



Highly effective flame retarded epoxy resin cured by DOPO-based co-curing agent



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ABSTRACT

A highly effective 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO)-based flame retardant (D-bp) was successfully synthesized via the addition reaction between DOPO and Schiff-base obtained in advance by the condensation of 4,4'-diaminodiphenyl methane (DDM) and 4-hydroxybenzaldehyde. D-bp was used as co-curing agent to improve the flame retardancy of DDM/diglycidyl ether of bisphenol A (DGEBA) system. Non-isothermal curing kinetics, thermal and flame-retardant properties of cured epoxy resins were studied by differential scanning calorimeter (DSC), thermogravimetric analysis (TGA), UL94 vertical burning test, limited oxygen index (LOI) and cone calorimeter test. The morphology of residues after cone calorimeter test was observed by scanning electron microscope (SEM). The results revealed that the epoxy thermosets exhibited excellent flame-retardancy and passed V-0 rating of UL 94 test with LOI of 39.7% when the phosphorus content was only 0.5 wt%.

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1. Introduction

Epoxy resin, one of the most important industrial materials, displays the characteristics of good chemical and corrosion resistance, high tensile strength and modulus, excellent dimensional stability and superior electrical properties, and has been widely used as the polymeric matrix of advanced composites, especially in semiconductor encapsulation applications [1–3]. Unfortunately, due to the flammability of epoxy resin, the utilization in some fields that require high flame resistance is limited [4].

Traditionally, halogen compounds are useful for improving the flame retardancy of epoxy resin [5–7]. However, the employment of bromine or chlorine-containing compounds would produce poisonous and corrosive smoke during combustion. Therefore, the development of halogen-free flame-retarded epoxy resin has become an extremely important subject [8–10]. In recent years, organophosphorous compounds have exhibited remarkable results in environment-friendly flame retarded epoxy resin [11–16].

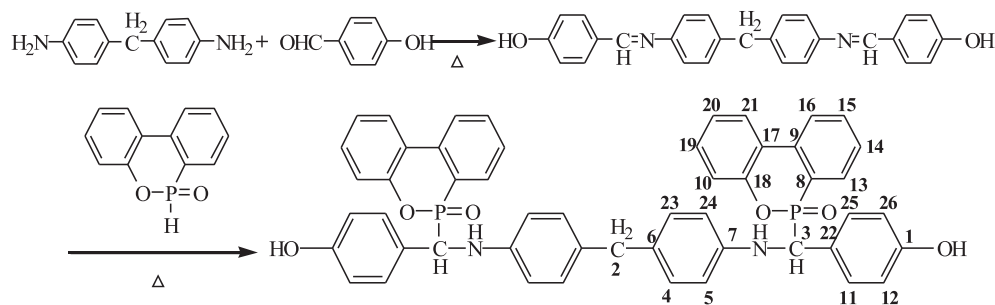
However, in order to achieve an excellent flame retardancy, the high addition amount of phosphorus element needs to be introduced, which consequently brings negative effects on the other properties of cured epoxy resins [17,18]. In addition, from the commercial point of view, the decrement in addition amount of flame retardants is beneficial to the reduction of cost. It is still worth challenging that the load of flame retardant reduces as low as possible in the cured epoxy resins via the improvement in flame-retardation efficiency.

Some studies indicated that the utilization of other flame-retardant elements, such as nitrogen, silicon, etc., would give a significant enhancement in the flame-retardation efficiency of phosphorus-based compound through the synergistic flame retardation effect [19–21]. 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) exhibited great potential to construct such synergism by utilizing the high reactivity of P–H bond [22–24]. Triazine [25], Schiff-base [26] or hexachlorocyclotriphosphazene [27,28] structures have attached into DOPO molecule to produce phosphorus-nitrogen synergism in the flame retardation of epoxy resin. It was found that the addition product between DOPO and Schiff-base presented a considerable enhancement in flame-retardation efficiency for epoxy resin [26,29–31]. Gu et al. [29] synthesized two novel DOPO-containing Schiff-base, which performed excellent flame retardancy with

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Scheme 1. Synthesis of D-bp.

Table 1
Formulations of the flame-retarded epoxy resins.

Sample	DGEBA (g)	DDM (g)	D-bp (g)	P (wt%)	N (wt%)
EP-0	100	25.3	0	0	2.85
EP-0.25	100	24.3	4.4	0.25	2.78
EP-0.5	100	23.2	8.9	0.5	2.70
EP-1	100	20.8	18.9	1	2.55

Table 2
Exothermic peak temperatures of D-bp/DDM/DGEBA cured at varying heating rates.

Heating rate (°C/min)	EP-0 (°C)	EP-0.25 (°C)	EP-0.5 (°C)	EP-1 (°C)
5	147.1	136.4	127.4	120.3
10	164.5	153.5	143.6	137.5
15	175.6	164.0	153.9	148.5
20	183.6	172.7	163.6	155.3

0.73 wt% phosphorus content. However, T_g of the cured epoxy resin decreased significantly from 160.3 °C to 141 °C. What's more, the structure of flame retardant contained methoxy group, which brought the negative effect to the flame-retardation efficiency. In order to achieve a breakthrough in flame retardancy, it is necessary to design the structure of DOPO-containing Schiff-base compounds.

In this paper, a highly effective DOPO-containing Schiff-base flame retardant (D-bp) was successfully synthesized by a simple one-pot method and used as co-curing agent to improve the flame retardancy of DDM/DGEBA system. The cured epoxy resins exhibited superior flame retardancy, which may attributed to the phosphorus-nitrogen synergistic flame retardation effect and well-

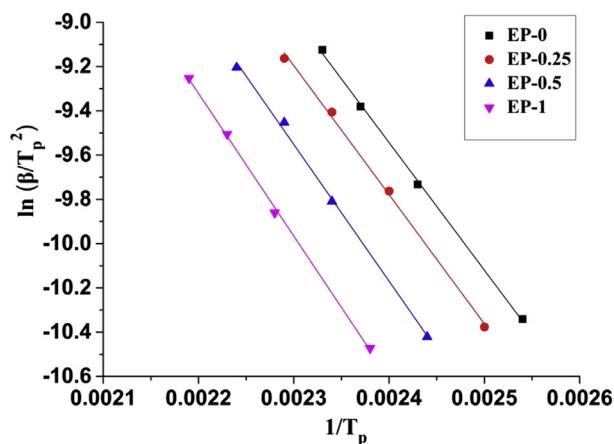


Fig. 1. The linear plot of $\ln(\beta/T_p^2)$ versus $1/T_p$ of D-bp/DDM/DGEBA according to Kissinger's method.

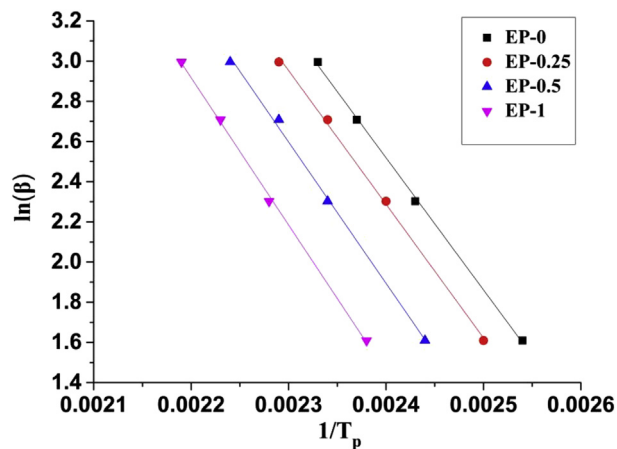


Fig. 2. The linear plot of $\ln(\beta)$ versus $1/T_p$ of D-bp/DDM/DGEBA according to Ozawa's method.

Table 3
Apparent activation energy of D-bp/DDM/DGEBA.

Sample	E_a^k (kJ/mol)	R^2	E_a^o (kJ/mol)	R^2
EP-0	53.6	0.999	60.9	0.999
EP-0.25	51.3	0.996	58.4	0.999
EP-0.5	48.5	0.997	55.3	0.999
EP-1	47.9	0.998	54.6	0.999

E_a^k : Calculated by Kissinger's method.

E_a^o : Calculated by Ozawa's method.

maintained crosslink density of the thermoset by introducing D-bp.

2. Experimental

2.1. Materials

9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and diglycidyl ether of bisphenol A (DGEBA, epoxide value of 0.51 mol/100 g) were purchased from Eutec Trading (Shanghai) Co., Ltd and Momentive Specialty Chemicals Inc., respectively. 4,4'-Diaminodiphenyl methane (DDM) and 4-hydroxybenzaldehyde

Table 4
Thermal properties data of cured epoxy resins at different contents of D-bp.

Sample	T_g (°C)	$T_d 5\%$ (°C)	$T_d max$ (°C)	Residues (%)
EP-0	161.1	368.0	386.7	15.7
EP-0.25	158.4	353.6	382.9	21.6
EP-0.5	157.9	336.5	381.1	26.9
EP-1	155.9	332.2	370.9	27.9

were obtained from Aladdin Chemistry (Shanghai) Co., Ltd. 1,4-Dioxane and ethanol were purchased from Guangzhou Chemical Reagent Factory and used without further purification.

2.2. Synthesis of D-bp

DDM (1.98 g, 0.01 mol), 4-hydroxybenzaldehyde (2.44 g, 0.02 mol) and 40 mL 1,4-dioxane were introduced into a 250 mL three-necked round-bottomed glass flask equipped with a stirrer and a nitrogen inlet. The reaction mixture was stirred at 55 °C for 2 h. Then, 20 mL 1,4-dioxane solution containing DOPO (4.32 g, 0.02 mol) was added into the system. Afterwards, the mixture was stirred at 55 °C for another 12 h (Scheme 1). After being cooled down to room temperature, the mixture was poured into ice water. The precipitate was filtered and washed two times with ethanol. The light yellow powder was obtained after vacuum-drying at 70 °C for 24 h. The yield was 92.4% [26,29–35].

D-bp: m.p. (DSC): 157.0 °C. MS m/z: calcd. for $C_{51}H_{40}N_2O_6P_2$: 838.24, anal., 839.24($M+1^+$), 861.24($M + Na^+$). Elemental analysis values: C, 72.44; H, 4.89; N, 3.33; O, 11.88. Calculated values: C, 73.03; H, 4.77; N, 3.34; O, 11.46; P, 7.40.

FT-IR (KBr, cm^{-1}): 3281 (–OH), 2902 (C–H), 1594, 1476 (P–Ph), 1274 (C–N), 1236 (P=O), 925 (P–O–Ph).

1H NMR (DMSO- d_6 , ppm): $\delta = 3.39$ – 3.44 (–CH $_2$ –), 4.83–4.88(NH), 5.27–5.31(NH'), 5.97–6.01(–CH–), 6.38–6.42(–CH–'), 6.38–6.42(H_4 , $H_{4'}$), 6.47–6.50(H_{23} , $H_{23'}$), 6.52–6.55(H_5 , $H_{5'}$), 6.61–6.63(H_{24} , $H_{24'}$), 6.64–6.66(H_{12} , $H_{12'}$), 6.68–6.70(H_{26} , $H_{26'}$), 7.01–7.03(H_{11} , $H_{11'}$), 7.13–7.15(H_{25} , $H_{25'}$), 7.18–7.19(H_{20} , $H_{20'}$), 7.28–7.32(H_{10} , $H_{10'}$), 7.38–7.44(H_{19} , $H_{19'}$), 7.51–7.53(H_{15} , $H_{15'}$), 7.66–7.70(H_{16} , $H_{16'}$), 7.72–7.74(H_{14} , $H_{14'}$), 7.96–7.99(H_{21} , $H_{21'}$), 8.15–8.17(H_{13} , $H_{13'}$), 9.36–9.39(–OH).

^{13}C NMR (DMSO- d_6 , ppm): $\delta = 157.3$ – 157.4 (C_1), 55.8–56.5(C_2), 54.5–55.2(C_3), 114.2(C_4), 115.3(C_5), 149.4(C_6), 145.4(C_7), 120.4–120.7(C_8), 122.1–122.3(C_9), 123.5–123.8(C_{10}), 124.2–124.3(C_{11}), 124.4–124.5(C_{12}), 126.0–126.3(C_{13}), 125.0–125.2(C_{14}), 125.3–125.5(C_{15}), 129.1(C_{16}), 128.6–128.9(C_{17}), 135.6–135.8(C_{18}), 133.7–134.1(C_{19}), 130.0–130.2(C_{20}), 131.0–131.3(C_{21}), 130.1, 132.2(C_{22}). ^{31}P NMR (DMSO- d_6 , ppm): $\delta = 28.60$, 31.36.

2.3. Preparation of flame-retarded epoxy resins

Flame-retarded epoxy resins were prepared via thermal curing reactions among DDM, D-bp and DGEBA. The stoichiometric formulations for D-bp/DDM/DGEBA system at different phosphorus

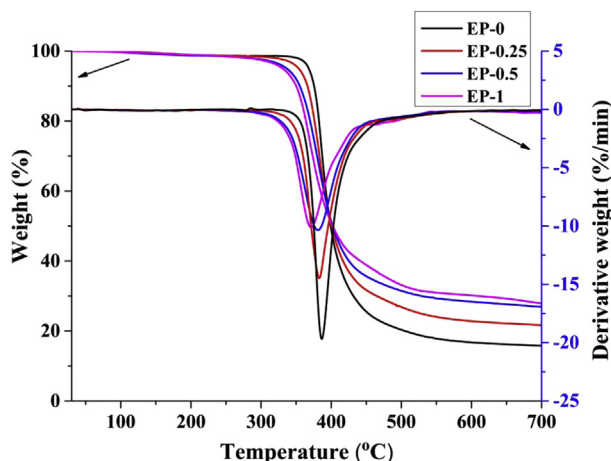


Fig. 3. TGA and DTG curves of cured epoxy resins at different contents of D-bp.

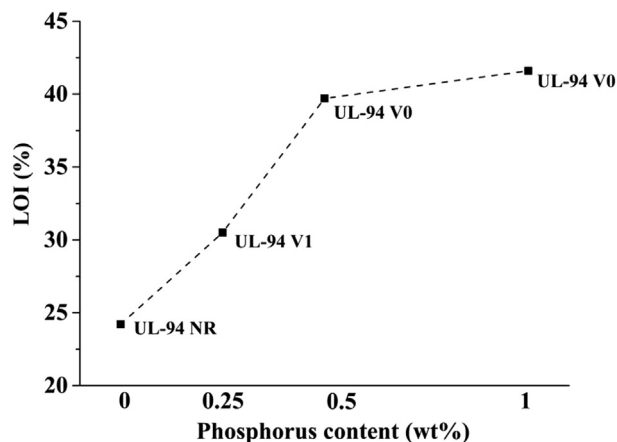


Fig. 4. LOI and UL-94 rating of cured epoxy resins at different phosphorus content.

content are listed in Table 1, where the sum amount of amino and phenol groups is equal to the epoxy groups. Firstly, DGEBA and D-bp were mixed and stirred at 140 °C for 10 min. Then, the homogeneous liquid was cooled down to 90 °C and blended with DDM. After becoming transparent, all samples were vacuum-degassed in a mold and sequentially cured for 1 h at 80 °C, 1 h at 100 °C, 1 h at 120 °C, 3 h at 150 °C and 2 h at 180 °C, respectively.

2.4. Characterization

Fourier transform infrared (FT-IR) spectra were recorded by Netzsch 870 FT-IR spectrophotometer with KBr pellet. 1H , ^{13}C and ^{31}P nuclear magnetic resonance (NMR) spectra were obtained from Bruker DRX 600 spectrometer by using DMSO- d_6 as solvent. Mass spectrometry (MS) was conducted using a Bruker maX is impact mass spectrometer. Elemental analysis was carried out on an Elementar Vario EL cube elemental analyzer.

DSC analysis was performed on a Netzsch DSC 200F3. Glass transition temperature (T_g) was determined from 30 °C to 200 °C at a heating rate of 10 °C/min under nitrogen atmosphere. The non-isothermal curing kinetics was investigated from 30 °C to 250 °C at varying heating rates (5, 10, 15 and 20 °C/min) under nitrogen atmosphere. TGA was carried out on a Netzsch 2209F1 thermogravimetric analyzer from 30 °C to 700 °C at a heating rate of 10 °C/min under nitrogen atmosphere.

LOI measurement was conducted on an oxygen index instrument (Fire Testing Technology Co., Ltd, UK) with the sheet dimension of $150 \times 6.5 \times 3.2$ mm 3 according to ASTM D2863-97. Vertical burning test was carried out on a UL 94 flammability meter (Fire Testing Technology Co. Ltd., UK) with the sheet dimension of $130 \times 13 \times 3.2$ mm 3 according to ANSL UL 94–1985. Cone calorimeter test was carried out on a FTI cone calorimeter with the sheet dimension of $100 \times 100 \times 5$ mm 3 according to ISO5660 under an external heat flux of 35 kW/m 2 .

Dynamic mechanical analysis (DMA) was conducted on a Netzsch DMA242C analyzer from 30 °C to 225 °C at a heating rate of

Table 5
Cone calorimeter test results of cured epoxy resins.

Sample	TTI (s)	P-HRR (kW/m 2)	THR (MJ/m 2)	EHC (MJ/kg)
EP-0	53	939.2	227.4	31.6
EP-0.25	48	757.1	154.1	29.0
EP-0.5	47	633.9	145.2	23.6
EP-1	39	535.1	121.9	20.5

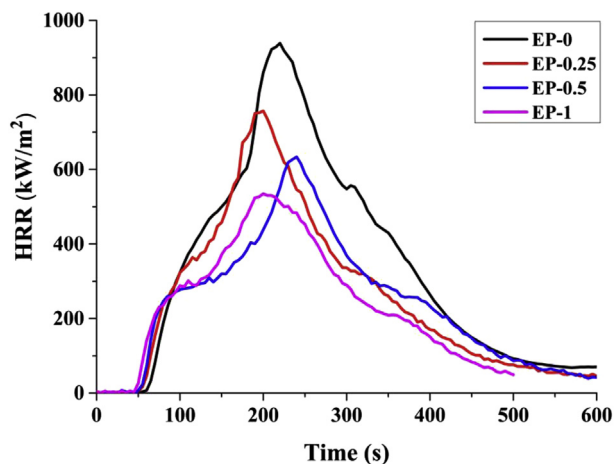


Fig. 5. Heat release rates of cured epoxy resins.

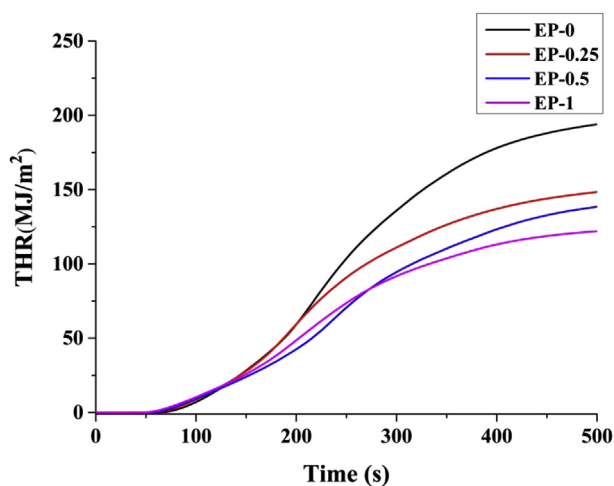


Fig. 6. Total heat release of cured epoxy resins.

3 °C/min and a frequency of 10 Hz under three-point bending mode.

The morphology of residues collected after cone calorimeter test was observed by a Nova Nano SEM430 scanning electron microscope with an accelerating potential of 20 kV.

3. Results and discussion

3.1. Curing behaviors and kinetics of D-bp/DDM/DGEBA

The non-isothermal curing kinetics of D-bp/DDM/DGEBA system was studied by DSC. The Kissinger's method and Ozawa's method were used to obtain the apparent activation energy during the curing process. Kissinger's method is expressed by Eq. 1 [36–39]:

$$\ln\left(\beta/T_p^2\right) = \ln(AR/E_a) - E_a/RT_p \quad (1)$$

where E_a is the apparent activation energy, R is the ideal gas constant, β is the heating rate, A is the pre-exponential factor and T_p is the exothermic peak temperature.

The exothermic peak temperatures of D-bp/DDM/DGEBA cured at various heating rates (5, 10, 15 and 20 °C/min) under nitrogen

atmosphere are summarized in Table 2. Accordingly, a linear plot of $\ln(\beta/T_p^2)$ versus $1/T_p$ is obtained (Fig. 1).

Ozawa's method is expressed by Eq. 2 [36,40]:

$$\ln \beta = -1.052(E_a/RT_p) + \ln(AE_a/R) - \ln F(\alpha) - 5.331 \quad (2)$$

The obtained linear plot of $\ln(\beta)$ versus $1/T_p$ is illustrated in Fig. 2.

The apparent activation energy of D-bp/DDM/DGEBA system, which is obtained from the slope of the corresponding straight line according to those two methods, is listed in Table 3. The utilization of D-bp can lower the activation energy of the system and accelerate the crosslinking reaction. This effect is proportional to the D-bp content and is possibly resulted from the reactivity of hydroxyl and secondary amino of D-bp. Based on the bimolecular reaction mechanism [41,42], the hydrogen atom of the hydroxyl and secondary amino group may act as the proton donor and form hydrogen bonds with the oxygen atom of epoxy group, increasing the polarization of epoxide ring, which is beneficial for the ring-opening reaction.

3.2. Thermal properties of D-bp/DDM/DGEBA

T_g is a major parameter for thermosetting resins. T_g s of D-bp/DDM/DGEBA were determined by DSC and the result is summarized in Table 4. Compared with the EP-0, T_g s of flame-retarded epoxy resins decrease slightly following the increase of D-bp content. It has been reported that the introduction of phosphorus-containing group would significantly reduce the crosslink densities of cured epoxy resins, thus decreasing T_g of the resins [26]. On the other hand, the rigidity of D-bp structure with high content of aromatic group may inhibit the mobility of macromolecular chains and constrain the thermal movement of polymer backbone [33]. Based on these two competing factors, the glass transition temperature of cured epoxy resins is well maintained despite of the introduction of small amount of D-bp.

Fig. 3 shows TGA and differential thermal gravity (DTG) curves of D-bp/DDM/DGEBA under nitrogen atmosphere. The related data of the temperature at 5% weight loss ($T_d 5\%$), the temperature at maximum decomposition rate ($T_d max$) and the residual mass at 700 °C (Residues) obtained from the curves are summarized in Table 4. It can be observed that there is only one sharp weight loss peak of the phosphorus-nitrogen containing epoxy, which is consistent with the previous report [10]. $T_d 5\%$ and $T_d max$ of D-bp/DDM/DGEBA decrease gradually with the increase of the D-bp content, nonetheless the $T_d 5\%$ values are all still above 300 °C. Moreover, it is noteworthy that the residual mass of D-bp/DDM/DGEBA is comparatively higher than 15.7% of EP-0 sample. The reasonable explanation is attributed to the fact that the O=P=O bond is less stable than the C–C bond [26,30]. The early degradation of phosphorus-containing group produces phosphate and polyphosphate in a relatively lower temperature, which prevent the further decomposition of the epoxy matrix and lead to a higher residual mass [21]. The charred layer accumulates on the surface of the material and acts as a protective barrier to inhibit the flame and heat transfer of the underlying substance, endowing a significant enhancement in the flame retardancy.

3.3. Flame retardancy of D-bp/DDM/DGEBA

Fig. 4 shows the UL-94 rating and LOI of D-bp/DDM/DGEBA. It can be observed that the introduction of D-bp into the system endows the cured epoxy with excellent flame retardancy. V-0 rating in UL-94 classification is successfully attained, as shown in EP-0.5 and EP-1. The LOI value of neat sample without D-bp is only

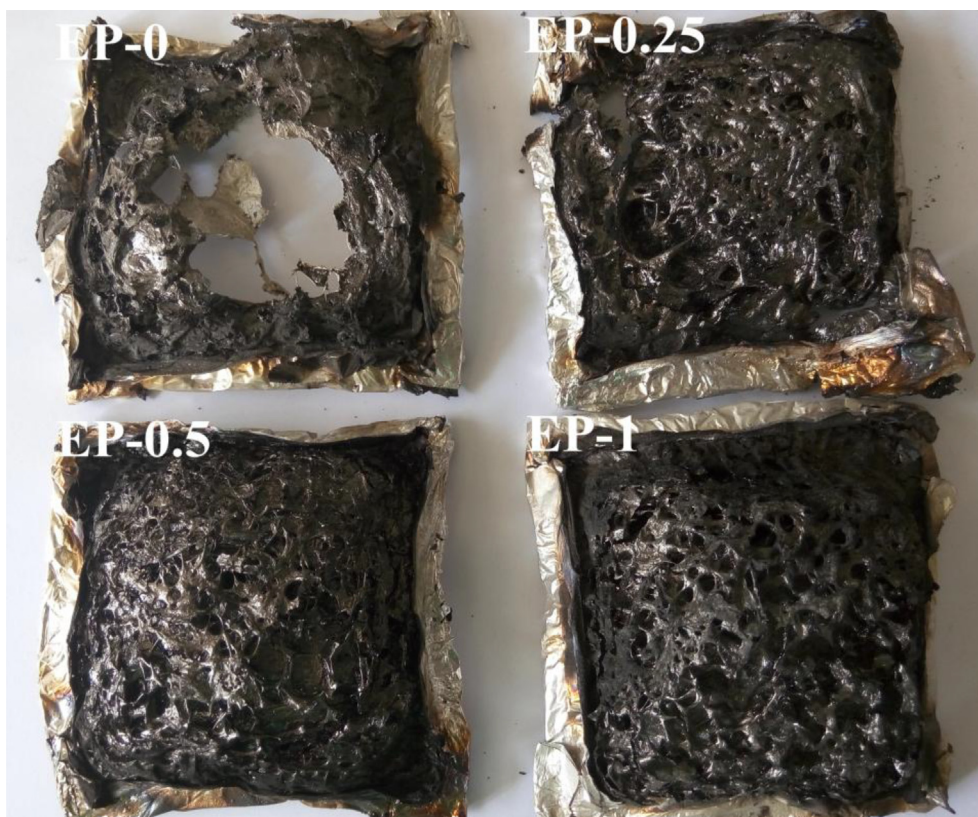


Fig. 7. Digital photos of the residues after cone calorimeter test.

24.2%, it raises drastically following the increase of D-bp content and further reaches 39.7% when the phosphorus content was only 0.5 wt%. The results are monitored by the content of phosphorus element and the synergistic effect between phosphorus and nitrogen elements. Phosphorus element plays a leading role for the flame-retardation due to $\text{PO}\cdot$ released from phosphorus-containing species during combustion, which exhibits the flame retardancy through the quenching mechanism of active radicals in gaseous phase. Besides, the degradation of phosphorus-containing group also produces phosphate and polyphosphate structure in the condensed phase, which promotes the configuration of dense carbon layer to prevent the heat transfer [8,25]. The presence of nitrogen element generates a lot of nitrogen gases to dilute the concentration of oxygen necessary for maintaining the combustion [21]. Therefore, the highly efficient flame retardancy can be obtained from the combination of these two major impacts.

Cone calorimeter test provide a useful method for studying the fire behavior of flame-retarded epoxy materials. The collected data, including time to ignition (*TTI*), peak of heat release rate (*P-HRR*), total heat release (*THR*) and effective heat of combustion (*EHC*), are listed in Table 5. It can be observed that *P-HRR* and *THR* of flame-retarded epoxy resins decrease significantly along with the increase of phosphorus content (Fig. 5 and Fig. 6). Besides, the gradual decrement of *EHC* is also observed. These three parameters confirm the amelioration in the flame retardancy of cured epoxy resins after the utilization of D-bp. The evident reduction in *TTI* value of flame-retarded epoxy resins occurs by reason of the early decomposition of unstable phosphorus-containing group of D-bp which promotes the disintegration of epoxy matrix in a relatively lower temperature [25]. As previously discussed in the section 3.2, D-bp catalyzes the formation of stable carbon layer structure earlier during combustion and brings better flame retardancy for the epoxy resins [18,28].

3.4. Morphology analysis of D-bp/DDM/DGEBA

3.4.1. Digital images

Generally, the char layer structure after combustion can deliver some important information which reflects the flammability characteristics of polymer materials. Digital photos of the residues after cone calorimeter test are shown in Fig. 7. It is obvious to see that EP-0 is depleted after combustion. However, accompanied by the introduction of D-bp, as shown in EP-0.25, EP-0.5 and EP-1, the structure of char layers becomes dense and distinctly intumescent charred. The above phenomenon suggests that D-bp can catalyze the formation of a compact char layer, which prevents the further decomposition of the epoxy matrix.

3.4.2. SEM photographs

Fig. 8 shows the morphology of D-bp/DDM/DGEBA residues after cone calorimeter test. As revealed, the residue of EP-0 displays a badly broken carbon layer structure and numerous open holes, verifying the failure to prevent the flame and heat transfer. The residue of EP-0.25 becomes denser and the holes are reduced, compared with that of EP-0. Moreover, the residues of EP-0.5 and EP-1 exhibit a thick and compact char layer, which surface is covered with the decomposition product of phosphorus-containing group. The formation of strong char layer may inhibit the transmission of heat during combustion, so that the cured epoxy resins would obtain an excellent flame retardancy.

3.4.3. FT-IR spectra

Fig. 9 shows the FT-IR spectra of the char layer structure for EP-0 and EP-0.5 after cone calorimeter test. It can be observed that the broad stretching vibration of N–H and O–H bonds is around 3443 cm^{-1} , which is attributed to the pyrolysis products of the

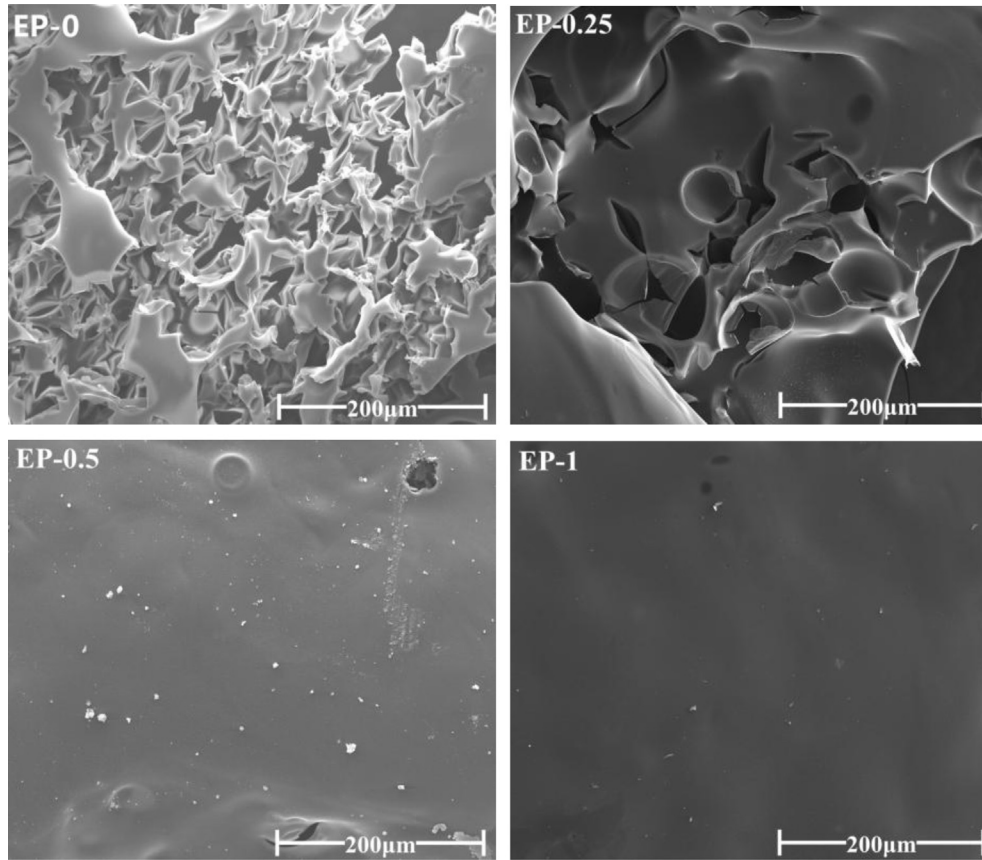


Fig. 8. SEM photographs of cured epoxy resins at different contents of D-bp (scale bar size: 200 μm).

hydroxy compounds and the ammonium compounds. Besides, the absorption peaks at 2354 and 1646 cm^{-1} are ascribed to the carbonized networks. It is worth noting that a broad absorption of P–O–P bond can be discerned at around 1102 cm^{-1} , suggesting that the char layer structure contains the phosphorus-containing compounds. The appearance of P–O–P structure is considered as a testimony, indicating that D-bp catalyzes the formation of carbon layer during the combustion and results in a dense and complex-structured char [43].

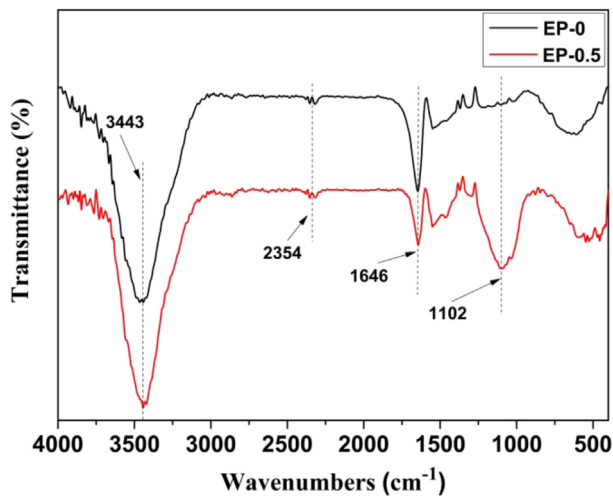


Fig. 9. FT-IR spectra of the char layer for the samples of EP-0 and EP-0.5.

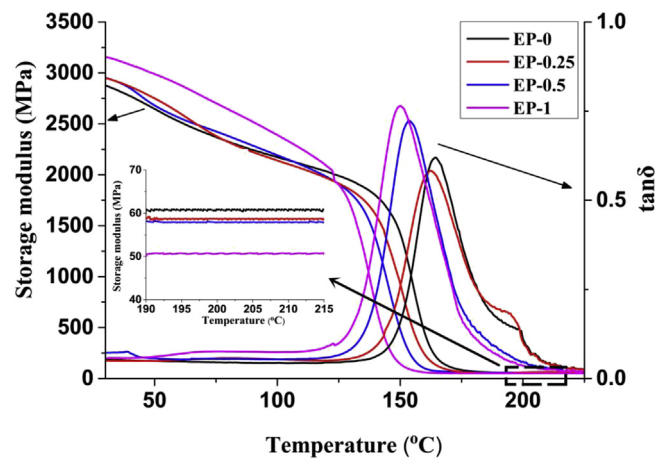


Fig. 10. Storage modulus and $\tan\delta$ of cured epoxy resins.

Table 6
Calculation results of ν_e according the DMA data.

Sample	E' (MPa)	T_g (°C)	ν_e (mol/m ³)
EP-0	60.1	164.5	4992
EP-0.25	58.7	162.4	4897
EP-0.5	57.9	157.5	4880
EP-1	50.8	150.1	4349

3.5. Dynamic mechanical analysis of D-bp/DDM/DGEBA

Fig. 10 exhibits the storage modulus (E') and loss tangent ($\tan\delta$) curves of D-bp/DDM/DGEBA. E' and the crosslink density (ν_e) can be described using the theory of rubber elasticity and follow the Eq. 3 [44,45]:

$$\nu_e = E'/3RT \quad (3)$$

where E' is the storage modulus at $T_g + 45$ °C in the rubbery plateau, R is the ideal gas constant, T is the thermodynamic temperature at $T_g + 45$ °C and T_g is obtained from the peak temperature of $\tan\delta$ in this section.

The calculation results of ν_e according to the above formulation are listed in Table 6. Clearly, the result indicates that the phosphorus loading in low content, as shown in EP-0.25 and EP-0.5, gives no significant impact on the ν_e . According to the literature, maintaining ν_e at the high extent is beneficial for improving the flame retardancy of polymeric thermoset [46]. In correlation with the discussion in the previous section, the flame retardancy of cured epoxy resin depends on many factors, which include the phosphorus content, synergistic effect of flame retardant elements and crosslink density. Therefore, despite the low content of phosphorus element, the cured epoxy resin still performs remarkable flame retardancy owing to the well-maintained crosslink density, as shown in EP-0.25 and EP-0.5. As for the EP-1 sample, since the crosslink density decreases evidently, the high flame retardancy is primarily induced by the high phosphorus content.

4. Conclusion

Incorporation of phosphorus–nitrogen containing co-curing agent D-bp lowers the apparent curing activation energy of DDM/DGEBA system. Probably owing to the combined effect of phosphorus–nitrogen synergistic flame retardation and well-maintained crosslink density, the modified epoxy thermoset exhibits excellent flame retardancy at the low phosphorus content, in which the V-0 grade of UL94 classification with LOI of 39.7% is achieved when the phosphorus content is only 0.5 wt%. Besides, T_g of the flame retarded epoxy thermoset remains relatively constant. Hence, D-bp is expected to be used as the highly effective halogen-free flame retardant for the application of epoxy resins as electronic materials.

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