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ORIGINAL PAPER

Highly efficient phosphorous-containing flame retardant for transparent epoxy resin with good mechanical properties

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Abstract

To develop transparent flame-retardant epoxy resin (EP) having good mechanical properties, a 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) derived flame retardant (PAHDOPO) was prepared by a neutralization reaction between 10-hydroxy-9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO-OH) and piperazine. When 7% PAHDOPO was added to EP, the obtained flame-retardant EP (EP7) can pass the UL-94 V-0 rating test and exhibit a high limiting oxygen index (LOI) value of 35.8%. Microscale combustion calorimetry investigation results proved that, compared with EP, the peak heat release rate (PHRR) and heat release capacity (HRC) of EP7 decreased by 34.6% and 33.6%, respectively. The observation of the char residue morphology indicated that the addition of PAHDOPO can lead to the formation of the continuous and dense char residue layer, which can improve EP flame retardancy. Meanwhile, compared with EP, EP7 exhibited similar transparency with less than 8% reduction in the average transmittance. Moreover, the mechanical properties of EP7 hardly decreased in comparison with EP. All these results indicated that PAHDOPO can be applied as a high-performance flame retardant of EP with good mechanical properties, transparency, and flame retardancy simultaneously.

Keywords DOPO · Piperazine · Flame retardant · Transparency · Mechanical property

Introduction

As a widely used polymer material, epoxy resin (EP) can be applied in adhesives, laminates, composites, and coatings because of its excellent thermal stability, chemical stability, and dimensional stability [1, 2]. At present, the application of EP is restricted in some fields because of its flammability. Thus, developing EP with high flame retardancy is gradually forming a hot research topic nowadays [3–5]. Traditional halogen flame retardants can be applied to improve flame retardancy. Nevertheless, the application of halogen flame retardants is limited because of the harmful gases released during the burning process, which can threaten the ecological environment and human health [6, 7]. Therefore, developing halogen-free flame retardants has become an inevitable choice [8, 9].

Due to the excellent flame retardancy, flame retardants, which contain phosphorus element, have been developed and successfully applied [10, 11]. Among the developed phosphorus-containing flame retardants, DOPO and DOPO derivatives showed promising flame retardant [12–14]. However, when DOPO was used in EP alone, the volatilization of DOPO during combustion can decrease the flame retardancy of DOPO, and the reaction of DOPO with EP can reduce the crosslinking degree of cured EP, resulting in the decrease of EP mechanical properties [15–17]. To overcome the shortcomings of DOPO, a lot of DOPO derivatives with good flame retardancy were synthesized. Gangireddy et al. [18] prepared a DOPO-derived flame retardant (DOPO-TPMP, TPMP means tri(1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octanemethyl) phosphate) for EP. The 36.1% LOI value can be obtained when the content of DOPO-TMPM in EP reached 10%. Phenethyl-bridged DOPO derivative (DiDOPO) also showed good flame retardancy. When the addition of DiDOPO in EP reached 10%, the obtained flame-retardant material achieved a 38.0% LOI value [19].

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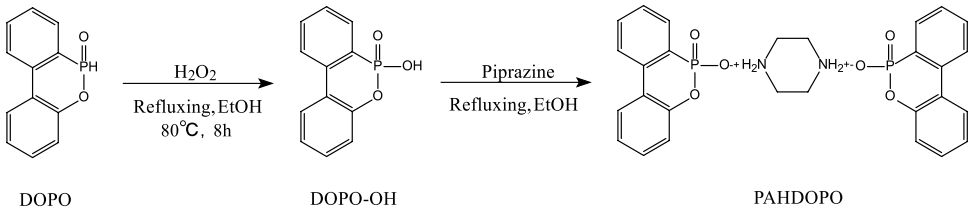
Scheme 1 The synthesis route of PAHDOPO



With the application of DOPO derivatives, two problems were exposed. One problem is that the presence of DOPO derivatives in EP can reduce the mechanical properties of EP. Enough amount of DOPO derivatives must be added to ensure the flame retardant level of EPs, leading to the reduction of mechanical properties [20, 21]. Developing DOPO-modified particles is a feasible path to solve this problem. When silicon oxide, [22] graphene, [23] and carbon nanotube [24] were modified by DOPO, the obtained DOPO-modified particle can increase the mechanical properties and flame retardancy of polymer materials simultaneously. Another problem exposed during the application of DOPO derivatives is that the presence of DOPO derivatives in EP can decrease the transparency of EP. However, sometimes in the field of coatings and decorative materials, epoxy resin is required to be not only flame retardant, but also transparent. [25]. Because most DOPO derivatives are white particles, the addition of these DOPO derivatives generates opaque EP materials [26]. As an important category of DOPO derivative, DOPO-derived curing agent was developed to solve this problem. During the curing process of EP, the DOPO-derived curing agent entered into the molecular structure of EP, leading to the high transparency of the prepared EP material [27, 28]. However, some EP material prepared with DOPO derivatives as curing agents showed relatively low mechanical properties [29]. Although the above-mentioned two problems can be solved by developing DOPO-modified particle and DOPO-derived curing agents, respectively, the preparation of these DOPO derivatives is difficult and the two problems cannot be solved simultaneously. Thus, developing DOPO derivatives that can improve the transparency and mechanical properties of flame-retardant EP is important for EP.

DOPO-derived salt is a kind of DOPO derivative with a simple preparation method and excellent flame retardancy. Shen et al. [30] prepared a DOPO-derived salt melamine dibenzo[c,e][1,2]oxaphosphate (MDOP) for EP via neutralization of 10-hydroxy-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO-OH) with melamine, which can be added in EP and pass the UL-94 V-0 rating when the MDOP content was approximately 5%. However, the mechanical properties of the prepared flame-retardant material decreased clearly with the addition of MDOP. Although DOPO-derived salt exhibited high flame retardancy in EP, the transparency and mechanical properties of flame-retardant EP decreased to varying degrees. Recently, piperazine-derived phosphorus-containing flame retardant has drawn a lot of attention because piperazine derivatives such as piperazine pyrophosphate (PAPP), 1,4-bis (diethylmethylenephosphonate) piperazine (BDEMPP), and piperazine-modified ammonium polyphosphate (PAz-APP) exhibited good charring ability and high flame retardancy during the burning of the polymer materials [8, 31, 32]. In addition, when BDEMPP was added to EP, the mechanical properties of the prepared flame-retardant material increased. Therefore, using piperazine to prepare high-efficiency flame retardants is a promising way, and it can be predicted that DOPO-piperazine-derived salt could be a high-performance flame retardant for EP.

In the present work, a phosphorus-containing flame retardant PAHDOPO salt was synthesized by a simple neutralization reaction between piperazine and DOPO-OH, which can be obtained by the oxidization of DOPO with hydrogen peroxide. After the structure examination of the prepared PAHDOPO by Fourier transform infrared spectra (FTIR), transparent flame-retardant EPs containing different PAHDOPO content were prepared. The thermal stability and flammability of these EPs were compared. Furthermore, the effect of the PAHDOPO addition on the mechanical properties of flame-retardant EP was explored.

Experimental

Materials

Diglycidyl ether of bisphenol A (E-51) was bought from Nantong Xingchen Material Co., Ltd., China. DOPO, hydrogen peroxide (H_2O_2, 30%), and ethanol were bought from Shanghai Aladdin Reagent Co., Ltd., China. Piperazine and 4,4'-Diaminodiphenylmethane (DDM) were bought from Shanghai Macklin Biochemical Co., Ltd., China.

Synthesis of PAHDOPO

PAHDOPO was prepared by a two-step reaction process. The synthesis route is shown in Scheme 1. Firstly, DOPO-OH was prepared according to the reported literatures [33, 34]. 0.2 mol DOPO and 300 mL ethanol were stirred in a three-neck flask until the complete dissolution of DOPO. Then, 240 mL H_2O_2 was added to the solution dropwise.

When H_2O_2 was completely added, the solution was heated up to 80 °C and reacted at this temperature for 8 h. After the reaction, the obtained mixture was cooled down to room temperature and DOPO-OH was separated by filtration. The obtained DOPO-OH was washed by ethanol and dried at 80 °C in a vacuum oven for 12 h. Secondly, PAHDOPO was prepared by the neutralization between DOPO-OH and piperazine. 0.2 mol DOPO-OH and 300 mL ethanol were stirred in a three-neck flask. Then, piperazine (8.2 g, 0.1 mol) was added and stirred constantly until the reaction mixture became neutral. The white PAHDOPO salt was separated by filtration. After being washed by distilled water and vacuum drying at 80 °C for 12 h, the final PAHDOPO product was obtained.

Preparation of flame-retardant EP

Firstly, PAHDOPO was blended vigorously with E51 at 80 °C for 1 h. The obtained homogeneous liquid was ultrasonically treated by an ultrasonic cell pulverizer (KS-250SDN, China) for 20 min. The melted DDM curing agent was immediately added and mixed with the treated liquid. After mixed completely, the obtained mixture was degassed under reduced pressure for 10 min to eliminate bubbles in the mixture. The degassed mixture was poured rapidly into a preheated Teflon mold, which was successively cured at 120 °C for 3 h and 150 °C for 2 h. The obtained flame-retardant EP was named as EPX, where the X indicates the weight percentage of PAHDOPO in EP. For instance, the flame-retardant EP with the 7% PAHDOPO was named as EP7. Formulation of flame-retardant EPs is shown in Table 1.

Characterization

FTIR test was carried out with an IR-prestige 21 infrared spectrometer, using the KBr pellet method. Vertical burning (UL-94) test was performed on a BKSSOD vertical burning tester according to the ASTM D3801 standard. The limiting oxygen index (LOI) value was tested using a YZS-75A oxygen index meter according to the ASTM D2863-97 standard with the sample dimension of $130 \times 6.5 \times 3.2$ mm^3. A FAA-PCFC microscale combustion calorimeter was applied to examine the flammability behavior of flame-retardant EP. Thermal gravimetric analysis (TGA) was applied on a Q50 thermal analyzer under the air from 50 °C to 700 °C. A Phenom ProX scanning electronic microscope was conducted to observe the char residue morphology after the UL-94 test. This instrument was also used to determine the sample elemental composition because of the energy-dispersive X-ray spectrometer (EDS) fitted on it. The transmittance of EP specimens with a thickness of 3.2 mm was examined by a JC-UT2000 UV–vis spectrophotometer in the range from 600 to 800 nm. According to the GB/T 1040.2–2006 standard, tensile strength of flame-retardant EPs was recorded by a TCS-2000 universal testing machine. According to the GB/T 1843–2008 standard, the Izod unnotched impact strength was measured on a JJ-20 pendulum impact testing machine.

Results and discussion

Characterization of PAHDOPO

Figure 1 presents the FTIR spectra of PAHDOPO, DOPO-OH, piperazine, and DOPO. The peaks at 1595 cm^{-1} and 2436 cm^{-1} in Fig. 1a come from the stretching vibration of P-Ph and P–H of DOPO, respectively [24, 35]. In Fig. 1b, the peak at 2436 cm^{-1} disappeared, and a new peak appeared at 925 cm^{-1}, which comes from the stretching vibration of P-OH in DOPO-OH [36]. This result demonstrates that, after DOPO was oxidized by H_2O_2, DOPO-OH was synthesized. In the spectrum of piperazine Fig. 1c, the peak at 3207 cm^{-1} and 1068 cm^{-1} can be ascribed to the stretching vibration of N–H and C-N of piperazine, respectively [37, 38]. Compared with Fig. 1c, it can be found that the peak of N–H stretching vibration

Table 1 Formulation, LOI, and UL-94 tests results of EP and flame-retardant EPs

Sample	EP (%)	PAHDOPO (%)	LOI (%)	UL-94		
				t_1/t_2 (s)	Dripping/cotton ignition	Rating
EP	100	0	23.9	-	Y/Y	NR
EP2	98	2	30.3	14.4/5.2	N/N	V-1
EP4	96	4	32.0	10.3/4.4	N/N	V-1
EP6	94	6	34.5	4.4/6.1	N/N	V-1
EP7	93	7	35.8	3.2/4.5	N/N	V-0
EP8	92	8	36.4	3.3/3.6	N/N	V-0

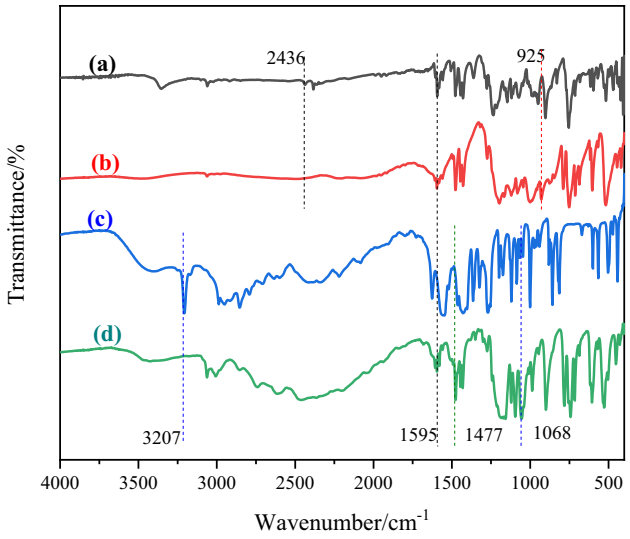


Fig. 1 FTIR spectra of **a** DOPO, **b** DOPO-OH, **c** piperazine and **d** PAHDOPO

at 3207 cm^{-1} in Fig. 1c disappeared, and a new peak at 1477 cm^{-1} appeared, indicating the existence of the bending vibration of -NH_2^+ [39]. These results proved the formation of PAHDOPO.

LOI and UL-94

To characterize the flammability of the prepared samples, the LOI and UL-94 tests were carried out and the testing results are summarized in Table 1. The UL-94 test result of pure EP is no rating and the LOI value of pure EP is only 23.9%, exhibiting the relatively high flammability of EP. When PAHDOPO was added to EP, the flame retardancy of EP was improved. Compared with EP, when 2%, 4% and 6% PAHDOPO was added, the LOI value of EP2, EP4 and EP6 increases to 30.3%, 32.0% and 34.5%, respectively. Meanwhile, the UL-94 test of EP6 almost passed the V-0 rating because the sum of the t_1 and t_2 of EP6 is 10.5 s, which is only 0.5 s higher than the V-0 rating standard. Flame retardancy of prepared samples increases with the increase of the PAHDOPO content. When the content of PAHDOPO is increased to 7%, the LOI value of EP7 achieved 35.8%, and EP7 easily obtained the UL-94 V-0 rating. With the further increase of the content of PAHDOPO, EP8 also exhibits high flame retardancy because its LOI value is 36.4% and the UL-94 test result is V-0 rating. To demonstrate the difference in combustion phenomenon between flame-retardant EPs and pure EP, the burning photos of the EP and EP7 samples during UL-94 tests are provided in Fig. 2. EP is easy to ignite, and after the first ignition, the ignition time of EP

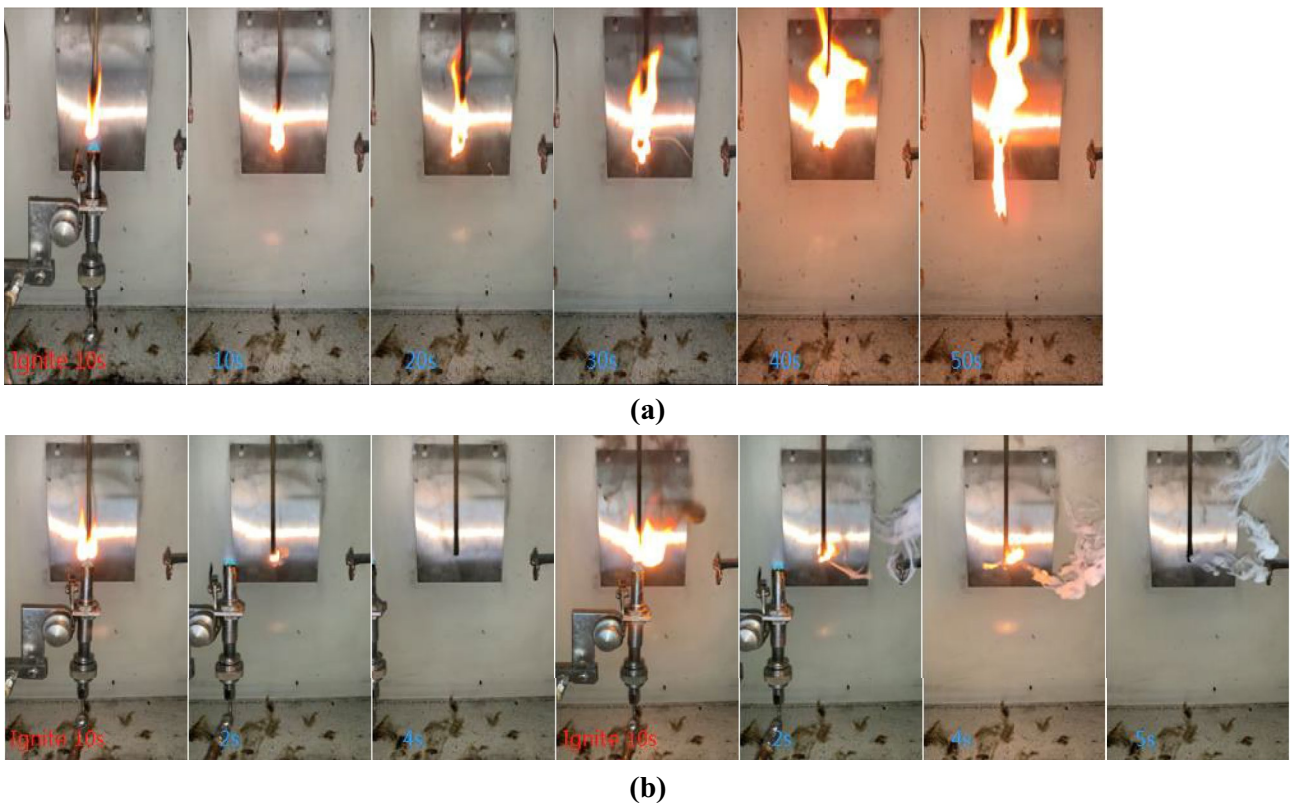


Fig. 2 The digital photos of the burning **a** EP and **b** EP7 samples during UL-94 tests

lasted more than 50 s. With the addition of 7% PAHDOPO in EP, the EP7 sample can self-extinguish rapidly after ignition. The flame retardancy of pure EP is greatly improved with the addition of PAHDOPO according to the above two test results. Since EP6, EP7, and EP8 showed relatively better performance in the LOI and UL-94 tests, these three samples were used in the following experiments.

Thermal stability analysis of PAHDOPO, pure EP and flame-retardant EPs

TG and DTG curves of PAHDOPO, pure EP, and flame-retardant EPs are illustrated in Fig. 3. The detailed thermal analysis data are shown in Table 2. In Fig. 3a, the initial thermal degradation temperature of PAHDOPO is about 335 °C, which can be identified by the temperature at the 5% weight loss ($T_{5\%}$). Two degradation stages can be seen in the TG curve of PAHDOPO. The first stage between 280 °C and 500 °C with a weight loss of approximately 86.1% is caused by the thermal decomposition of the C-N heterocycle and DOPO group [40, 41]. The second stage above 500 °C with a weight loss of 6.8% can be attributed to the degradation of phosphorus-containing derivatives formed in the first thermal degradation stage [42]. When the temperature reached 700 °C, the char residue of PAHDOPO is 7.1%. As reported in the literature, pure EP exhibits two weight loss stages below 700 °C with the $T_{5\%}$ of 388.1 °C and 2.0% char residue at the thermal decomposition temperature of 700 °C [43]. The difference in thermal degradation behavior between PAHDOPO and EP can greatly affect the thermal decomposition process of flame-retardant EPs. Compared with EP, with the addition of PAHDOPO, the $T_{5\%}$ and T_{max} of flame-retardant EPs are all lower than those of EP, while the residue at 700 °C of flame-retardant EPs is higher than that of EP. When the content of PAHDOPO increased from 6 to 8%, the $T_{5\%}$ of flame-retardant EPs decreased from 346.1 °C to 337.9 °C and the char residue at 700 °C increased from 4.2% to 6.2%. With the addition of PAHDOPO, the resultant relative low $T_{5\%}$ and high char residue at 700 °C are good for improving the flame retardancy of EPs [44].

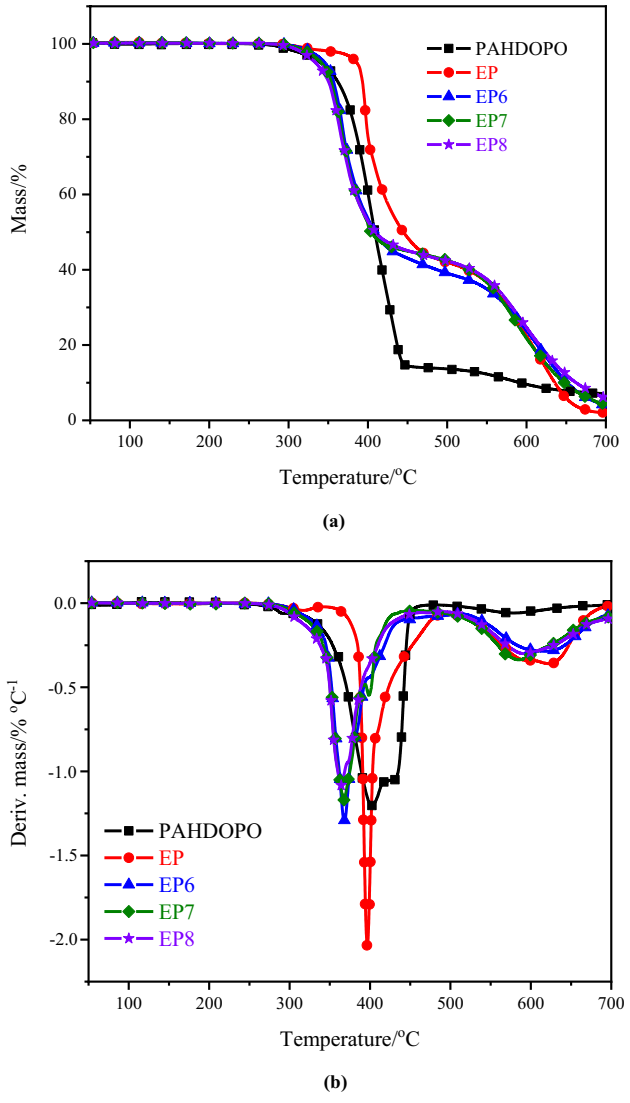


Fig. 3 **a** TG and **b** DTG curves of PAHDOPO, EP, and flame retardant EPs under air atmosphere

Table 2 Detailed TGA data of PAHDOPO, pure EP, and flame-retardant EPs

Sample	$T_{5\%}$ (°C)	T_{max} (°C)	Residue at 500 °C (%)	Residue at 700 °C (%)
PAHDOPO	334.5	402.9	13.7	7.1
EP	388.1	396.6	42.0	2.0
EP6	346.1	367.7	39.1	4.2
EP7	343.3	366.7	42.5	4.3
EP8	337.9	363.3	42.3	6.2

MCC measurement of flame-retardant EPs

To accurately and rapidly demonstrate the flame retardancy of polymers, microscale combustion calorimetry (MCC) is always used [45]. Figure 4 shows the obtained heat release rate (HRR) curves of flame-retardant EPs and pure EP. The detailed combustion data are presented in Table 3. All the HRR curves in Fig. 4 show one sharp peak. However, the addition of PAHDOPO greatly affects the combustion data. The HRC of EP is 554.3 J g^{-1} K^{-1}, while the HRC of EP6, EP7, and EP8 decreased to 400.5, 388.8, and 368.3 J g^{-1} K^{-1}, respectively. Since HRC reflects the amount of substances that can promote combustion in materials, the lower HRC means the better flame

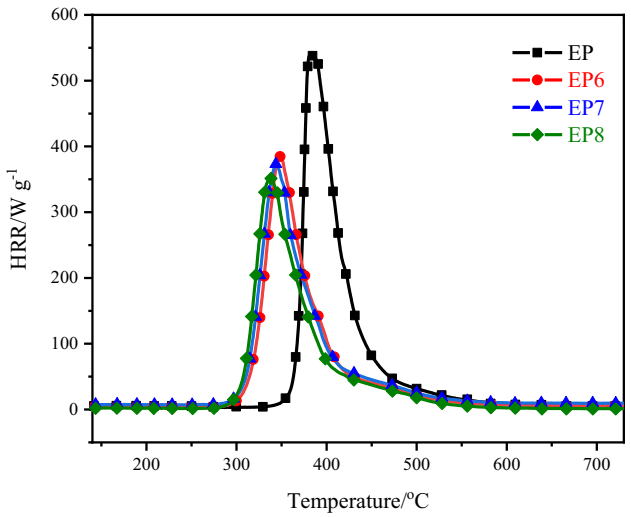


Fig. 4 HRR curves of EP and flame-retardant EPs

retardancy [46]. Thus, the decrease of HRC of EP6, EP7, and EP8 indicates the high flame retardancy of the prepared flame-retardant EPs. As for PHRR, the PHRR of EP is 537.7 W g^{-1}. When the content of PAHDOPO is 6%, the PHRR of EP6 decreases to 384.5 W g^{-1}. With the content of PAHDOPO increasing to 8%, the PHRR of EP8 decreased to 351.4 W g^{-1}. This indicates that PAHDOPO can efficiently prevent the combustion and thermal decomposition of EP, resulting in the improvement of the flame retardancy of pure EP [47]. The THR of EP and flame-retardant EPs also shows a similar trend as PHRR. The THR of EP was 29.4 kJ g^{-1}. When PAHDOPO was added to EP, the THR of flame-retardant EPs decreased. The THR of EP6, EP7, and EP8 are 26.2, 25.7, and 25.6 kJ g^{-1}, respectively, which are lower than the 29.4 kJ g^{-1} of pure EP. This investigation result indicates that the addition of PAHDOPO can restrain the EP decomposition and enhance the flame retardancy of EP [48]. Moreover, the T_{PHRR} of the prepared flame-retardant EPs shifts to low temperatures compared with pure EP. It can be observed from Table 3 that the T_{PHRR} of EP6, EP7, and EP8 decreased from 384.5 °C to 348.1 °C, 343.5 °C, and 337.8 °C, respectively. This phenomenon demonstrates that the prepared flame-retardant EPs have lower thermal stability than that of pure EP, which is in accordance with the above TGA result. Therefore, the MCC results confirmed the improvement of the flame retardancy of pure EP caused by the addition of PAHDOPO.

Table 3 MCC measurement results of pure EP and flame-retardant EPs

Sample	HRC (J g^{-1} K^{-1})	PHRR (W g^{-1})	THR (kJ g^{-1})	T_{PHRR} (°C)
EP	554.3	537.7	29.4	384.5
EP6	400.5	384.5	26.2	348.1
EP7	388.8	373.2	25.7	343.5
EP8	368.3	351.4	25.6	337.8

Char residue analysis

The elemental composition and morphology of the char residues were measured by EDS and SEM, and the results are presented in Fig. 5. As depicted in Fig. 5a, the char residue surface of EP shows the loose hole-and-crack morphology. The diameter of the holes is about 50 µm, and the width of the cracks is around 30 µm. This loose hole-and-crack structure can neither prevent the propagation of flame nor the contact between oxygen and the EP matrix. Therefore, without the presence of PAHDOPO, the complete combustion of EP happens. On the contrary, the char residue surface morphology of EP6, EP7, and EP8 is becoming more and more continuous and denser. It can be observed from Fig. 5b that the gaps or holes became smaller than EP on the surface of EP6 char residue. Although there are a little small gaps on the char residue surface of EP7 and EP8 (Fig. 5c, d), the main body of the char residue became continuous and dense. Thus, the continuous and dense char residue layer formed during the combustion of EP7 and EP8 can be responsible for the oxygen isolation, heat insulation, and internal EP protection, which provides the higher flame retardancy compared to the char residue formed during the combustion of EP [49]. Usually, DOPO derivatives always achieve high flame retardancy by eliminating the free radicals formed in the gas phase during the burring of polymers [50]. Nevertheless, some DOPO derivatives can act on the gas and condensed phase simultaneously [51]. To illustrate whether PAHDOPO can act on the condensed phase, the elemental compositions of the char residue layers of pure EP, EP6, EP7, and EP8 were examined by EDS. Table 4 and Fig. 5 present the related results. The main elements that were found in the char residues of EP6, EP7, and EP8 are C, P, N and O. The proportion of the C, O, and N elements are 49.13%, 32.78%, and 18.09%, respectively, in the EP char residue and no P element can be found. Compared with the elemental composition of EP char residue, P element can be detected in the char residue of EP6, EP7, and EP8. The content of P element increased from 2.85% in EP6 to 3.47% in EP8. The detection of P element in the char residues of EP6, EP7, and EP8 indicates that the thermal decomposition products from the P element can act on the condensed phase and lead to the formation of the continuous and dense char layer [52]. Thus, EDS results demonstrate that the PAHDOPO can act on the condensed phase to promote the flame retardancy of EP during the combustion process.

Proposed possible flame-retardant mechanism

Based on the above investigation results, a possible flame-retardant mechanism of PAHDOPO was proposed

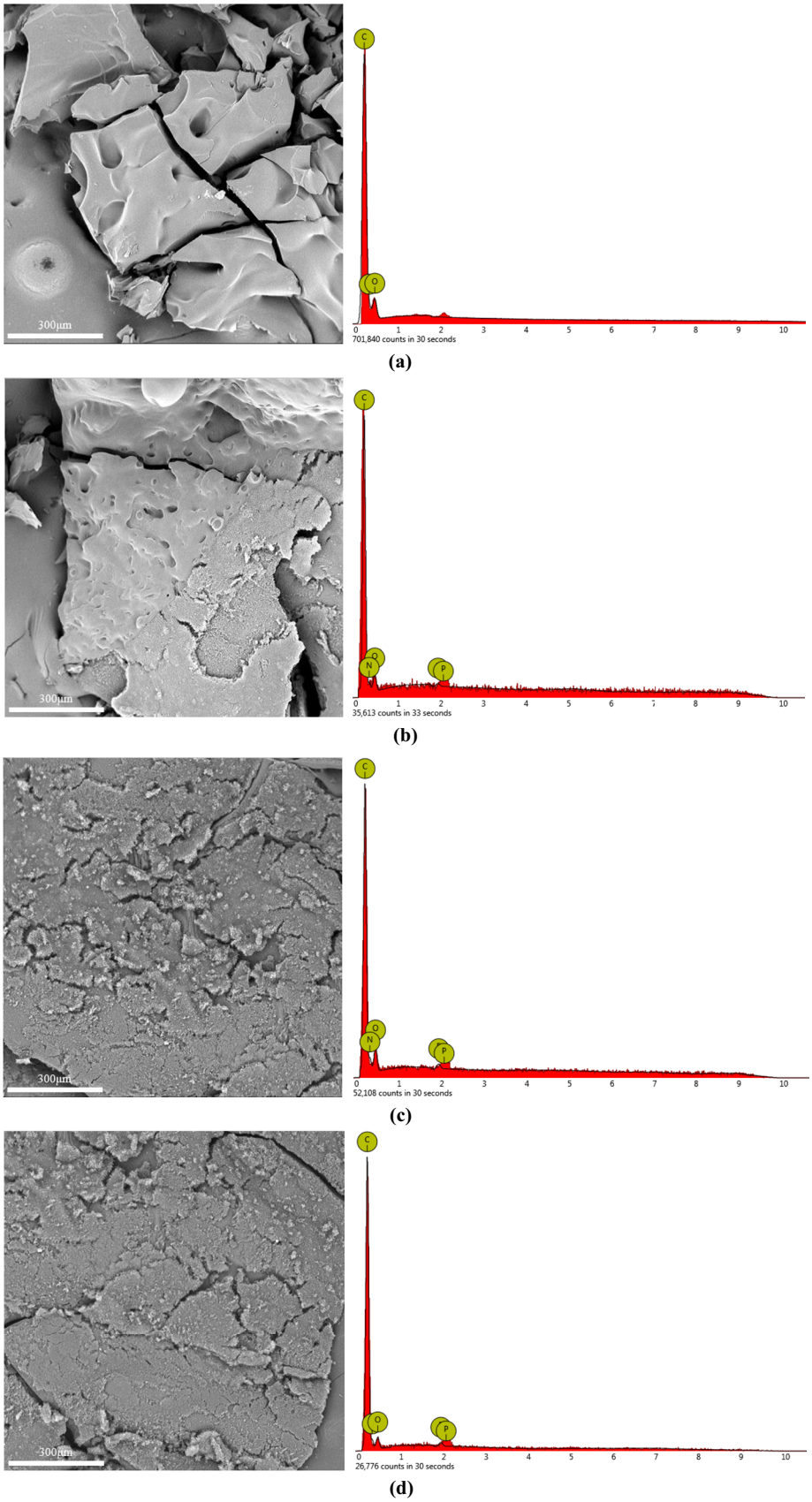
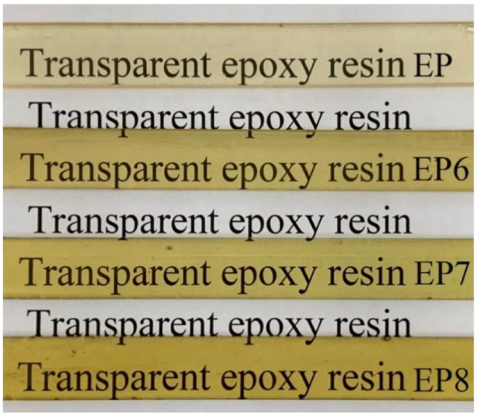


Fig. 5 SEM and EDS results of char residues from **a** EP, **b** EP6, **c** EP7, and **d** EP8 after the UL-94 test

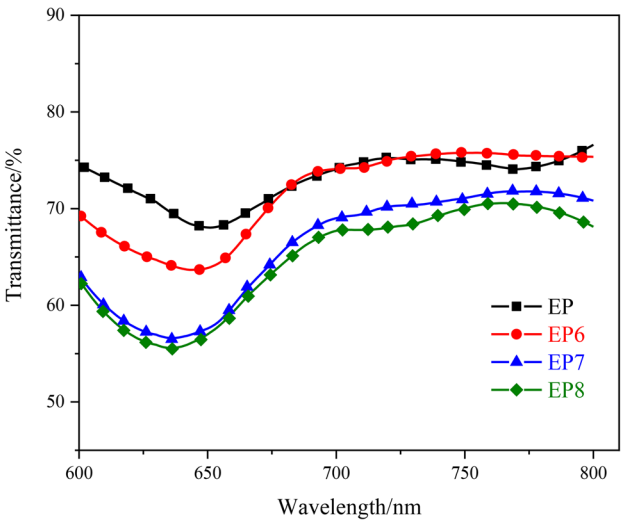
Table 4 Element proportion of char residues of pure EP, EP6, EP7 and EP8

Sample	O (%)	C (%)	N (%)	P (%)
EP	49.13	32.78	18.09	-
EP6	44.25	39.72	13.18	2.85
EP7	48.36	32.51	15.87	3.26
EP8	34.45	43.64	18.44	3.47

as shown in Scheme 2. This mechanism mainly involves two aspects. On the one hand, PAHDOPO can act on the gas phase. During the burning process, with the decomposition of the DOPO group in PAHDOPO, PO_2·and PO· radicals were produced in the gas phase, which can quench the HO· and H· free radicals to terminate the combustion process of EP [53]. Simultaneously, incombustible gases such as NH_3 and H_2O produced by the decomposition of the piperazine group in PAHDOPO can dilute the concentration of combustible volatiles and O_2 to achieve the high performance of PAHDOPO [54]. On the other hand, PAHDOPO can act on the condensed phase. The phosphoric acid derivatives generated during the decomposition of PAHDOPO can catalyze EP to form a continuous and dense char layer containing the C-O-P structure in the condensed phase [20, 55]. Moreover, with the decomposition of the piperazine group in PAHDOPO, some special bonds such as P-N–C and C = C can be generated, which also helps to form a continuous and dense layer [8]. Thus, the ultimately formed continuous and dense char residue layer can retard the thermal and mass exchange between the combustion region and EP matrix to protect EP from combustion. Therefore, PAHDOPO shows good flame retardancy performance.



(a)



(b)

Fig. 6 **a** Digital photos of EP, EP6, EP7, and EP8 specimens, **b** transmittances of EP and flame-retardant EPs

Scheme 2 Schematic diagram of the proposed flame-retardant mechanism

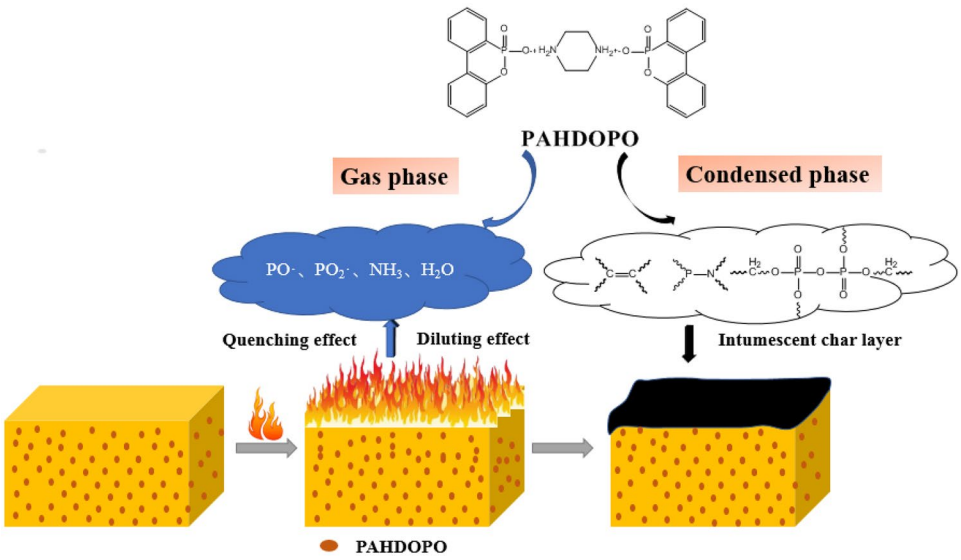


Table 5 Mechanical properties of pure EP and flame-retardant EPs

Sample	Tensile strength (MPa)	Izod unnotched impact strength (kJ m^{-2})
EP	72.1 ± 4.0	30.0 ± 2.0
EP6	74.2 ± 4.8	28.9 ± 2.2
EP7	82.5 ± 6.5	29.2 ± 2.5
EP8	87.3 ± 6.1	29.6 ± 2.4

Transparency of flame-retardant EPs

The digital photographs of the specimens are shown in Fig. 6 to reveal the good transparency of the prepared specimens in the visible light region. The appearance of EP is light yellow and transparent. When PAHDOPO was added, the color of flame-retardant EPs gradually deepened, but their transparency changes little. It can be observed from Fig. 6a that although the color of EP8 becomes chrome yellow, the text under EP specimens is still clearly visible. To quantitatively demonstrate that the addition of PAHDOPO had little influence on the EP transparency, the transmittances of specimens were examined. The average transmittance of EP, EP6, EP7, and EP8 in the wavelength range from 600 to 800 nm is 72.1%, 71.5%, 66.4%, and 64.9%, respectively. Compared with EP, the average transmittance of EP8 decreases by less than 8%, demonstrating that the addition of PAHDOPO can hardly affect the transparency of EP.

Comparison of the mechanical properties

Investigation on the effect of the addition of PAHDOPO on the mechanical properties of EP was further carried out. Mechanical properties data, including the tensile strength and Izod unnotched impact strength, are shown in Table 5. With the addition of PAHDOPO, the mechanical properties of EP did not decrease significantly. According to the experimental result, tensile strength increased clearly when the PAHDOPO content increased. Compared with the 72.1 MPa tensile strength of EP, the tensile strength of EP6, EP7, and EP8 increases to 74.2 MPa, 82.5 MPa, and 87.3 MPa, respectively. As to the impact strength, EP and flame-retardant EPs exhibited similar properties. The respective impact strength of EP, EP6, EP7 and EP8 is 30.0 kJ m^{-2}, 28.9 kJ m^{-2}, 29.2 kJ m^{-2}, and 29.6 kJ m^{-2}. The difference in impact strength between EP and the flame-retardant EPs is less than 3%. It has been reported that there are some interactions between the DOPO group and EP, and these interactions, including the π-π interaction and hydrogen bond caused by the DOPO group, can improve the dispersion of DOPO derivatives in EP [56, 57]. Therefore, the good dispersibility and compatibility of PAHDOPO in EP leads to the good mechanical properties of the prepared flame-retardant EPs.

Developing EP with excellent transparency, flame retardancy, and mechanical properties is an important work in the field of EP materials in recent years. Table 6 presents some recent research work related to the additive-type flame retardant (FR) used for the preparation of EP composite with good transparency, flame retardancy, and mechanical properties. Due to the variety of EPs, Table 6 can only roughly reflect the performance of different FRs. All these FRs showed good transparency, flame retardancy, and mechanical properties. All the prepared flame-retardant EPs passed the UL-94 V1 rating when the content of FR was lower than 10%. The flame-retardant EP with the addition of PAHDOPO showed relatively high tensile strength of 83 MPa. In terms of transparency, PAHDOPO and PDB showed similar performance. When PAHDOPO and PDB were added, the prepared flame-retardant EPs have the similar transparency at 600 nm of higher than 60%. Thus, PAHDOPO exhibited similar performance on the aspects of transparency, flame retardancy, and mechanical properties as reported FRs.

Table 6 Comparison of the flame retardancy, transparency, and mechanical properties of the flame-retardant EP prepared in this work with other reported literature data

FR	Content of FR (%)	Transparency at 600 nm (%)	Thickness (mm) [a]	UL-94	LOI (%)	Tensile strength (MPa)	Ref.
PAHDOPO	7	63	3.2	V0	35.8	83	This work
PDB	7	65	3.2	V0	28.6	-	[58]
DCA	5	35	1	V1	31.6	-	[59]
BDEMPP	9	85	1	V1	28.3	52	[32]
BMP	10	-	-	V0	35.5	67	[60]
DOA	7.5	70	1	V1	36.5	81	[56]

[a] thickness of the sample used in the transparency test

Conclusion

A DOPO-derived salt (PAHDOPO) was prepared by the reaction between DOPO-OH and piperazine in this work. The addition of PAHDOPO can improve significantly the flame retardancy of pure EP. Flame-retardant EP containing 7% PAHDOPO can not only pass the V-0 rating in the UL-94 test but also obtain a 35.8% LOI value. MCC test results indicated that the THR, HRC, and PHRR of flame-retardant EPs were reduced obviously. The high performance of PAHDOPO was assigned to the fact that PAHDOPO can positively act on the gas phase and the condensed phase simultaneously during combustion. In addition, adding PAHDOPO to EP has little influence on EP transparency. When 8% PAHDOPO was added to pure EP, the average transmittance of the prepared flame-retardant EPs decreased by less than 8%. In the mechanical property testing, compared with EP, the addition of PAHDOPO cannot lead to the decrease of the mechanical properties of the prepared EP samples. The good mechanical properties of the PAHDOPO-containing EPs are caused by the good compatibility and dispersibility of PAHDOPO in EP. Thus, this work used DOPO and piperazine as reagents to synthesize a high-performance flame retardant, PAHDOPO, which can be applied in the preparation of the transparent flame-retardant EP with good mechanical properties.

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Data availability The data that support the findings of this study are available from the corresponding author upon reasonable request.

Declarations

All authors certify that they have no affiliations with or involvement in any organization or entity with any financial interest or non-financial interest in the subject matter or materials discussed in this manuscript.

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