesized imidazolium dibenzoxalic acid phosphate (IDOP) by a simple method and used it as a potential flame-retardant curing agent. When the addition amount was 15 wt%, the LOI of the IDOP/EP composite material increased to 37%

and the 15 wt% IDOP/EP passed successfully vertical combustion test (V-0 rating). However, by comparison with EP, the TSP of IDOP/EP had increased, and the smoke suppression performance had not been improved. Yan [34] used DOPO derivatives (DiDOPO) in combination with graphene nanosheets (GNS) to enhance fire resistance of EP. When 1.5 wt% GNS and 1.5 wt% DiDOPO was introduced to EP, the LOI could be increased to 32.2% as well as a V-0 rating was accorded, whereas TSR was risen from 3867 m²/m² of EP to 7072 m²/m². To improve simultaneously the flame retardance and smoke suppression, an appropriate and feasible approach is to design and synthesize the DOPO-based flame retardant with gaseous phase activity and charring effect [35-37]. Chen [38] synthesized a oligomer named DOPMPA composed of DOPO and piperazine that presented good intumescent flame retardant activity. The EP/DOPMPA composite with 13 wt% flame retardant accorded a V-0 rating and possessed a LOI of 34% as well as had a reduction of 64% and 78.4% in THR and TSP.

Therefore, we designed and prepared a novel flame retardant (POBDBI) containing benzimidazolone and DOPO groups for improving the flame retardance and smoke suppression of EP. In addition, the corresponding flame retardant mechanism was also revealed.

2. Experimental

2.1 Materials

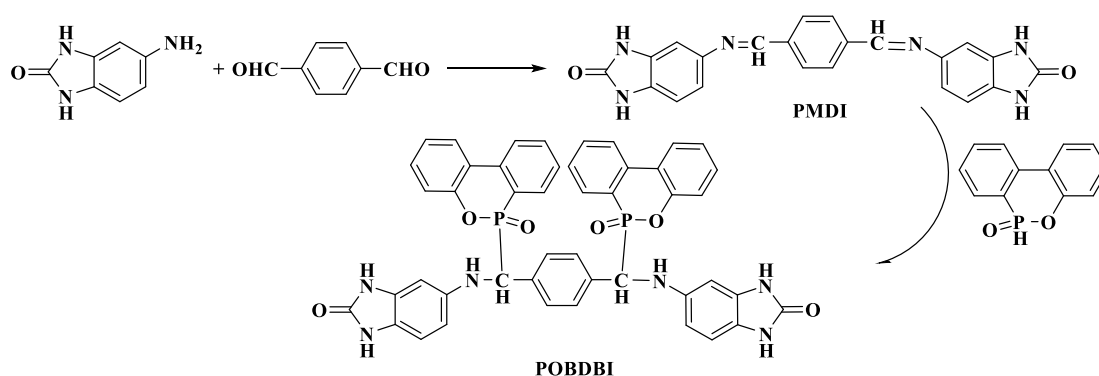
EP (DGEBA) was provided by Nantong Xingchen Synthetic Material Co., Ltd. (Nantong, China). 4, 4- Diamino diphenylmethane (DDM), absolute ethyl alcohol

and Dimethyl sulfoxide (DMSO) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). DOPO, p-phthalaldehyde and 5-amino-2-benzimidazolinone were all purchased from Shanghai Aladdin Chemical Reagent Co., Ltd. (Shanghai, China). Distilled water was provided by our Lab.

2.2 Synthesis of POBDBI

As seen in Scheme 1, 5-amino-2-benzimidazolinone (0.08 mol, 11.9384 g), p-phthalaldehyde (0.04 mol, 5.3652 g) and absolute ethyl alcohol (200 mL) were added into a 500mL three-neck flask equipped with a magnetic stirrer and reflux condenser. Subsequently, the reaction solution was continuously stirred for 4 hours at 70 °C. Lastly, the intermediate product (PMDI) was obtained by suction filtration, wash with distilled water and dried at 70 °C for 10 h under vacuum (yield: 99%).

The obtained intermediate product PMDI (0.04 mol, 15.8467 g) and DMSO (200 mL) was introduced to a flask equipped with a magnetic stirrer and a reflux condenser. Afterwards, DOPO (0.08 mol, 17.2958 g) was introduced to the reaction system and reacted at 100 °C for 10 hours. After accomplishing, the solution was poured into distilled water and a large amount of precipitation appeared in the solution. Finally, the solid was obtained by suction filtration, washed with distilled water and cold alcohol, and then dried in a vacuum drying cabinet at 70 °C for 10 h (yield: 91%).



Scheme 1. Route for synthesis of POBDBI.

2.3 Preparation of flame retardant epoxy thermosets

Firstly, EP and POBDBI were mixed with a magnetic stirrer at 140 °C for 60 minutes. Secondly, when the temperature dropped to 90 °C, DDM was added to DGEBA/POBDBI, and fully agitated for 5 minutes. The mixture was quickly filled into the mold, and then cured at 100 °C for 120 minutes and at 150 °C for 180 minutes in a convection oven. EP thermosetting were prepared according to similar procedures, but without the addition of POBDBI. Table 1 listed the corresponding formulations of epoxy thermosetting.

Table 1. LOI and UL-94 results and specific formulas of the EP and its composites

Sample	DGEBA (g)	DDM (g)	BPOPA (g)	P content (wt%)	UL-94	LOI (%)
EP	100	25	0	0	No rating	26.2±0.3
EP/POBDBI-0.5	100	25	8.96	0.5	V-1	32.5±0.3
EP/POBDBI-0.75	100	25	13.96	0.75	V-1	35.5±0.3
EP/POBDBI-1.0	100	25	19.32	1.0	V-0	36.5±0.3

2.4 Preparation of DGEBA/DDM/POBDBI mixture

First, different qualities (as seen in Table 1) of DGEBA, DDM and POBDBI were dispersed in acetone under the ultrasonic environment. Afterwards, the DGEBA/DDM/POBDBI mixtures were obtained by removing solvent acetone using rotary evaporator at room temperature. DGEBA/DDM and DGEBA/POBDBI

mixtures were obtained using a similar method. All the samples were used for DSC test.

2.5 Characterization

A Nicolet 6700 FTIR instrument was utilized to record FT-IR spectra of DOPO, PMDI, POBDBI and the chars after burning. The wavenumber range was 400-4000 cm^{-1} .

The NMR tests (^{31}P NMR and ^1H NMR) were carried out to further determine the structure of POBDBI using a Bruker Avance Spectrometer (400 MHz). And DMSO- d_6 was used as solvent.

Thermogravimetric analysis was conducted by a TGA instrument (NETZSCH, DSC-204 F1, Germany). About 4 mg POBDBI, EP and its composites (powder) were heated from 25 to 700 $^{\circ}\text{C}$ with a heating rate of 10 $^{\circ}\text{C}/\text{min}$ under N_2

Differential scanning calorimeter (DSC) tests were performed on a NETZSCH 204F1 DSC instrument (NETZSCH, Germany) to characterized glass transition temperatures (T_g) of EP and EP/POBDBI composites, and investigated the influence of flame retardant POBDBI on curing process of DGEBA/DDM mixture. The above-mention samples were heated from 30 to 250 $^{\circ}\text{C}$ with a heating rate of 10 $^{\circ}\text{C}/\text{min}$ N_2 atmosphere.

Flammability was studied using an oxygen index meter (HC-2C, Jiangning) following ASTM D2863-97 and vertical combustion instrument (CZF-4, Jingning) following ASTM D3801-2010. The sample size of LOI and UL-94 tests was 130 mm \times 6.5 mm \times 3.2 mm and 130 mm \times 13 mm \times 3.2 mm, respectively. The LOI value of

every sample was the average value of three parallel tests.

The combustion behavior of EP and EP/POBDBI composites was studied by a FTT cone calorimeter instrument following ISO 5660. The samples with the size of 100 mm × 100 mm × 3.2 mm were exposed to heat radiation with the heat flux of 35 kW/m². Every spline were tested twice in cone calorimeter test, and the result was average of two parallel tests.

The smoke density of EP and its composites were investigated by a FTT0064 smoke density instrument (according to ISO-5659). The samples with the size of 75 × 75 mm × 3.2 mm were tested under flame combustion at a heat flux of 25 kW/m².

Gaseous products of POBDBI was analyzed by a CDS 5200 GC/MS. POBDBI (about 2.0 mg) was first treated in the pyrolyzer by heating from indoor temperature to 500 °C under helium atmosphere. The injector temperature was held at 40 °C for 3 min, then heated to 280 °C and held for 10 minutes. The GC/MS interface temperature was 280 °C, and the cracker temperature was 500 °C.

SEM was utilized to observe the microstructure of carbon residue after combustion using a HITACH S4800 instrument.

Char residues components were analyzed by XPS test under ultrahigh vacuum conditions. The XPS instrument (Thermo fisher Scientific Co., USA) made use of a K-Alpha+ spectrometer and Al K α source ($h\nu = 1486.6$ eV).

3. Results and discussion

3.1 Structural characterization of POBDBI

The IR spectra of PMDI, DOPO and POBDBI were presented in Fig. 1. As seen, the obvious P-H bond (2430 cm^{-1}) appeared in IR spectrum of DOPO. For PMDI, also the characteristic peak of C=N (1606 cm^{-1}) was found. For POBDBI, some typical phosphaphenanthrene groups, such as the P=O (1232 cm^{-1}), P-O-C_{Ar} (1201 and 925 cm^{-1}) and P-C_{Ar} (1595 and 1475 cm^{-1}), were observed [39]. Besides, the disappearance of C=N and P-H bonds and the appearance of typical absorption peak of DOPO groups indicated that the DOPO groups were successfully incorporated into POBDBI.

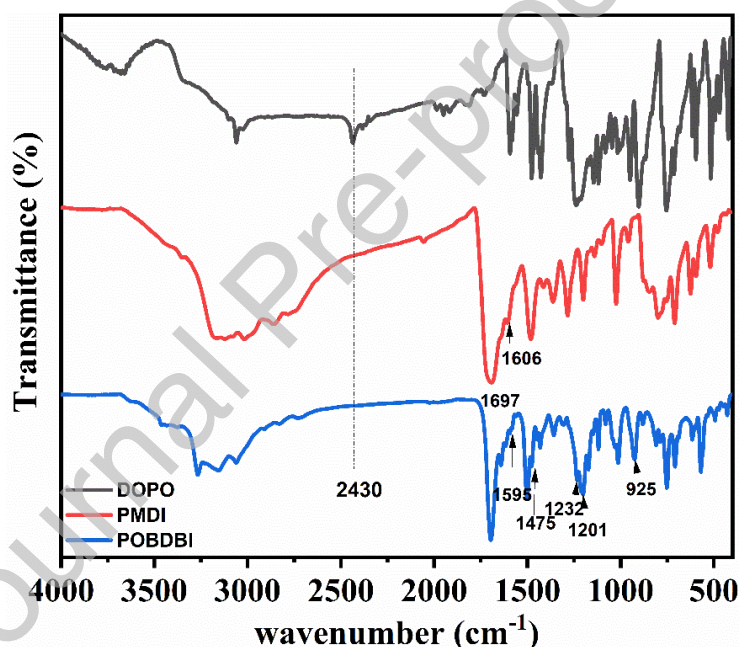


Fig. 1. FTIR spectra of DOPO, PMDI and POBDBI

The ^1H NMR and ^{31}P NMR spectra of POBDBI were further analyzed. In Fig. 2, the dual peaks at 5 ppm corresponded to the H protons in the -CH-P (H_a) structure; the peak at 5.8-5.9 ppm belonged to the H atoms of C-NH-Ph (H_b); the peaks between 6.2 and 8.3 ppm were due to the H atoms in benzene ring structure (H_c); the peaks between 10.0 and 10.2 ppm were attributed to the atoms of N-H (H_d) in

benzimidazolidone groups. Besides, the ratio of the proton peak area well matched the proportion of different H atoms in POBDBI, which indicated POBDBI was successfully synthesized. Fig. 3 presented the ^{31}P NMR spectra of POBDBI, it was found that two peaks at 28.3 and 31.2 ppm appeared, which might be due to the influence of chiral carbon atoms [39]. Based upon the above analyses, it was concluded that POBDBI had been synthesized successfully.

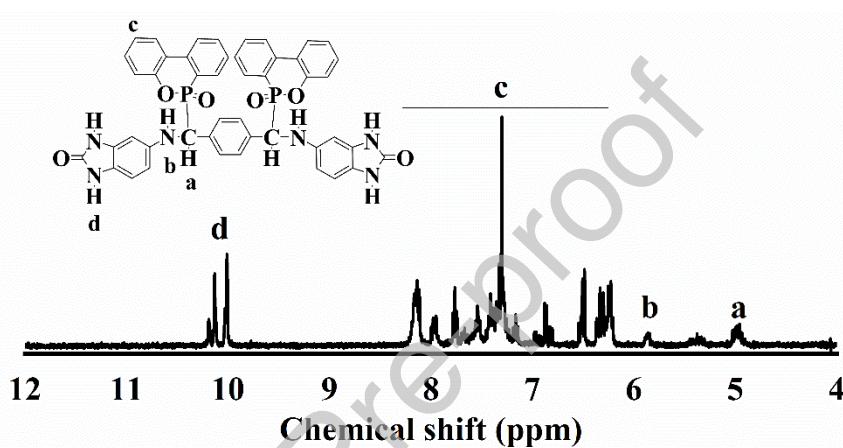


Fig. 2. ^1H NMR spectrum of POBDBI.

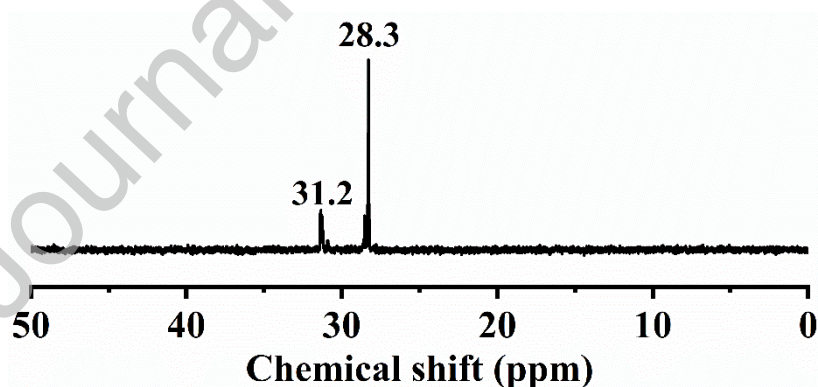


Fig. 3. ^{31}P NMR spectrum of POBDBI.

3.2 The study on curing behavior of DGEBA/DDM mixtures

To investigate the influence of POBDBI on curing process of DGEBA/DDM, the DSC test was carried out. As seen in Fig. 4, a wide exothermic peak (163.4 °C) was observed in DGEBA/DDM curve. While the introduction of POBDBI has no obvious

effect on the exothermic peak and curing process of DGEBA/DDM, and their exothermic peak temperature were 160.8 °C for DGEBA/DDM/POBDBI-0.5, 161.2 °C for DGEBA/DDM/POBDBI-0.75 and 161.4 °C for DGEBA/DDM/POBDBI-1.0, indicating that no chemical reaction between POBDBI and epoxy groups. Besides, it found that no exothermic peak existed in DGEBA/POBDBI curves within 250 °C, which illustrated the hydrogen protons in POBDBI were inactive.

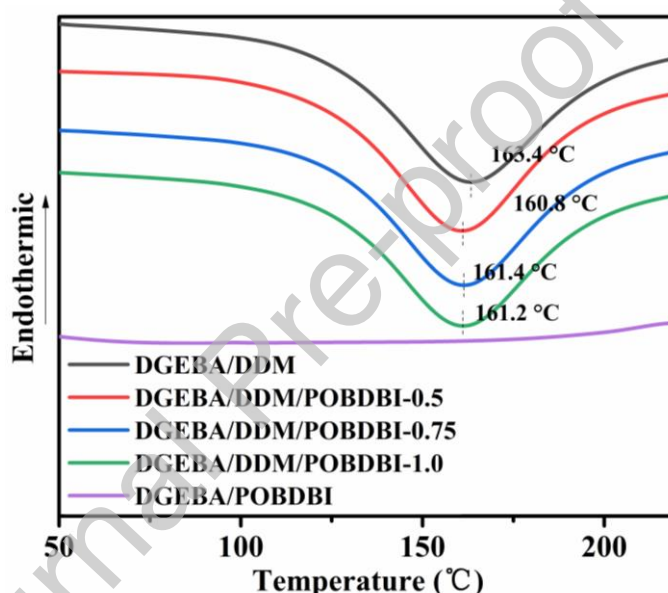


Fig 4. DSC curves of DGEBA/DDM, DGEBA/DDM/POBDBI and DGEBA/POBDBI with a heating rate of 10 °C/min

3.3 Thermal stability of epoxy thermosets

Fig. 5 presented the TGA and DTG curves of POBDBI, EP and its composites under N₂. Some characteristic data of thermal stability, including T_{5%} (the temperature at 5 wt% weight loss), T_{max} (the maximum mass loss temperature), R_{max} (the maximum mass loss rate) and residual mass were listed in Table 2.

As seen, the initial decomposition temperatures($T_{5\%}$) of POBDBI was 193.7 °C, and presented mainly five stage decompositions with 45.3 wt% residual mass at 700 °C. The $T_{5\%}$ and T_{\max} of EP were 356.8 and 478.1 °C, respectively. When POBDBI was added, the $T_{5\%}$ of EP/POBDBI systems decreased to 331.1 for EP/POBDBI-0.5, 318.3 for EP/POBDBI-0.75 and 311.1 °C for EP/POBDBI-1.0 respectively, which was caused by the decomposition of POBDBI in advance. Besides, the addition of POBDBI yielded a slight decrease in T_{\max} of EP composites and an increase in the residual mass at 700 °C. For example, the char yield was increased from 17% to 20.3% for EP/ POBDBI-0.5, 20.8% for EP/ POBDBI-0.75 and 21.6% for EP/POBDBI-1.0, respectively. Overall, the increased residual mass of the composites suggested the potential fire-retardant activity in condensed phase.

The T_g of EP and EP/POBDBI composites was also investigated by DSC test, and the relevant data were showed in Fig. 6. From Fig.6, a single peak was observed in all samples. After the addition of POBDBI, a slight decrease in the T_g value for cured resin was noticed, which from 155.3 °C for EP to 146.8 °C for EP/POBDBI-1.0. As well known, the T_g of EP material is closely connected with the cross-link density of network and stiffness of molecular chain segments [40]. It was conclude from Fig 4 that POBDBI did not react with epoxy groups during curing process of DGEBA/DDM mixtures. Thus the decrease of T_g was resulted from the reduce of crosslinking density of EP caused by larger steric hindrance of DOPO group of POBDBI.

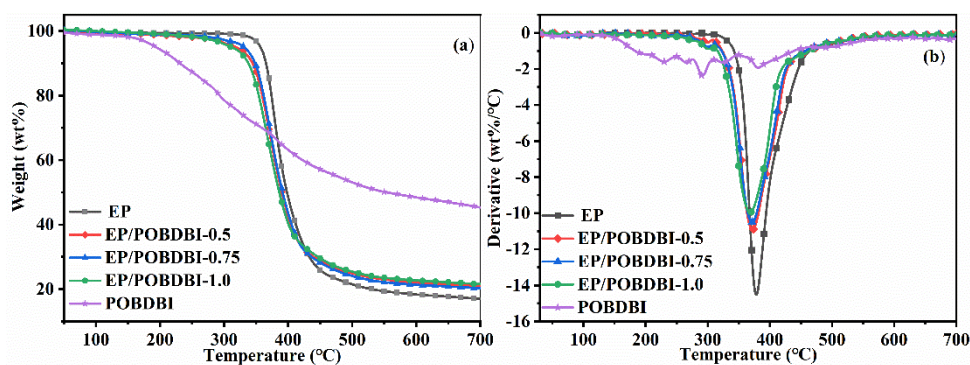


Fig. 5. TG (a) and DTG (b) curves of POBDBI, EP and EP/POBDBI composites.

Table 2. The results of TG and DTG of EP, and flame-retardant EPs

Sample	T _{5%} (°C)	T _{max} (°C)	R _{max} (%/min)	Residue at 700 °C (wt%)
EP	356.8	378.1	-14.527	17.0
EP/POBDBI-0.5	331.1	372.0	-10.934	20.3
EP/POBDBI-0.75	318.3	371.1	-10.503	20.8
EP/POBDBI-1.0	311.1	368.2	-9.973	21.6
POBDBI	193.7	291.6	-2.380	45.3

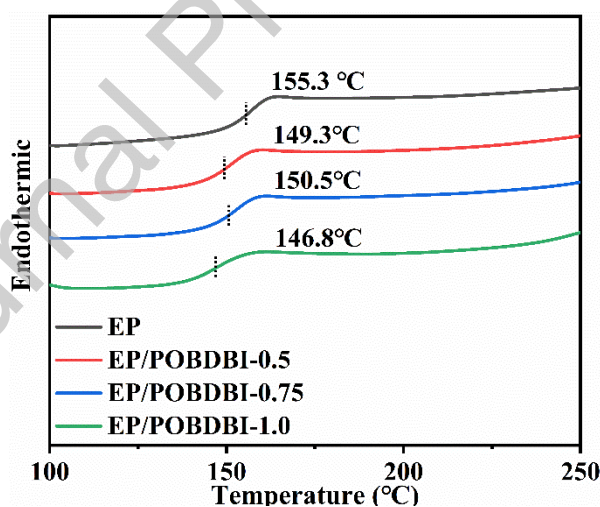


Fig. 6. DSC curves of EP and EP/POBDBI formulations.

3.4 Fire behavior and flame-retardancy

As seen in Table1, the LOI of EP was 26.2%, and it had no UL-94 rating, which presented the inherent flammability of thermosetting resin. In contrast, EP composites exhibited good flame retardancy and anti-dripping property when POBDBI was added.

As detailed, the LOI values of EP composites were achieved to 32.5% for EP/POBDBI-0.5, 35.5% for EP/POBDBI-0.75 and 36.5% for EP/POBDBI-1.0, respectively. As for UL-94 tests, EP/POBDBI-0.5 easily passed V-1 rating and showed good anti-dripping behavior when the phosphorus content was 0.5%. With the phosphorus content reached to 1.0%, the samples successfully passed a V-0 rating.

The combustion behavior of EP and EP/POBDBI composites were studied by cone calorimeter test, which also provided some key parameters, i.e., the time of ignition (TTI), PHRR, THR, TSP, and average effective heat of combustion (av-EHC) of volatiles. And the according test data were showed in Table 3. TTI of all EP/POBDBI composites modified by POBDBI was slightly increased compared with EP, which meant EP/POBDBI was hard to ignite. It was reasonably inferred that since the degradation of POBDBI in advance generate noncombustible gases and phosphorus-containing fragment, which delayed fire combustion by dilution and trapping effects. From Fig.7, EP burned quickly after ignition with a PHRR value of 1073 kW/m², and its THR value reached 75.1%. For EP composites modified POBDBI, the PHRR values were reduced significantly compared with EP, and their values decreased to 709, 804 and 547.5 kW/m², respectively. THR of EP/POBDBI composites were also decreased, it proved POBDBI effectively inhibited the heat release. In addition to the heat release of combustion, the smoke release during combustion is also an important indicator for judging flame retardancy. The TSP values of EP/POBDBI composites decreased from 71.4 m² of EP to 39.3, 34 and 36.7 m², and the results was attributed to the formation of high quality and stable char

residue. As seen in Fig 7(d) and Fig.8, for EP, a small amount of broken char residue was observed (11.5 wt% of residue mass), while the residua mass of EP/POBDBI composites was increased with the addition of POBDBI as well as char residues morphologies became more continuous, and these results were mainly because POBDBI promoted effectively the carbonization of EP.

The av-EHC values of EP/POBDBI composites were all reduced, which proved POBDBI work in gaseous phase, and it was largely contributed to the fuel-dilution and trapping effect of active free radicals. What's more, the increase in av-COY and decrease in av-CO₂Y illustrated that the existence of incomplete combustion in gaseous phase, which further proved the gas-phase flame-retardant effect of POBDBI.

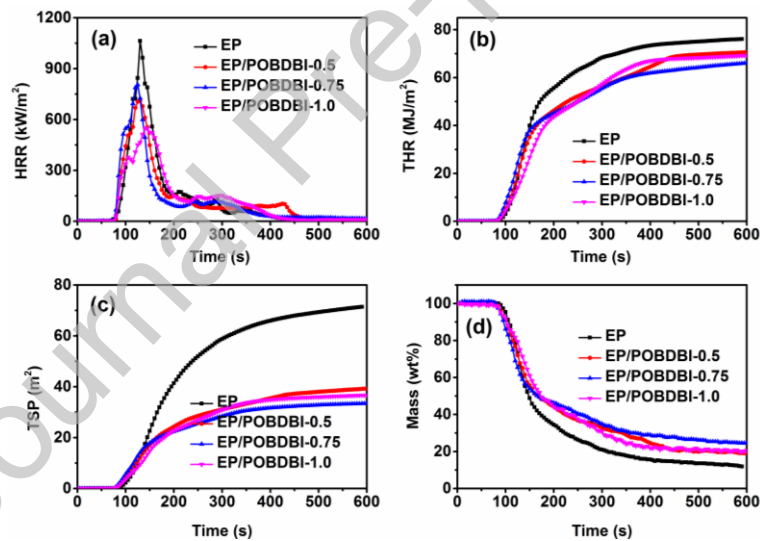


Fig. 7. HRR(a), THR(b), TSP(c) and mass lost (d) curves of EP and EP/POBDBI composites

Table 3. The combustion data of EP and EP/POBDBI composites.

Sample	TTI (s)	PHRR (kW/m ²)	THR (MJ/m ²)	TSP (m ²)	av-EHC (MJ/kg)	av-COY (kg/kg)	av-CO ₂ Y (kg/kg)	Char (wt%)
EP	60±1	1073±55	76±2	71.4±3	22.1±1	0.094±0.01	1.550±0.07	11.5±2

EP/POBDBI-0.5	70±2	709±38	70±2	39.3±2	20.8±1	0.108±0.01	1.443±0.05	19.2±3
EP/POBDBI-0.75	62±3	804±42	66±3	34±2	20.5±1	0.134±0.01	1.392±0.07	24.4±2
EP/POBDBI-0.1	70±1	547.5±35	69.5±3	36.7±2	19.4±1	0.109±0.01	1.336±0.06	21±2

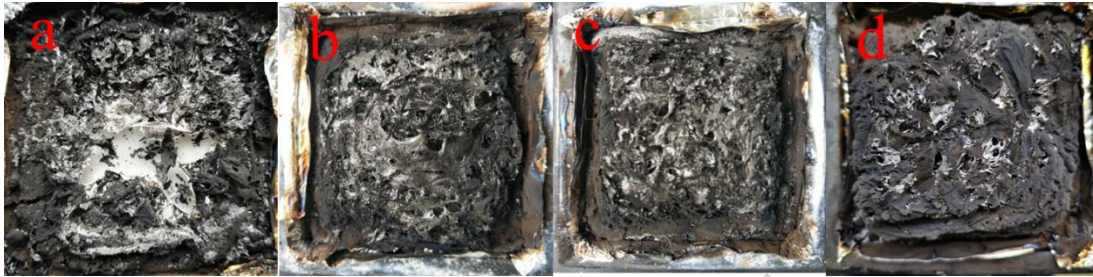


Fig. 8 The digital photos of EP (a), EP/POBDBI-0.5 (b), EP/POBDBI-0.75 (c) and EP/POBDBI-1.0 (d)

The smoke density of materials was further investigated and the relevant curves were presented in Fig.9. Compared with EP, the $D_{s,max}$ (the maximum of smoke density) values of EP/POBDBI-0.75 and EP/POBDBI-1.0 decreased by 30.6% and 26.6% respectively, further suggesting that POBDBI was able to effectively inhibit the smoke release.

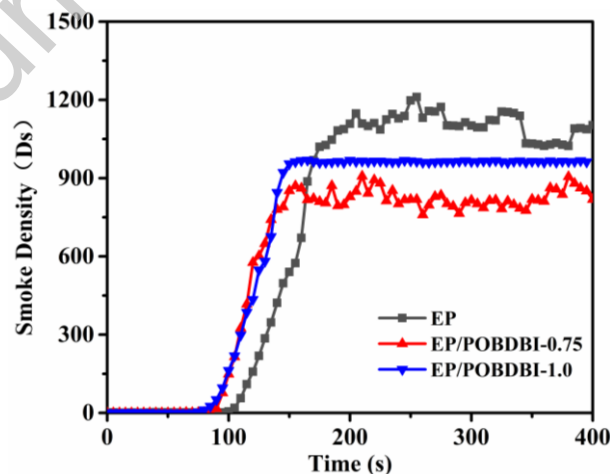


Fig.9 The smoke density curves of EP and its composites

3.5 Flame-retardant mechanism

Py-GC/ MS was utilized to in-depth study the flame-retardant mechanism in gaseous phase by analyzing the pyrolytic products of POBDBI. The total ion chromatogram (TIC) of POBDBI was presented in Fig. 10, along with the relevant pyrolytic products. As seen in Fig. 10, the main pyrolytic products were diphenyl, benzimidazolone, o-phenylphenol and dibenzofuran. Notably, the existence of dibenzofuran provided evidence that PBOBDBI produced phosphorus free radicals in gaseous phase. Diphenyl and o-phenylphenol were degradation products of DOPO group which were released by splitting of P-C bond in POBDBI. And PO and PO₂ radicals were generated in during degradation process. Besides, some nitrogenous compounds dilute the oxygen and combustible gases concentration, such as NH₃ and N₂. Fig. 11 was pyrolysis process diagram of POBDBI.

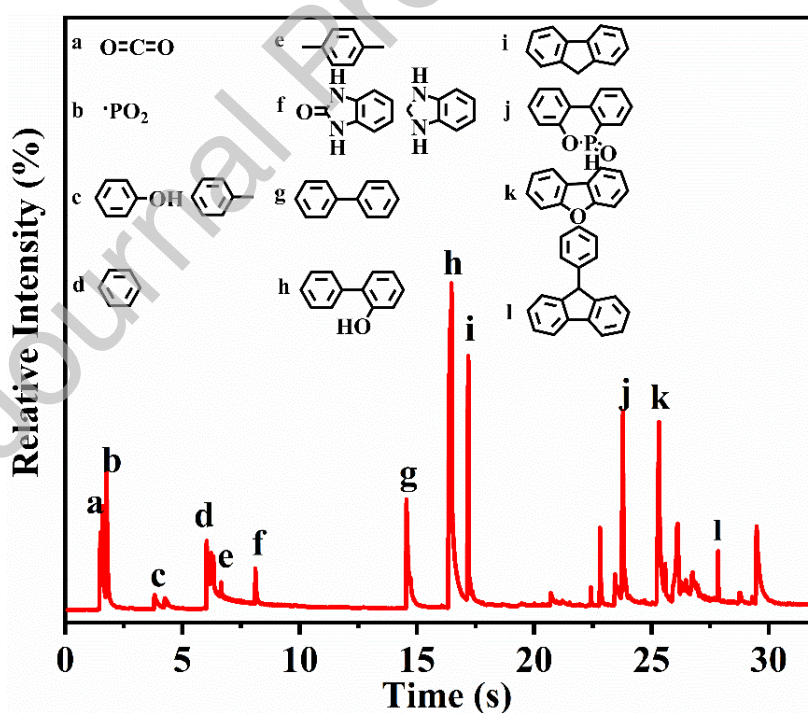


Fig. 10. Pyrogram of POBDBI and corresponding pyrolysis products.

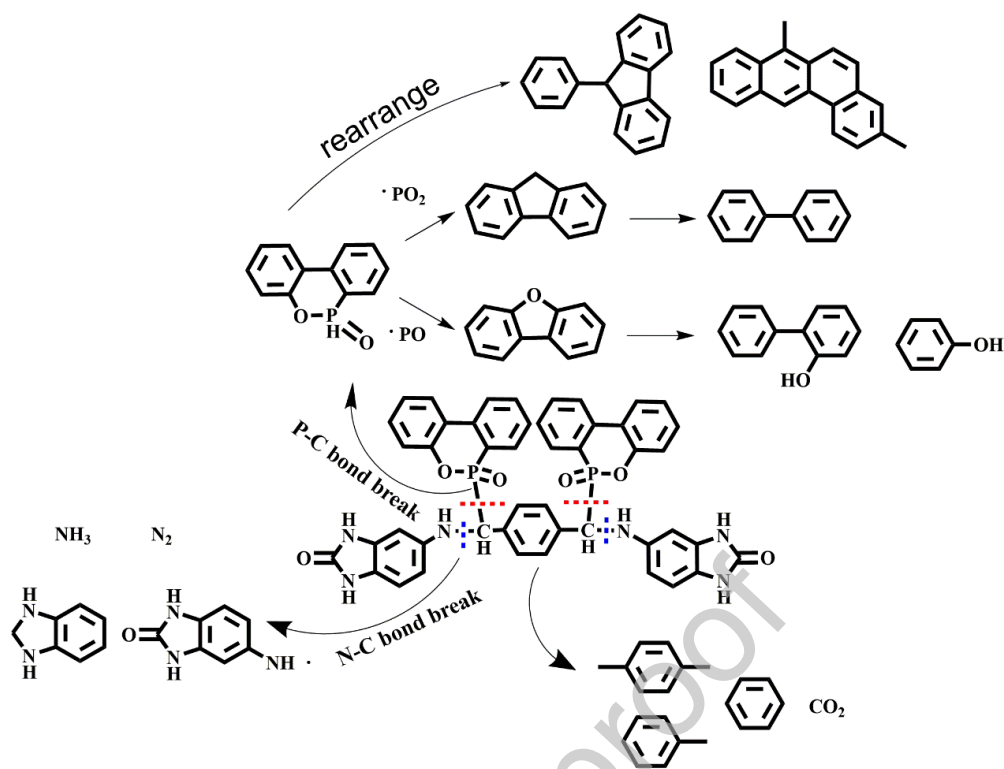


Fig. 11. Pyrolysis process diagram of POBDBI

Fig. 12 showed digital photos and the microstructure of char layer of EP and EP/POBDBI-1.0. As shown in Fig. 12 (a), a very small amount of residual carbon left in EP, indicating that EP had poor flame retardancy. However, the carbon residue of EP/POBDBI-1.0 presented a dense and expanded structure. It confirmed that POBDBI could promote the carbonization of EP and played a role in condensed phase. As seen in microstructure images, lots of cavities and holes were easily observed on exterior and interior chars for EP, whereas that of EP/POBDBI-1.0 exhibited more cohesive, compact and continuous. Besides, the interior char layer had intumescent characteristics and a honeycomb structure compare with that of EP, which proved the excellent shielding effect of the char layer. The compact char layer was capable to server as a protective layer for the underlying material by effectively inhibiting the

communication of oxygen combustible gas between the vapor phase and the condensed phase.

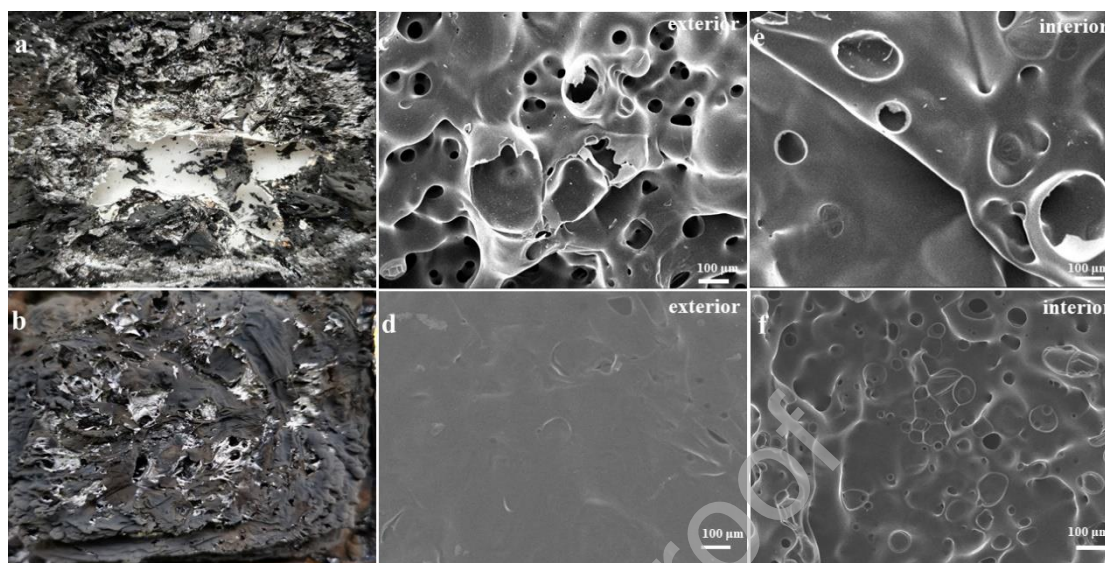


Fig. 12. Digital photos of EP (a) , EP/POBDBI-1.0 (b) and SEM images of exterior and interior char residues of EP (c,e) , exterior and interior char residues of EP/POBDBI-1.0 (d,f) after cone calorimeter test.

The component of chars was further investigated via FTIR spectroscopy and XPS, as shown Fig. 13. From Fig. 13, the peak at 1574 cm^{-1} was due to C=C bond [4], indicating that carbonization reaction occurred during combustion. For EP/POBDBI-1.0, some phosphorus-containing groups such as P-O (1058 cm^{-1}) and P=O (1143 cm^{-1}) left in char residue after combustion [41, 42]. Besides, as seen in P2p XPS spectrum, two characteristic peaks, i.e., P-O-C (133.2 eV) and P-O-P (134.2 eV) [22, 27], was observed in EP/POBDBI-1.0. These phosphoric-containing acid produced by degradation of POBDBI dehydrated and esterified EP to promote the formation of stable chars containing P-O-C and P-O-P bonds, which exerted condensed-phase flame-retardant effect.

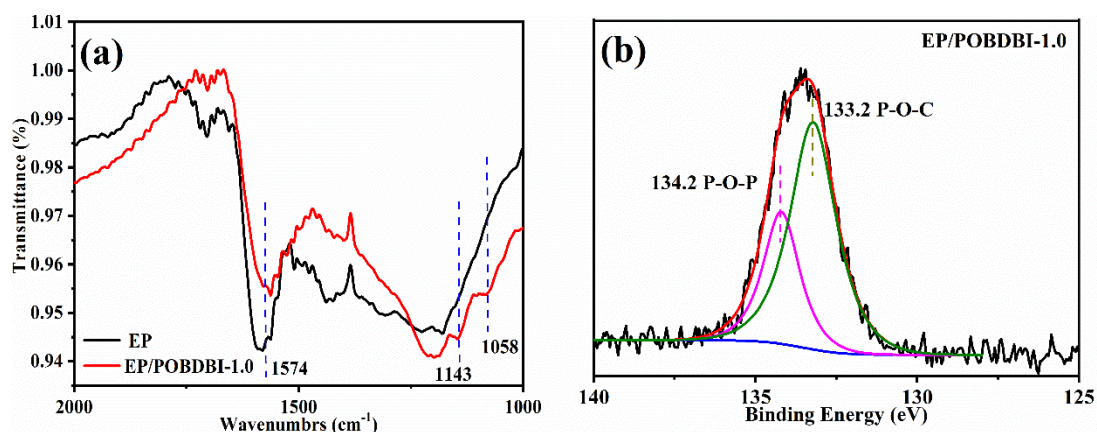


Fig. 13. FTIR (a) and P2p XPS spectra (b) of EP and EP/POBDBI-1.0 after cone calorimeter test.

4. Conclusions

A novel benzimidazolone derivative flame retardant (POBDBI) was successfully synthesized, and used it to flame retard EP. POBDBI made EP obtain good flame retardancy and smoke suppression properties. The LOI of EP/POBDBI-1.0 was as high as 36.5% when the phosphorus content is 1.0 wt% and it accorded a V-0 rating as well as PHRR were significantly decreased. Moreover, the addition of POBDBI decreased TSP by 48.5%. Besides, since the steric hindrance effect of POBDBI reduced the crosslinking density of the molecular chain to a certain extent, Tgs of EP/POBDBI were somewhat lower than that of EP. The enhancement in flame retardancy should be attributed to two aspects: on the hand, POBDBI decomposed to produce pyrophosphoric acid and metaphosphoric acid to catalytic carbonization of matrix and improve the quality of the carbon layer, which played an excellent shielding effect to block the flow of substances and energy in the condense and gaseous phases; on the other hand, some phosphorous-containing originated from the

thermal degradation of POBDBI captured active free radicals and interrupt the chain reaction.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: