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The synergistic effect of maleimide and phosphaphenanthrene groups on a reactive flame-retarded epoxy resin system

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ABSTRACT: A novel reactive flame-retarded epoxy resin system was prepared by copolymerizing diglycidyl ether of bisphenol-A (DGEBA) with 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), N,N'-bismaleimide-4,4'-diphenylmethane (BDM) and 4,4'-diamino-diphenyl sulfone (DDS). Curing behavior, thermal and flame-retardant properties of the cured epoxy resins were investigated by differential scanning calorimeter (DSC), thermogravimeric analysis (TGA), limited oxygen index (LOI) measurement, UL94 test and cone calorimeter. The results indicated that phosphaphenanthrene group was introduced into the multicomponent system by addition reaction of DOPO with BDM. Compared with traditional DOPO-DGEBA systems, the EP/DDS/BDM/DOPO thermosets showed greatly improved glass transition temperatures (210-223°C). The results of combustion tests indicated that the addition of BDM or DOPO into DGEBA could improve the flame resistance of the thermosets. Most importantly, the flame-retardant property was further improved when BDM and DOPO coexisted in the epoxy resin systems. For example, compared to the control samples, the EP/DDS/BDM/DOPO-15 thermoset displayed better flame retardancy with higher LOI value and UL94 rating, lower peak of heat release rate (pk-HRR) and average of effective heat of combustion (av-EHC) under the same content of BDM and phosphorus, strongly confirming the synergistic effect of BDM and DOPO. In addition, in a particular proportion, BDM and DOPO synergistically functioned in the condensed-phase and gaseous-phase at the same time. The flame retardant mechanism was studied by TGA and cone calorimeter coupled with the analysis of the char residues.

Keywords: Epoxy resin; DOPO; Maleimide; Synergistic effect; Flame retardant.

1. Introduction

Epoxy resins (EPs) are widely used in coating, adhesive, laminating, and electronic industry due to their attractive characteristics of high tensile strength and modulus, high adhesion to substrates, good chemical and corrosion resistance, excellent dimensional stability and superior electrical properties [1-5]. However, conventional epoxy resins are flammable and can not satisfy high flame-resistance requirement of advanced materials [6, 7]. So far, research works on improving the flame retardancy of epoxy resins are very attractive for advanced application. The incorporation of halogen into the epoxy resins can increase flame resistance. Currently, halogen-containing compounds are not preferred for environmental reasons [8, 9]. Therefore, there is a trend to develop and apply halogen-free flame retardants.

Epoxy resins modified by phosphorus-containing flame retardants are considered to be more environmentally friendly and have been widely used [10-14]. Among the phosphorus-containing flame retardants, DOPO and its derivatives have received considerable attention due to their high reactivity and flame retarded efficiency [15-17]. Without co-additive, epoxy resins modified with DOPO can not show high thermal stability and good mechanical properties due to the decreased crosslinking density, and single flame retardant composition limits the further enhancing of flame retardancy of the modified epoxy resins [18-20]. Therefore, flame retardants with multiple flame-retardant functional groups have been used. A few works have been reported about the synergistic effect of multiple flame-retardant functional groups on flame retardancy of epoxy resins [21-27].

Maleimide modified epoxy resins provide a convenient approach of enhancing the thermal stability, flame retardancy and mechanical properties due to their high crosslink density and thermal stable maleimide groups [28-30]. Therefore, when maleimide and phosphaphenanthrene groups coexist in epoxy resin systems, the cured products may exhibit outstanding integrated properties.

In this work, a novel flame-retarded epoxy resin system was prepared by copolymerizing DGEBA with DOPO, BDM and DDS. Research on the curing behavior of the multicomponent system revealed that phosphaphenanthrene and maleimide groups were integrated into one molecule which functioned as reactive flame retardant. Thermal and flame retardant properties of the cured epoxy resins were investigated by differential scanning calorimeter (DSC), thermogravimeric analysis (TGA), limited oxygen index (LOI) measurement, UL94 test and cone calorimeter. Compared to the traditional DGEBA-DOPO system, the EP/DDS/BDM/DOPO systems showed enhanced thermal stability and flame retardancy. The flame retardant mechanism of the EP composites based on BDM and DOPO was studied.

2. Experimental

2.1. Materials

Diglycidyl ether of bisphenol-A (DGEBA) with an epoxide equivalent weight (EEW) of about 188 g/equiv was provided by Yueyang Baling Huaxing Petrochemical Co., Ltd.

N,N'-bismaleimide-4,4'-diphenylmethane (BDM) was obtained from Puyang Willing Chemicals Co., Ltd. 9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was purchased from Huizhou Sunstar Technology Co., Ltd. 4,4’-Diamino-diphenyl sulfone (DDS) was purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Preparation of EP/DDS/BDM/DOPO thermosets and the control samples

EP/DDS/BDM/DOPO thermosets were prepared via a thermal curing process. At first, BDM was dissolved in DGEBA at 120°C under vigorous stirring. After complete dissolution of BDM, DOPO was added under N_2 atmosphere. After stirring at 120°C for 20 min, stoichiometric DDS (with respect to epoxy) was thoroughly blended at 120°C until a homogeneous solution was obtained. The mixture was then degassed under vacuum for 5 min to remove trapped air, and then poured directly into preheated mould and thermally cured in air convection oven for 2 h at 125°C, 150°C, 180°C, 200°C and 230°C, respectively.

The control samples were prepared as follows. EP/DDS/BDM thermoset was obtained similar to the way of EP/DDS/BDM/DOPO thermosets without the addition of DOPO and thermally cured for 2 h at 160°C, 180°C, 200°C and 230°C, respectively. EP/DDS and EP/DDS/DOPO thermosets were prepared with the method reported in the literature [10]. All the details of formula are listed in Table 1.

Table 1

Formulas of the cured epoxy resins

Sample code	DGEBA (g)	DDS (g)	BDM (g)	DOPO (g)	BDM content (wt.%)	P content (wt.%)
EP/DDS	100	33	0	0	0	0
EP/DDS/BDM	100	33	26.95	0	16.85	0
EP/DDS/DOPO	100	33	0	12.25	0	1.21
EP/DDS/BDM/DOPO-5	100	33	30	5	17.86	0.43
EP/DDS/BDM/DOPO-10	100	33	30	10	17.34	0.83
EP/DDS/BDM/DOPO-15	100	33	30	15	16.85	1.21
EP/DDS/BDM/DOPO-20	100	33	30	20	16.39	1.57

2.3. Preparation of uncured samples for DSC analysis

The EP/DOPO mixture (the weight ratio is 2:1) was obtained by dissolving DOPO in DGEBA at 125°C and then cooled to room temperature. The BDM/DOPO mixture (the molar ratio is 1:2) was prepared by grinding BDM and DOPO in an agate mortar. In addition, tiny amounts of the uncured EP/DDS/BDM and EP/DDS/BDM/DOPO mixtures prepared in 2.2 were taken out for DSC measurement.

2.4. Preparation of prepolymers for IR analysis

The EP/DOPO (the weight ratio is 2:1) mixture were placed in air convection oven at 125°C for 2h, and marked as EP/DOPO-125°C-2h. In addition, tiny amounts of EP/DDS/DOPO and EP/DDS/BDM/DOPO mixtures prepared in 2.2 were taken out after cured for 2h at 125°C, and labeled as EP/DDS/DOPO-125°C-2h and EP/DDS/BDM/DOPO-x-125°C-2h (x=5,10, 15, 20).

2.5. Measurements

Fourier Transform Infrared (FTIR) spectra were obtained using a Nicolet 6700 infrared spectrometer. The powdered samples were thoroughly mixed with KBr and then pressed into pellets.

Differential scanning calorimetry (DSC) thermograms were recorded with Perkin–Elmer DSC 4000 at a heating rate of 10°C/min under nitrogen atmosphere from 50 to 320°C.

Thermogravimetric analysis (TGA) was performed using NETZSCH STA449F3 at a heating rate of 10°C/min under nitrogen atmosphere from 50 to 800°C.

The LOI values were measured at room temperature on a JF-3 oxygen index meter (Jiangning Analysis Instrument Company, China) according to ISO4589-1984 standard and dimensions of all samples were 130×6.5×3 mm^3. Vertical burning (UL-94) tests were carried out on the NK8017A instrument (Nklsky Instrument Co., Ltd, China) with the dimension of 130×13×3 mm^3 according to UL-94 test standard. Cone calorimeter measurements were performed on an FTT cone calorimeter according to ISO 5660 under an external heat flux of $50kW/m^2$. The dimension of samples was 100×100×3 mm^3.

Morphological studies on the residual chars were conducted using a JSM-5610LV scanning electron microscope (SEM) at an acceleration voltage of 25 kV.

3. Results and discussion

3.1. Research on the reactivity of the mixtures

The curing behavior of a multivariate copolymerization system determines its crosslinking network, and thereby the properties of the thermoset, so the curing behavior is the first issue needing to be studied. In our study, the reactivity of the

EP/DDS/BDM/DOPO mixtures was investigated by DSC at a heating rate 10°C/min under nitrogen atmosphere.

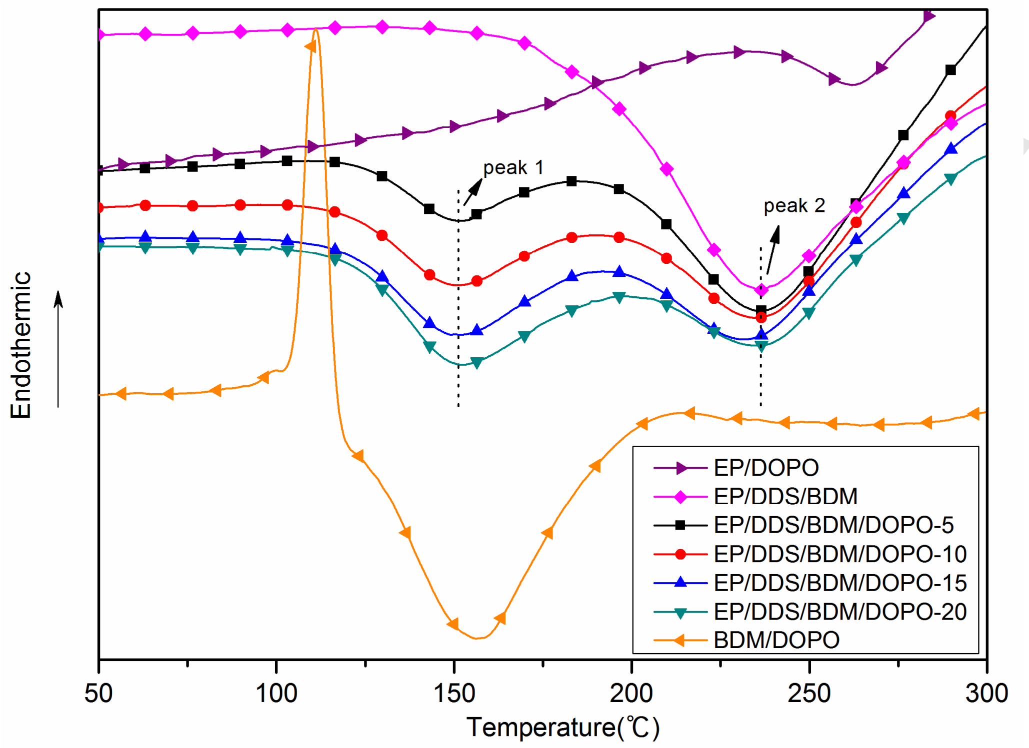

Fig. 1. DSC traces of uncured mixtures

As shown in fig. 1, the EP/DOPO mixture did not show obvious exothermic peak before 160°C, indicating that the low reactivity between DGEBA and DOPO at this temperature region. The BDM/DOPO mixture showed a sharp endothermic peak at 110°C, which was ascribed to the melting of DOPO. However, the curve of BDM/DOPO mixture went downwards immediately after the melting of DOPO, and then a very distinct exothermic peak appeared, indicating a much higher reactivity of BDM/DOPO mixture compared with that of DGEBA/DOPO mixture before 160°C. In addition, the EP/DDS/BDM mixture exhibited only one exothermic peak, which involved with the ring-opening reaction, homopolymerization of maleimide groups and Michael-addition reaction between diamine and maleimide groups [28, 29]. However, when DOPO was added into the EP/DDS/BDM mixture, another exothermic peak (peak 1) appeared as shown in fig. 1. Moreover, the integrated peak area of peak 1 increased with the increasing content of DOPO whereas peak 2 showed an opposite trend. The emerging peak 1 was due to the addition reaction of DOPO with BDM. With the increasing content of DOPO, more DOPO would react with BDM, resulting in a more obvious exothermic peak; on the contrary, the content of reactive double bonds of maleimide groups decreased, leading to a drop in exothermicity of peak 2. From what has been discussed above, it is supposed that during the curing process of EP/DDS/BDM/DOPO mixtures given in 2.2, DOPO will mainly react with BDM. This was further confirmed by the following FTIR analysis.

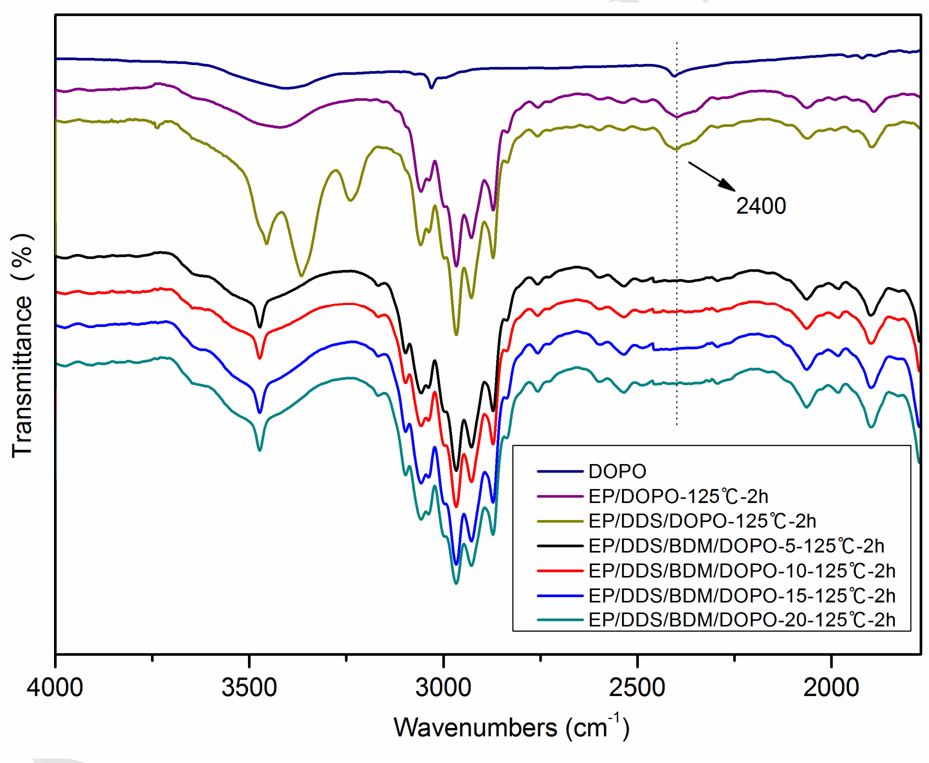

Fig. 2. FTIR spectra of different prepolymers

Fig. 2 shows FTIR spectra of different samples prepared in 2.4. The FTIR spectra of EP/DOPO and EP/DDS/DOPO prepolymers had the distinct P-H absorption at 2400cm^{-1}, proving the low reactivity between DOPO and DGEBA at

125°C. However, with the incorporation of BDM, the P-H absorption disappeared in the spectra of EP/DDS/BDM/DOPO prepolymers, suggesting a thorough reaction between P-H bond in DOPO and double bond in BDM, which was consistent with the DSC analysis. This special way of introducing DOPO into epoxy resin might impart enhanced properties to the thermosets.

3.2. Thermal properties of cured epoxy resins

The glass transition temperatures (Tgs) of the investigated EP composites were measured by DSC and the results are summarized in table 2. The Tg value of EP/DDS/BDM was increased by 15°C while that of EP/DDS/DOPO was reduced by 34°C compared with that of EP/DDS. The improvement was attributed to both of the rigidity of maleimide groups and high crosslinking density of the cured epoxy resins. The decrease in the Tg of EP/DDS/DOPO was due to a reduction in crosslinking density caused by the addition of DOPO. Unexpectedly, with the introduction of DOPO, the EP/DDS/BDM/DOPO thermosets exhibited a slightly higher T_g than that of EP/DDS/BDM in spite of the decreased crosslinking density. As listed in table 2, the Tg of EP/DDS/BDM/DOPO-15 was increased to 223°C, 7°C higher than that of EP/DDS/BDM. Only with the further increase of DOPO content, the T_g started to fall. Nevertheless, the Tg of EP/DDS/BDM/DOPO-20 (210°C) was still higher than those of EP/DDS (201°C) and EP/DDS/DOPO (167°C). Incorporating the bulky rigid DOPO group into the epoxy resin systems would increase the rotational barrier of the thermosets which compensated somewhat for the loss in crosslink density, and therefore improved the Tgs of the EP/DDS/BDM/DOPO thermosets [18].

Table 2
Thermal parameters of the cured epoxy resins

Sample code	Tg (°C)	$T_{5\%}$ (°C)	T_{max} (°C)	Char yields at different temperatures (%)				
				400 (°C)	500 (°C)	600 (°C)	700 (°C)	800 (°C)
EP/DDS	201	369	410	75.3	26.3	23.8	22.2	20.9
EP/DDS/BDM	216	366	404	72.5	33.6	29.3	26.5	24.8
EP/DDS/DOPO	167	341	370	45	32.3	30	28.5	26.9
EP/DDS/BDM/DOPO-5	218	351	384	58.5	42.7	38.2	34.4	31.7
EP/DDS/BDM/DOPO-10	220	346	375	54.8	40.9	36.7	33.4	31
EP/DDS/BDM/DOPO-15	223	344	368	54.5	41.5	37.8	35.6	33.9
EP/DDS/BDM/DOPO-20	210	339	364	53	41	38	36	34.1

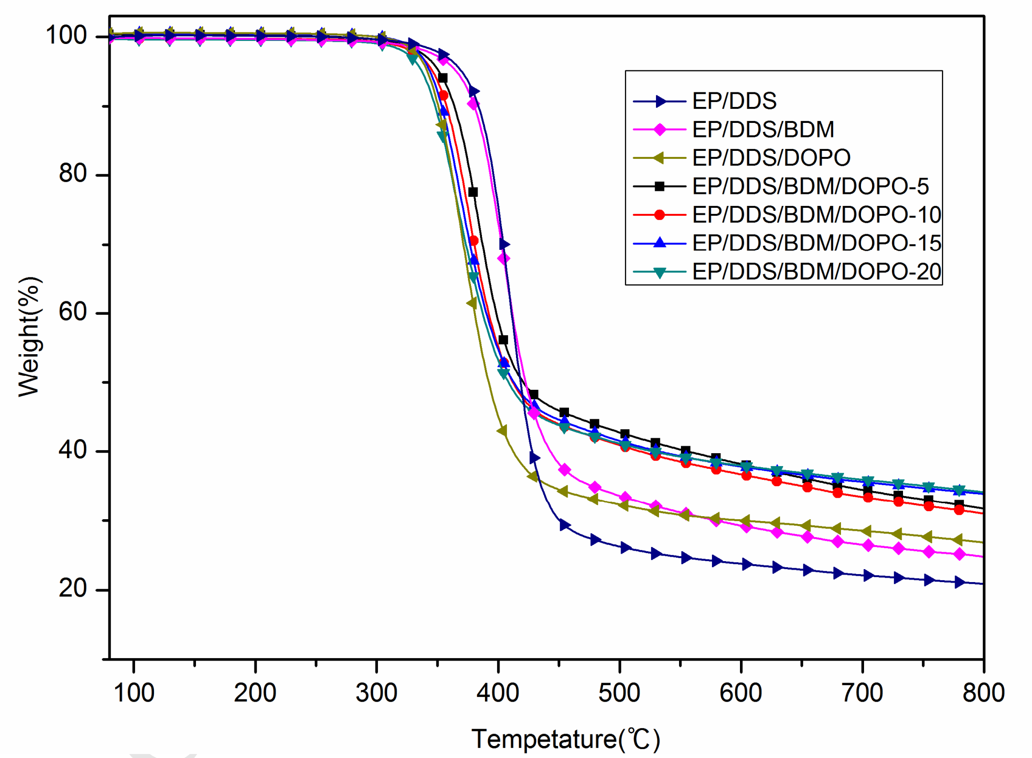

Fig. 3. TGA curves of the cured epoxy resins under N_2 atmosphere

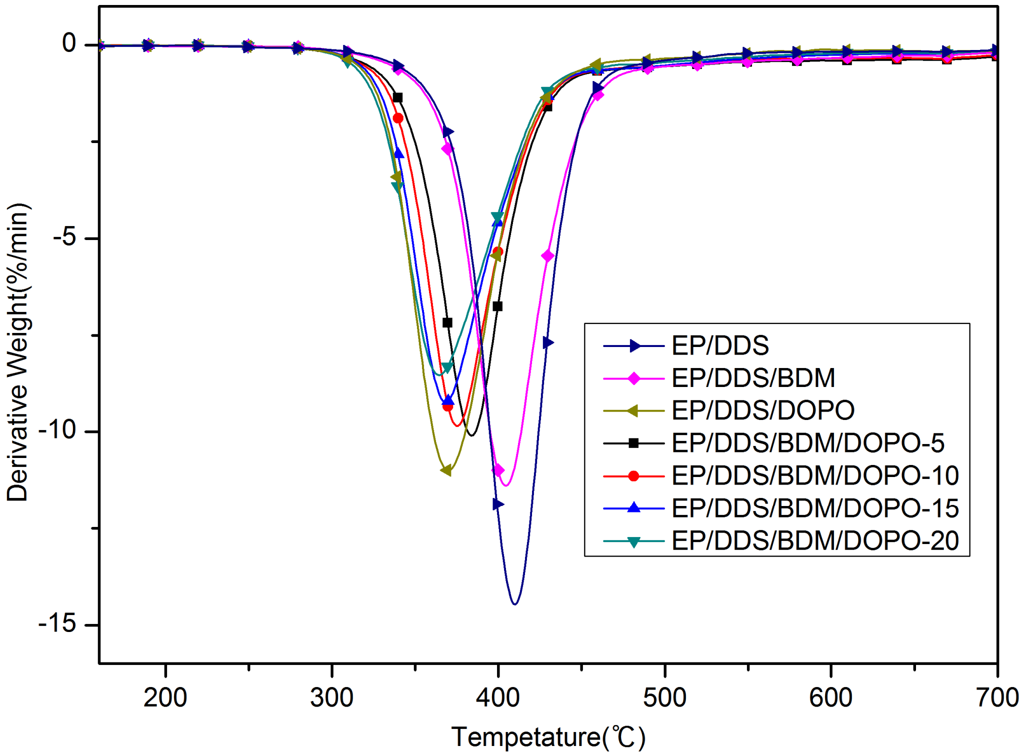

Fig. 4. DTG curves of the cured epoxy resins under N_2 atmosphere

Thermal stability of the cured epoxy resins was assessed by TGA under nitrogen atmospheres. TGA and DTG curves of the EP composites are presented in Fig. 3 and Fig. 4. The characteristic thermal decomposition data, such as temperature at 5% weight loss ($T_{5\%}$), temperature at maximum weight loss rate (T_{max}) and char yields at different temperatures are listed in tables 2. The $T_{5\%}$, T_{max} and Char yields at 400°C of DOPO-containing epoxy resin systems were lower than those of EP/DDS and EP/DDS/BDM systems. In addition, the $T_{5\%}$, T_{max} and Char yields at 400°C of the EP/DDS/BDM/DOPO thermosets decreased with the increasing content of DOPO. The pyrolysis of DOPO groups induced the decomposition of the EP matrix in advance. The induced decomposition effect could also be enhanced with increasing mass fraction of DOPO, leading to the decreased thermal stability. The char yields of EP/DDS/BDM and EP/DDS/DOPO were higher than that of EP/DDS from 500°C to 800°C, indicating that incorporating BDM or DOPO into DGEBA could promote the char formation. More notably, all of the EP/DDS/BDM/DOPO thermosets had higher char yields compared with EP/DDS/BDM and EP/DDS/DOPO at the temperature interval of 500 to 800°C, suggesting that the EP composites with difunctional group of phosphaphenanthrene and maleimide performed better in charring at higher temperature region.

Further study by the contrast tests strongly proved the synergistic effect of phosphorus and maleimide on char formation of the cured epoxy resins. The char yields of EP/DDS/BDM/DOPO-15 were higher than that of EP/DDS/BDM and EP/DDS/DOPO from 500 to 800°C. The char yields of EP/DDS/BDM, EP/DDS/DOPO and EP/DDS/BDM/DOPO-15 at 800°C were 24.8%, 26.9% and 33.9%, respectively, suggesting that there were chemical reactions between phosphorus and maleimide during the decomposition of the EP composites. The DOPO groups decomposed first to form phosphate and polyphosphate which could promote the charring of maleimide to form highly crosslinked and rigid char layer [31, 32].

3.3. LOI and UL94 rating tests

The flame-retarded properties of the EP composites were determined by LOI and UL94 vertical burning tests. The corresponding data are listed in table 3. The LOI value of EP/DDS was only 22.5%, whereas the LOI values of EP/DDS/BDM and EP/DDS/DOPO were increased to 27% and 35.5%, respectively. However, EP/DDS/BDM could not pass the UL94 test. Incorporating a small amount of DOPO into EP/DDS/BDM system could further enhance its flame retardancy. With a phosphorus content of 0.43wt.%, the LOI value of EP/DDS/BDM/DOPO-5 was increased to 32.5%, and the sample could reach the UL94 V-1 rate. When the phosphorus content reached 1.21wt.%, the EP/DDS/BDM/DOPO-15 had the maximum LOI value of 38.8% and reached the UL94 V-0 rate. However, the LOI value decreased when DOPO was further added. The LOI value of EP/DDS/BDM/DOPO-20 was decreased to 33.4% when the phosphorus content reached 1.57wt.%. Excess DOPO content led to a deviation from the optimal ratio of the flame retardant contents and thus resulted in a negative effect on the LOI performance of the cured epoxy resins.

Table 3

LOI and UL94 test results of the cured epoxy resins

Sample code	BDM content (%)	P content (%)	LOI (%)	UL-94 (3mm)
EP/DDS	0	0	22.5	NR
EP/DDS/BDM	16.85	0	27	NR
EP/DDS/DOPO	0	1.21	35.5	V-1
EP/DDS/BDM/DOPO-5	17.86	0.43	32.5	V-1
EP/DDS/BDM/DOPO-10	17.34	0.83	34.5	V-0
EP/DDS/BDM/DOPO-15	16.85	1.21	38.8	V-0
EP/DDS/BDM/DOPO-20	16.39	1.57	33.4	V-0

The enhanced flame resistance of the EP/DDS/BDM/DOPO thermosets was ascribed to the synergistic effect of BDM and DOPO. The LOI value of EP/DDS/BDM/DOPO-15 was 38.8%, whereas those of EP/DDS/BDM with the same BDM content and EP/DDS/DOPO with the same phosphorus content were 27% and 35.5%, respectively. As discussed above, the synergistic effect of phosphorus and maleimide on char formation was observed. High char yield can reduce the release of combustible gases and decrease the exothermicity of the pyrolysis reactions, consequently to limit the resins’ flammability. The flame-retardant mechanism will be further discussed in the subsequent section.

3.4. Cone calorimeter analysis of the cured epoxy resins

Cone calorimetry test was used to investigate the flame-retarded behaviors of DOPO and BDM on the EP thermosets. The characteristic parameters, such as the time to ignition (TTI), average of heat release rate (av-HRR), peak of heat release rate (pk-HRR) and average of effective heat of combustion (av-EHC) are summarized in table 4.

Table 4

Combustion parameters of the EP composites obtained from cone calorimeter test

Sample code	TTI (s)	pk-HRR (kW/m^2)	av-HRR (kW/m^2)	av-EHC (MJ/kg)
EP/DDS	49	1067	328	28
EP/DDS/BDM	50	763	230	30.7
EP/DDS/DOPO	38	536	265	22.7
EP/DDS/BDM/DOPO-5	42	331	154	25.2
EP/DDS/BDM/DOPO-10	39	634	142	25.4
EP/DDS/BDM/DOPO-15	40	491	158	18.4
EP/DDS/BDM/DOPO-20	37	484	195	25.3

As shown in table 4, the TTI of EP/DDS/BDM was similar to that of neat EP/DDS whereas those of DOPO-containing thermosets were shortened to some extent. According to the above discussion on TGA, DOPO groups decomposed in advance and induced the degradation of EP matrix, which weakened the resistance to ignition. Therefore, the TTIs of the DOPO-containing thermosets decreased. Of course, the degradation of DOPO-containing thermosets ahead of time contributed to charring earlier during combustion. The char layer hindered the heat and oxygen from reaching the inner resin matrix, and thus promoted the flame-retarded properties.

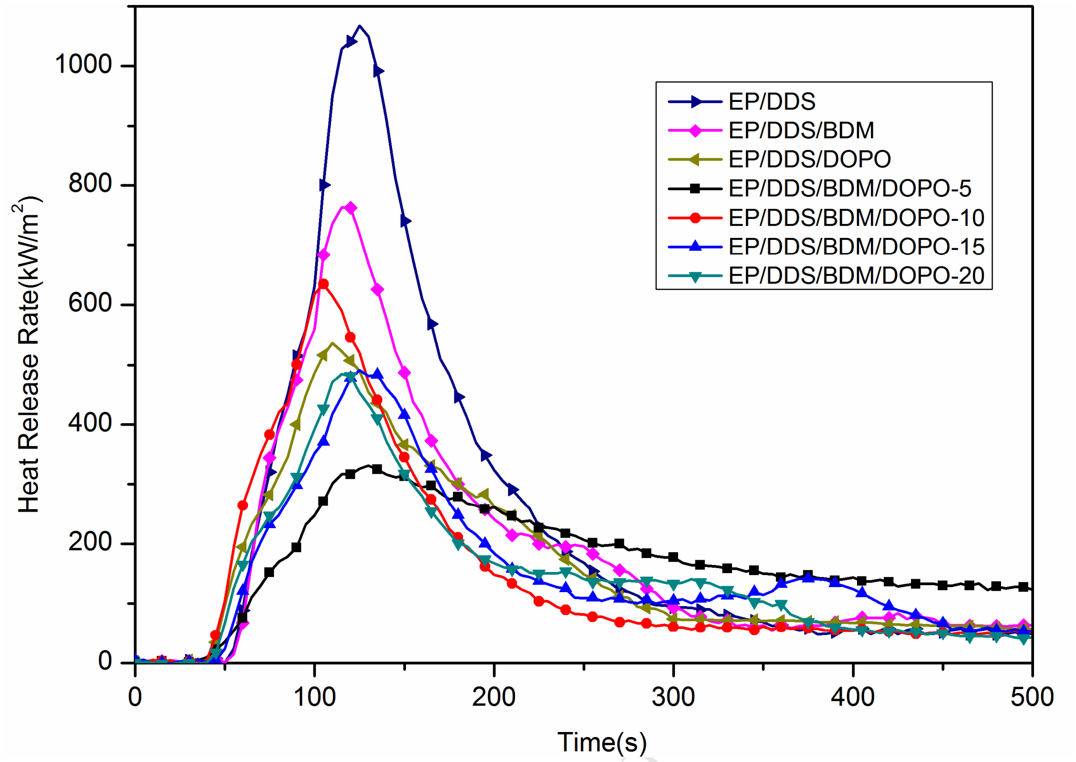

Fig. 5. HRR curves of cured epoxy resins

The curves of heat release rate (HRR) are shown in fig. 5. As presented in fig. 5, the neat EP/DDS burned rapidly after ignition and HRR reached a sharp peak with a peak heat release rate (pk-HRR) of 1067 kW/m^2. With the addition of BDM and/or DOPO, the av-HRR and pk-HRR of the modified EP composites decreased sharply. Notably, the av-HRR of the EP composites with both DOPO and BDM were significantly lower than that of EP composites with DOPO or BDM, which indicated the synergistic effect of DOPO and BDM on the decrease of HRR. The synergistic effect of DOPO and BDM on char formation as mentioned in the previous TGA analysis was one reason for the further decreased HRR.

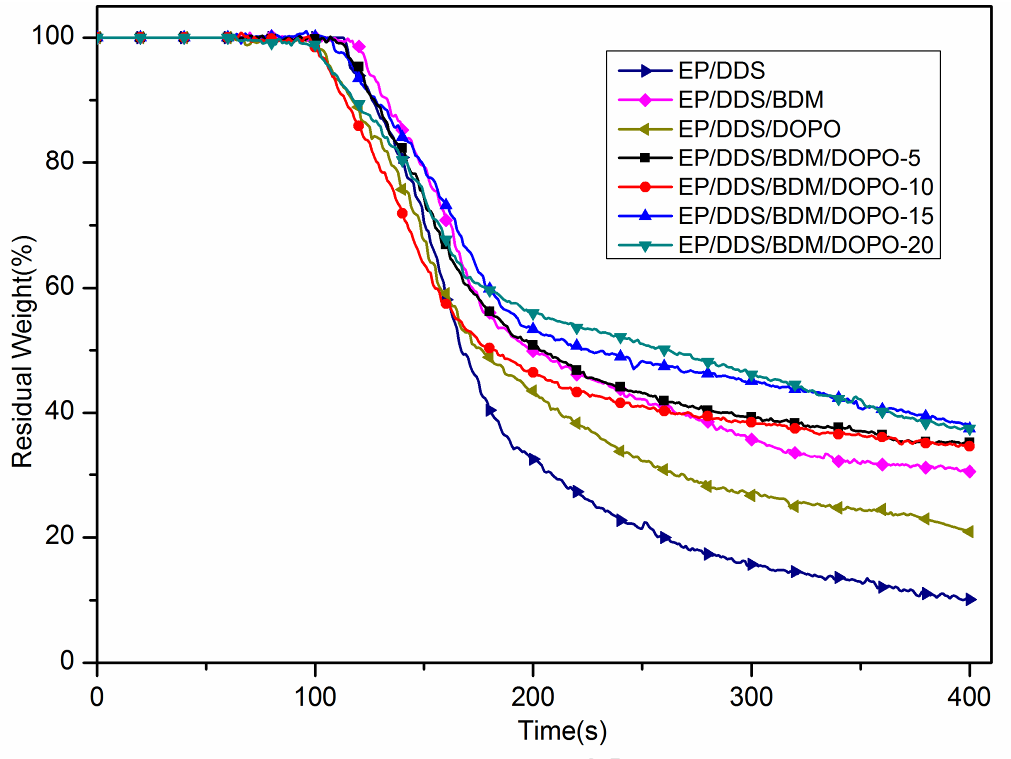

Fig. 6. Mass loss curves of cured epoxy resins from cone calorimeter test

The enhanced flame-retardant properties of the EP/DDS/BDM/DOPO thermosets were further explained by average of effective heat of combustion (av-EHC) accompany with the mass loss curves of EP composites obtained from cone calorimeter test (fig. 6). Av-EHC, which is the ratio of average of heat release rate (av-HRR) to the average mass loss rate from the cone calorimetry test, discloses the burning rate of volatile gases in gaseous-phase flame during combustion. As shown in table 4, EP/DDS/BDM had the highest av-EHC among all the samples, suggesting that the flame retardant effect of BDM mainly functioned in the condensed-phase through charring, which was consistent with the mass loss curves and TGA results, since the char yields after TGA and cone calorimetry tests were both higher than that of EP/DDS. With the introduction of DOPO, the char yield of EP/DDS/DOPO was higher than that of EP/DDS, which indicated the condensed-phase flame-retardant effect of DOPO. In addition, av-EHC of EP/DDS/DOPO was decreased to 22.7 MJ/kg, indicating that DOPO also worked in the gaseous-phase through flame-retardant quenching effect. As shown in fig. 6 and table 4, EP/DDS/BDM/DOPO-5, EP/DDS/BDM/DOPO-10 and EP/DDS/BDM/DOPO-20 had the similar av-EHC (about 25 MJ/kg) and char yields at 400s (about 36%), indicating that their flame-retardant effect in condensed-phase and gaseous-phase might be parallel, and thereby resulted in the similar flame-retarded properties. This was in accordance with the LOI and UL94 tests since they had the similar LOI value (33-34%) and UL94 rating (V-0 or V-1). Interestingly, EP/DDS/BDM/DOPO-15 had the lowest av-EHC of 18.4 MJ/kg compared with those of EP/DDS/DOPO and EP/DDS/BDM, suggesting that there was a synergistic flame-retardant effect of BDM and DOPO in the gaseous-phase. Moreover, the char yield at 400s was the highest, indicating that BDM and DOPO synergistically functioned in the condensed-phase, which was consistent with the TGA results. The synergistic effect of BDM and DOPO worked in the gaseous-phase and condensed-phase simultaneously imparted the best flame-retardant performance to the EP/DDS/BDM/DOPO-15 thermoset. It is evident that there is an optimal ratio of BDM and DOPO in the EP composites, which can maximize the flame-retardant effect in the gaseous-phase and condensed-phase at the same time.

3.5. Analysis of the char residues

The FTIR spectra of the char residues of the cured epoxy resins after cone calorimeter test are shown in fig. 7. The absorbance peaks of EP/DDS at 1594 and 1510 cm^{-1} indicated the formation of polyaromatic carbons [33], which were observed in other spectra curves as well. For the EP/DDS/BDM, except the peaks at 1594 and 1510 cm^{-1}, new absorbance peaks of C=O at 1766 and 1709 cm^{-1}and C-N at 1372 cm^{-1} as clearly recorded gave direct evidence of the abundance of maleimide structure in the char residue, which suggested that most of the maleimide groups was carbonized during combustion. For the EP/DDS/DOPO, the new absorbance peak at 753cm^{-1} indicated the existence of P-O-C in the char residue [31], which further proved the flame-retarded effect of DOPO in condensed-phase. Apparently, all the absorbance peaks of C=O, C-N and P-O-C could be observed in the char residue of EP/DDS/BDM/DOPO-15. The coexistence of phosphate ester compounds and maleimide structures in the char residue endowed EP/DDS/BDM/DOPO-15 with the best flammability property.

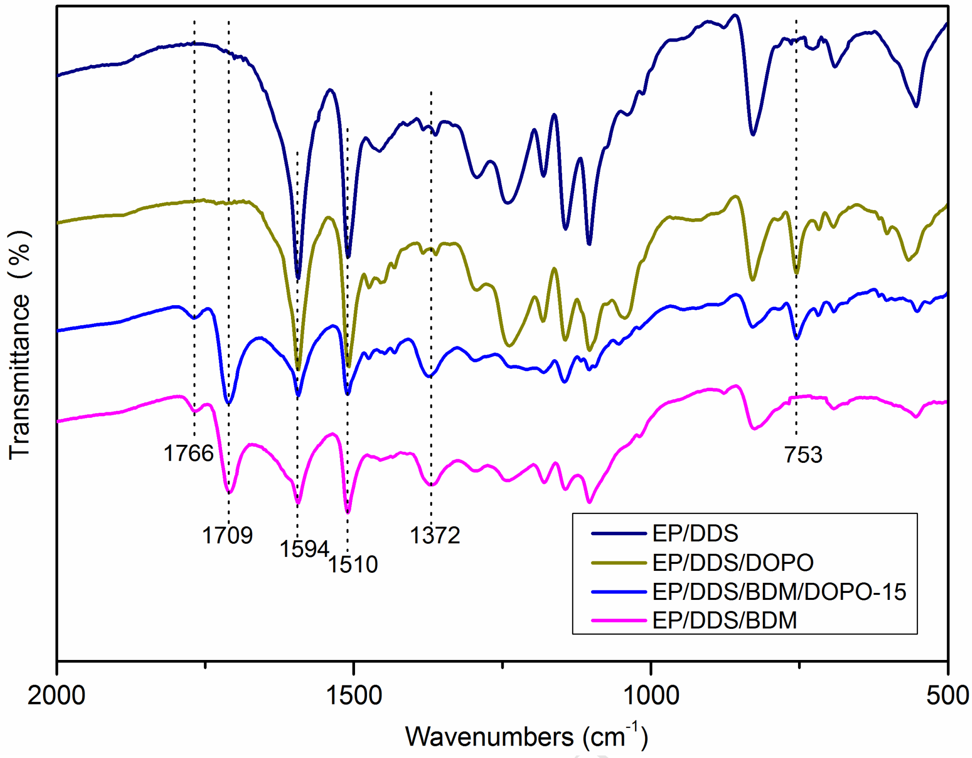

Fig. 7. The FTIR spectra of the char residues after cone calorimeter test

Morphological study of the char residues were conducted by visual observation and SEM. The SEM and digital images of the char residues after cone calorimeter test are shown in fig. 8. As shown in fig. 8, the char of EP/DDS showed a small amount of residual with a fragmentary structure whereas those of EP/DDS/DOPO, EP/DDS/BDM and EP/DDS/BDM/DOPO-15 with higher char yields exhibited intumescent structures. Moreover, EP/DDS/BDM and EP/DDS/BDM/DOPO-15 had a highly crosslinked and rigid char layer, which was visually stronger than that of EP/DDS/DOPO. This crosslinked and rigid char layer was due to the charring of maleimide groups.

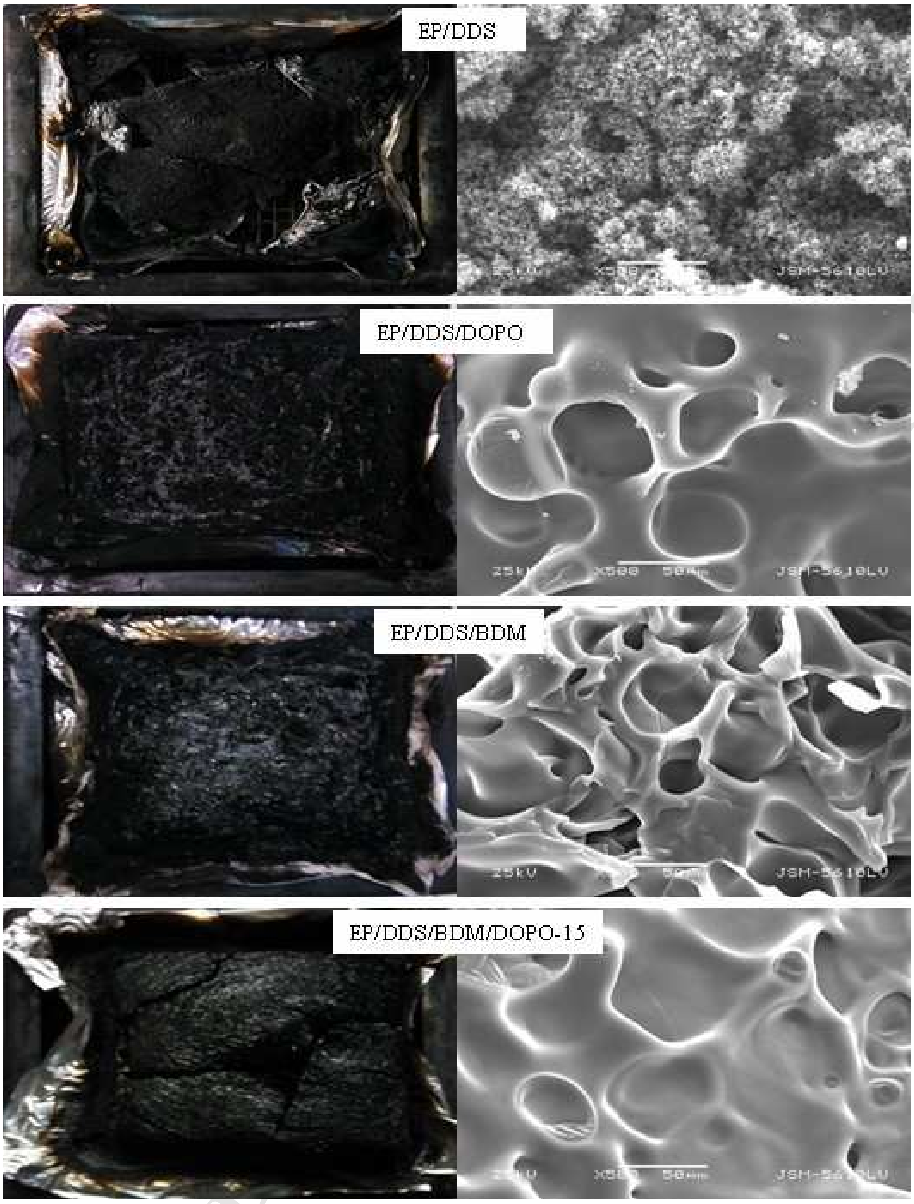

Fig. 8. The SEM and digital images of the char residues after cone calorimeter test

The char residues were further investigated by SEM. As shown in fig. 8, the char of EP/DDS exhibited a fluffy and flocculent structure which was unable to serve as a protective layer. The char of EP/DDS/BDM showed a lacunary and rigid-skeletal structure, which was due to the charring of maleimide groups and exhaustive combustion of EP matrix. This is consistent with the visual observation. In addition, the char layer of EP/DDS/BDM/DOPO-15 was more continuous and compact than that of EP/DDS/DOPO.

From the above FTIR and morphological studies of the char residues, the synergistic flame-retardant mechanism of DOPO and BDM in condensed-phase can be summarized as follows. Firstly, the phosphaphenanthrene groups, which were linked with maleimide groups, decomposed at lower temperature to form phosphorus-containing organic compounds which induced the decomposition of EP matrix in advance to form phosphorus-rich thick char. Secondly, most of the maleimide groups in the cured epoxy resins, which were rigid and thermal stable, would not degrade until charring and finally became the char source and highly crosslinked char skeleton; in addition, the phosphate compounds could promote the charring effect of maleimide groups, further increasing the char source and crosslinking density of the char skeleton. Finally, the phosphate compounds functioned as a bridge to link the carbonized EP matrix with the rigid char skeleton formed by the charring of maleimide groups. The strong char skeleton could provide sufficient support to prevent the char layer from collapsing and the carbonized EP matrix could attach to the char skeleton to form a continuous structure. A compact, strong and continuous char layer led to the promoted flammability property.

4. Conclusions

A novel reactive flame-retarded epoxy resin system was prepared by copolymerizing DGEBA with DOPO, BDM and DDS. Research on the curing behavior of the multicomponent system revealed that phosphaphenanthrene and maleimide groups were integrated into one molecule which functioned as reactive flame retardant in epoxy resins. The thermal and flame retardant properties of the thermosets were investigated. The results indicated that the EP composites containing multiple flame-retardant functional groups exhibited excellent flame retardancy as well as good thermal stability. EP/DDS/BDM/DOPO-15 system, loaded with 16.85 wt.% BDM and 1.21 wt.% phosphorus, had the highest LOI value (38.8%), UL94 rate (V-0) and glass transition temperature (223°C). In addition, the pk-HRR, av-HRR and av-EHC of the EP/DDS/BDM/DOPO-15 system were lower than those of the control samples. An obvious synergistic effect between DOPO and BDM was observed, which could be explained as follows. The maileimide groups were carbonized to provide char source and highly crosslinked char skeleton; on the other hand, the phosphaphenanthrene groups broke down to form phosphorus-containing organic compounds which induced the decomposition of EP matrix to form phosphorus-rich thick char; the phosphate compounds functioned as a bridge to link the carbonized EP matrix with the rigid char skeleton formed by the charring of maleimide groups. A compact, strong and continuous char layer led to the promoted flammability property.

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