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Performance Comparison of Flame Retardant Epoxy Resins Modified by DPO–PHE and DOPO–PHE

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Abstract: Two phosphorus-containing flame retardants, (bis(4-hydroxyphenyl)methyl)diphenyl phosphine oxide (DPO–PHE) and 1-(bis(4-hydroxyphenyl)methyl)-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO–PHE) were synthesized and characterized. The two target compounds both were used as a flame retardant and a co-curing agent of 4,4'-diaminodiphenylsulfone of bisphenol A diglycidyl ether to prepare flame-retardant epoxy resins (EP/DPO–PHE and EP/DOPO–PHE). The thermal and flame-retardant properties of the thermosets were investigated by thermogravimetric analysis (TGA), limited oxygen index (LOI) measurement, and UL-94 vertical burning testing (UL-94). The results indicated that both flame retardants can improve the flame retardancy of epoxy thermosets. TGA results indicated that the char yields of EP/DPO–PHE–P-0.9 and EP/DOPO–PHE–P-0.9 thermosets were increased from 19.1% of EP/P-0 to 25.3% and 27.8%, respectively. Compared with that of EP/P-0, the LOI of the EP/DPO–PHE–P-0.5 thermoset increased from 23.7% to 30.1%, and the sample reached UL-94 V-0. Meanwhile, the LOI of the EP/DOPO–PHE–P-0.7 thermoset increased from 23.7% to 28.9%, and the sample reached UL-94 V-0. Cone calorimetry test, scanning electron microscopy of burning residues, and pyrolysis–gas chromatography/mass spectrometry indicated that both flame retardants mainly act through the gas–phase mechanism. In addition, no condensed-phase activity of DPO–PHE was observed, whereas the condensed-phase activity of DOPO–PHE was negligible. Immersion experiments showed that the water absorption activity of flame retardant epoxy resins fluctuates. Compared with DOPO–PHE, DPO–PHE was more effective as a higher flame-retardant and exhibited better characteristics for improving the T_g, thermal stability, and water absorption of modified resins.

Keywords: Epoxy resin, Flame retardant, diphenylphosphine oxide, DOPO, Curing agent

1. Introduction

Among various organophosphorus flame retardants, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) is a commercialized product. It is mainly used as a halogen-free flame retardant for epoxy resins, particularly in electronics (printed wiring boards and semiconductor encapsulation) and transportation (automotive, high speed trains, and aircraft) requiring high flame-retardant property [1–5].

Although epoxy resins modified using DOPO can meet flame-retardant requirements, several problems have yet to be addressed [6–19]. The value of T_g is decreased [14–16], water absorptivity is high, and the decomposition temperature is decreased [6,8,17–19]. These changes can be attributed to the pre-reaction application of DOPO in which the functionality of the epoxy resin is decreased and finally affects the property of cured epoxy resin [20–21]. Owing to the special chemical structure, the introduction of the DOPO skeleton into epoxy resin may also significantly affect thermal stability and water absorptivity [20–24].

One widely known method to overcome these problems is the use of DOPO-based multifunctional flame retardants. Thus, a number of DOPO derivatives combined with -OH, -NH_2, or -NH- active groups were designed and synthesized [25–31]. These compounds can act as a flame retardant and a curing agent during the curing process of epoxy resins and confer enhanced flame-retardant property, larger T_g values, and higher thermal stability on epoxy resins [30,32–34].

Dai et al. reported on a DOPO derivative combined with -OH and -NH- groups. The limited oxygen index (LOI) of the cured resins increased from 24.5% to 33.5%, but the $T_{5\%}$ of thermosets decreased from 347 °C to 314 °C [35]. Lin et al. synthesized a trihydroxygen DOPO derivative referred to as DOPOtriol [36]. The flame retardancy of modified epoxy resin increased with phosphorus content. A UL-94 V-0 grade was achieved with a phosphorus content of 1.87 wt%. Meanwhile, the T_g value of the cured resins increased from 138 °C to 159 °C as the phosphorus content increased from 0 wt% to 2.4 wt%. However, rosolic acid, the raw material of DOPOtriol, is difficult to obtain in the industry. Xiong et al. prepared two DOPO derivatives, P–Ph and P–DDS–Ph, which were used as flame retardant curing agents for *o*-cresol novolac epoxy resin [5]. The flame-retardant epoxy resin showed increased T_g. However, the LOI of epoxy resins modified using P–DDS–Ph (with phosphorus content of 3.0 wt%) was 27%, and that of epoxy resins cured with P–Ph (with phosphorus content of 3.6 wt%) was 26%. Although DOPO derivatives can generally be used as flame retardants, the properties of modified epoxy resins still need to be improved. Thus, more studies still need to be conducted to identify efficient flame retardants for epoxy resins.

Schartel et al. studied the char forming mechanism and fire behavior of phosphorus flame retardants for epoxy resins with different oxidation state and reported on the structure–property relationships of some specially designed flame retardants [37–38]. These fundamental studies clearly showed that the chemical structure of the flame retardants, thermal decomposition temperature range of both the flame retardants and the resins, and oxidation state of the phosphorus together influence the performance of phosphorus-based flame-retardant epoxy resins.

We have recently focused on the synthesis and application of DOPO and diphenyl phosphine oxide (DPO) derivatives [39–42]. Two compounds, 1-(bis(4-hydroxyphenyl)methyl)-9,10-dihydro-9-oxa-10-phosphaphenan-threne-10-oxide (DOPO–PHE) and (bis(4-hydroxyphenyl) methyl) diphenylphosphine oxide (DPO–PHE) have drawn interest. Lin et al. synthesized DOPO–PHE, which was used to prepare poly(ether sulfone)s; however, no application in epoxy resin has been reported [43]. In a patent, Yasushi et al indicated that DPO–PHE could be used as a flame retardant for epoxy resins but reported no information on its further application

[44]. Two phenyl hydroxy groups are present in both DOPO–PHE and DPO–PHE (**Fig. 1**), and either can be used as a reactive flame-retardant curing agent for epoxy resin [45]. Notably, these two compounds vary from the DOPO and DPO groups with respect to structure. The higher phosphorus content in DPO–PHE used as a flame retardant can lead to reduced dosage. Moreover, the distinct skeletons of DOPO and DPO may lead to different performances in flame retardant epoxy resins.

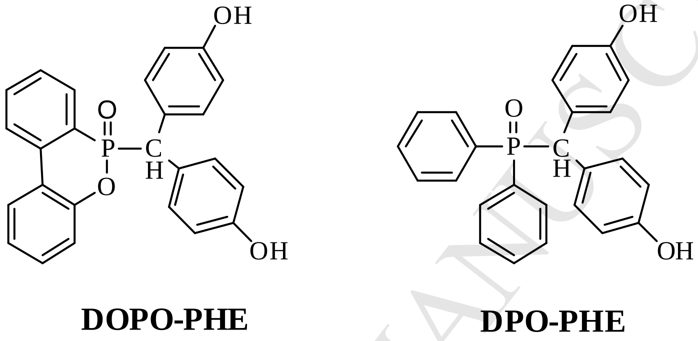


Fig. 1 Structures of DOPO–PHE and DPO–PHE

In this study, flame-retardant epoxy resins were prepared by curing diglycidyl ether of bisphenol-A (DGEBA) with 4,4'-diaminodiphenylsulfone (DDS). During the process, DOPO–PHE and DPO–PHE were used as co-curing agents. The thermal and flame-retardant properties of the epoxy resins were investigated by thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), LOI, UL-94 vertical burning, and cone calorimetry testing (CCT). The water absorptivity of the epoxy resins was investigated using immersion experiments. To explore the flame retardancy mechanism, flame-retardant epoxy thermosets were studied by pyrolysis–gas chromatography–mass spectrometry (Py–GC/MS), and residues after CCT were investigated by scanning electron microscopy (SEM).

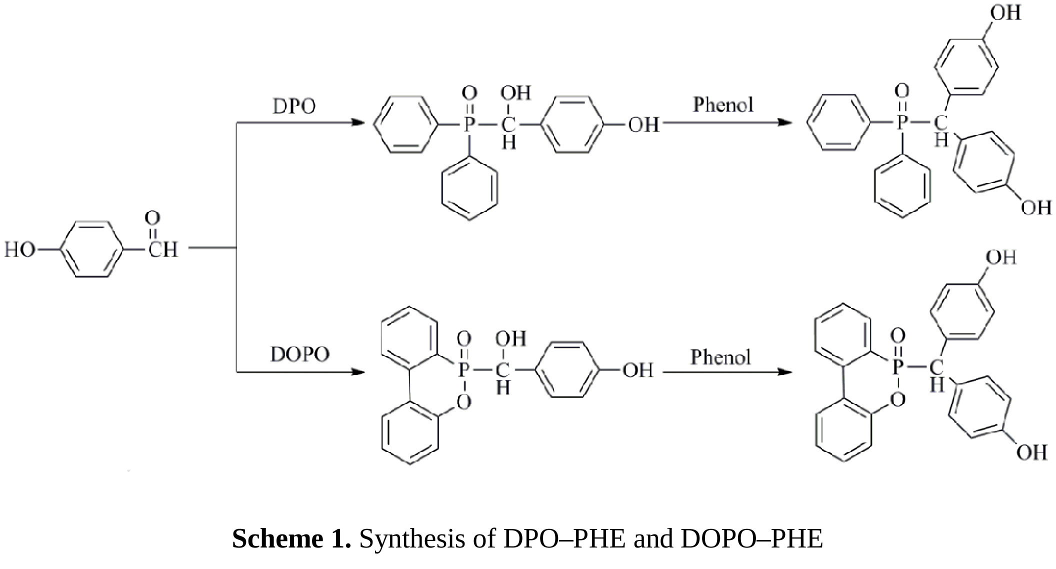
2. Experimental

2.1. Materials

DGEBA (E-44) was purchased from Zhenjiang Danbao Resin Co., Ltd. (Jiangsu, China). DP) and DOPO were supplied by Qingdao Fusilin Chemical Science and Technology Co., Ltd. (Qingdao, China). 4,4'-Diaminodiphenylsulfone (DDS), 4-hydroxybenzaldehyde, *p*-toluenesulfonic acid (*p*-TSA), phenol, dichloroethane, ethyl acetate, and dichloromethane were purchased from Aladdin Industrial Corporation (Shanghai, China). All chemicals were used as received.

2.2. Synthesis of flame retardants

DPO–PHE and DOPO–PHE were synthesized in accordance with the literature [43] by using a two-step reaction as shown in **Scheme 1**.



Scheme 1. Synthesis of DPO–PHE and DOPO–PHE

Step 1: DPO (0.3 mol, 60.66 g), 4-hydroxybenzaldehyde (0.31 mol, 37.88 g), and dichloroethane (150 mL) were added into a round glass flask (250 mL) equipped with a mechanical stirrer, reflux condenser, and thermometer. The mixture was stirred at 80 °C for 7 h. The precipitate was then filtered, washed with ethyl acetate, and dried at 70 °C. About 83.57 g of intermediate (white powder, 85.9% yield) was obtained.

Step 2: The aforementioned intermediate (0.3 mol, 120.12 g) and dichloroethane (200 mL) were added into a round glass flask (500 mL) equipped with a mechanical stirrer, reflux condenser, and thermometer. The temperature was increased to 80 °C. Phenol (0.31 mol, 29.17 g) and *p*-TSA (4.80 g, 4 wt% relative to intermediate) were then added and stirred for 13 h. The precipitate was filtered, washed with dichloromethane, and dried at 70 °C. About 111.7 g of DPO–PHE (pink powder, 93% yield) was obtained (m.p. 300 °C).

By replacing DPO with DOPO, DOPO–PHE (75.4% total yield) was synthesized using the same method.

2.3. Preparation of epoxy thermosets

Epoxy thermosets were prepared via thermal curing of DGEBA with DDS, and DPO–PHE (or DOPO–PHE) was used as a co-curing agent to prepare flame-retardant epoxy thermosets. For the thermosets modified using DPO–PHE (or DOPO–PHE), the amounts of reactive hydrogen in DPO–PHE (or DOPO–PHE) and DDS were equal to the amount of epoxy groups in DGEBA. The corresponding formulations of epoxy thermosets are listed in **Table 1**.

The preparation process of the thermoset modified using DPO–PHE (or DOPO–PHE) was as follows: DGEBA and DPO–PHE (or DOPO–PHE) were heated to 200 °C and stirred until DPO–PHE (or DOPO–PHE) was completely dissolved in DGEBA. DDS was then added into the mixture. After DDS was dissolved into DGEBA, the mixture was poured into preheated molds and cured at 120 °C for 2 h and then at 150 °C for 2 h. The obtained samples were labeled in accordance with the flame retardant and mass content of the P element in epoxy thermosets. For example, EP/DPO–PHE–P-0.3 indicates that the flame retardant was DPO–PHE, and the mass content of the P element in the thermosets was 0.3 wt%. The epoxy thermoset without flame retardants (EP/P-0) was also prepared following a similar procedure.

Table 1 Formulations of the epoxy resin thermosets.

Samples	DGEBA (g)	DDS (g)	DPO–PHE (g)	DOPO–PHE (g)	P (wt%)
EP/P-0	100	28.55	-	-	0
EP/DPO–PHE–P-0.3	100	26.97	5.12	-	0.3
EP/DPO–PHE–P-0.5	100	25.86	8.69	-	0.5
EP/DPO–PHE–P-0.7	100	24.71	12.40	-	0.7
EP/DPO–PHE–P-0.9	100	23.25	16.31	-	0.9
EP/DOPO–PHE–P-0.3	100	26.96	-	5.30	0.3
EP/DOPO–PHE–P-0.5	100	25.85	-	9.01	0.5
EP/DOPO–PHE–P-0.7	100	24.70	-	12.87	0.7
EP/DOPO–PHE–P-0.9	100	23.49	-	16.89	0.9

2.4. Characterization

FTIR spectroscopy was conducted using a Nicolet 380 (Thermo Fisher, United States) infrared spectrometer with a KBr pellet, and the wavenumber ranged from 4000 cm^{-1} to 500 cm^{-1}.

^1H and ^{31}P nuclear magnetic resonance (NMR) spectra were measured using a Bruker Avance III HD spectrometer (500 MHz, Bruker, Germany). The solvent used was dimethylsulfoxide-d_6.

Mass spectroscopy (MS) was conducted on an Agilent LC-MS 1100 instrument (Agilent, America). High-resolution MS data were recorded on a Thermo Fisher Scientific LTQ FT Ultra instrument.

Thermal gravimetric analysis (TGA) was conducted using a Mettler Toledo TGA/1600LF instrument (Mettler-Toledo, Switzerland) with a heating rate of 10 °C/min from 100 °C to 600 °C under a nitrogen flow of 50 mL/min. The epoxy resins of about 5–10 mg was measured in an alumina crucible.

DMA was performed on a Mettler Toledo DMA1 (Mettler-Toledo, Switzerland). The sample with dimensions of 35 mm × 6.5 mm × 3 mm (every sample was accurately measured before testing) was mounted on a double cantilever clip. The frequency was set to 1.0 Hz, and the samples were tested from 100 °C to 200 °C with a heating rate of 5 °C/min under air.

Pyrolysis–gas chromatography–mass spectrometry (Py–GC/MS) was conducted using PY-3030D/7890B-5977A (Agilent, United States). The sample weighed about 2.0 mg, the injector temperature was 250 °C, and the temperature of GC/MS interface was 280 °C, and the cracker temperature was 500 °C.

The LOIs were measured using a BG-5207 oxygen index meter (BinGo, China) in accordance with the ISO4589-1984 standard. All samples measured 130 mm × 6.5 mm × 3 mm. Vertical burning testing was conducted using a BG5210 instrument (BinGo, China) measuring 130 mm × 13 mm × 3 mm in accordance with the UL-94 test standard. The flammability of the samples was evaluated using a cone calorimeter (FTT, UK), and heat flux was set to 50 kW/m^2. The samples measured 100 mm × 100 mm × 3 mm.

A morphological study on char residues was conducted using a Nova Nano SEM450 scanning electron microscope (SEM) (FEI, America) at an acceleration voltage of 10 kV.

The water absorption property of the epoxy thermosets was measured and calculated as described in the literature [22]. To evaluate the relationship between water absorptivity and time, water absorptivity was measured at intervals of 4 h.

3. Results and Discussion

3.1. Synthesis and characterization of flame retardants

In the literature [43], DOPO–PHE was synthesized by the reaction of DOPO, 4-hydroxybenzaldehyde, and phenol by using a one-pot reaction at 130 °C. In the current study, the target compounds were synthesized using a two-step method, and the reaction temperature was kept considerably lower (80 °C). Total yield was increased, and the products were easily purified.

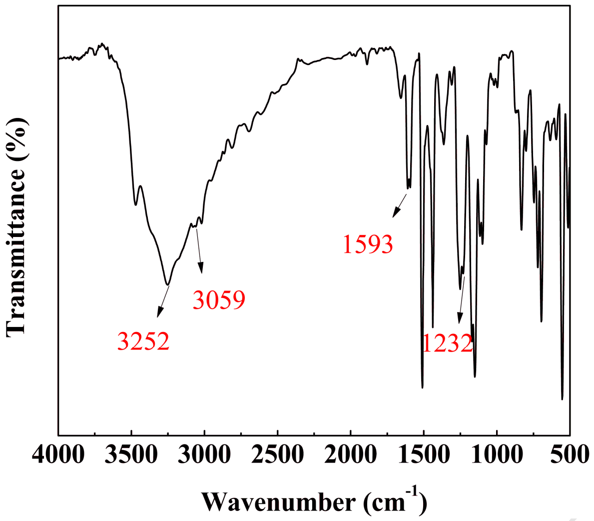


Fig. 2 FTIR spectrum of DPO–PHE

The chemical structure of DPO–PHE was characterized by FTIR, ^{1}H NMR, ^{31}P NMR, and MS. The results are depicted in **Figs. 2** and **3**. **Fig. 2** shows the FTIR spectra of DPO–PHE. In the spectrum of DPO-PHE, the peaks at 3252 cm^{-1} are ascribed to the vibration of -OH. The peaks at 3059 cm^{-1} are ascribed to the vibration of Ph-H, and the absorption peak of the Ph skeleton still exists at 1593 cm^{-1}. The vibration of -P=O presents its signal at 1232 cm^{-1}. As seen in the ^{1}H NMR spectrum (**Fig. 3(a)**), the signal at 9.1 ppm is ascribed to -OH, and the double peaks at 5.3 ppm are attributed to aliphatic hydrogen. In addition, the signals emitted by aromatic hydrogen are located at 6.5-7.8 ppm. The ^{31}P NMR spectrum of DPO–PHE is presented in **Fig. 3(b)**, and the ^{31}P NMR spectrum of DPO–PHE exhibits an intensive singlet resonance signal at 29.78 ppm. As shown in **Fig. 3(c)**, the *m/z* of DPO–PHE is 423.1121 [M+Na]$^+$. On the basis of the aforementioned analyses, DPO–PHE has been successfully synthesized.

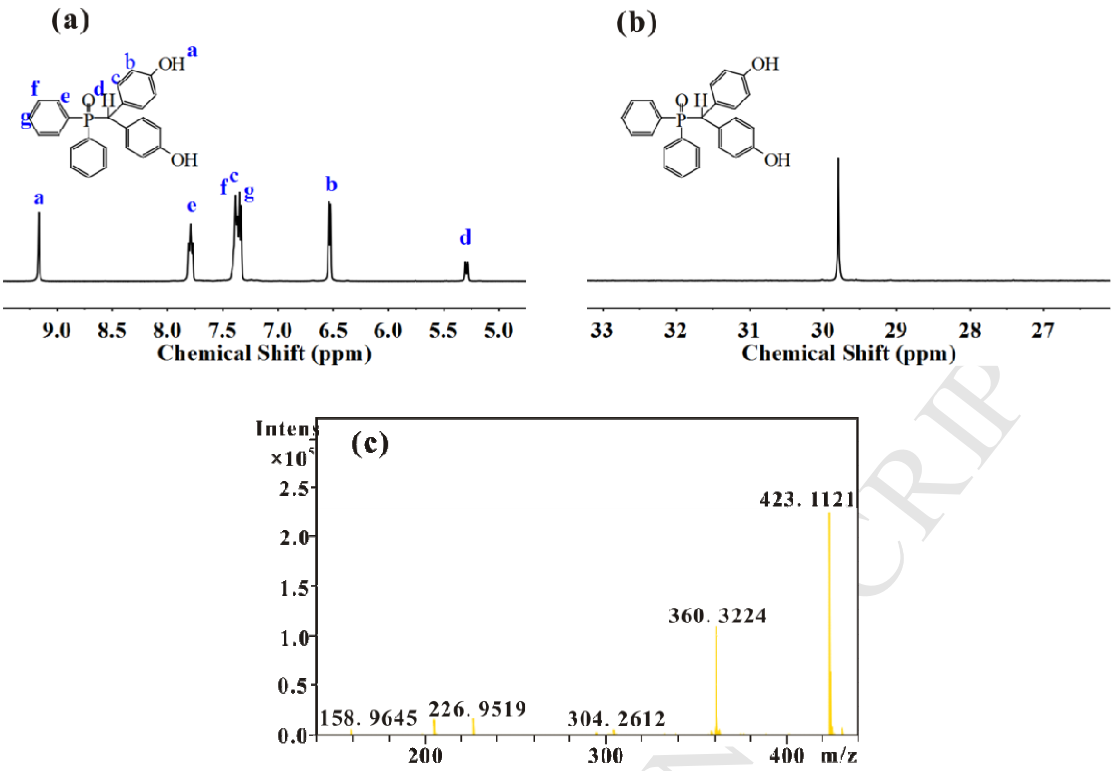


Fig. 3 ^{1}H NMR (a) and ^{31}P NMR (b) spectra of DPO–PHE in $(CD_3)_2SO$; MS spectrum (c) of DPO–PHE

The chemical structure of DOPO–PHE was characterized by ^{1}H NMR and MS. As shown in **Fig. 4(a)** the chemical shifts corresponding to the -OH group and aromatic protons of DOPO–PHE were observed at 9.36 ppm and 8.15–6.63 ppm, respectively. The MS spectrum of DOPO–PHE is shown in **Fig. 4(b)**, the *m/z* of DOPO–PHE is 415.1106 $[M+H]^+$. The ^{1}H NMR and MS spectra of DOPO–PHE were consistent with those reported in the literature [43].

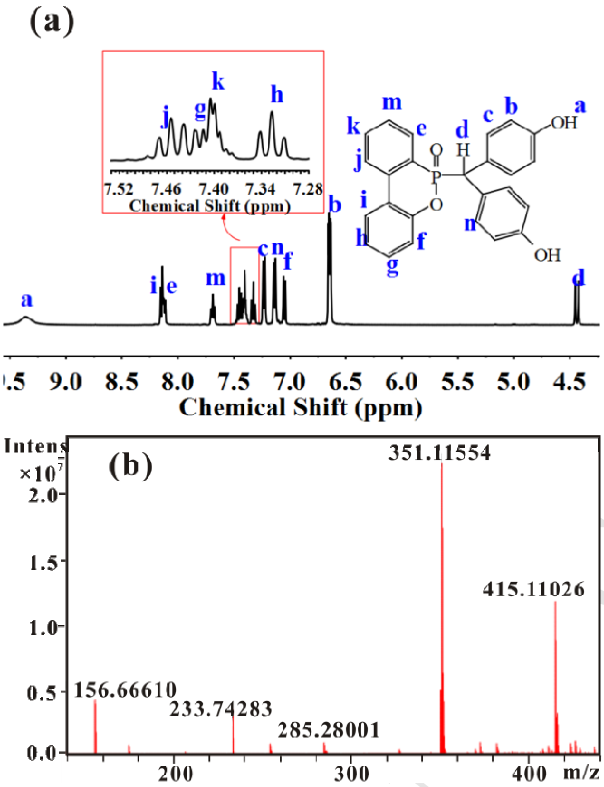


Fig. 4 ^{1}H NMR (a) spectra of DPO–PHE in $(CD_3)_2SO$; MS spectrum (b) of DOPO–PHE

3.2 Thermal stability of epoxy thermosets

The thermal stabilities of epoxy thermosets were evaluated by TGA. **Fig 5** presents the TG and DTG curves of the epoxy thermosets. The corresponding characteristic data are summarized in **Table 2,** which lists the 5 wt% mass loss temperature ($T_{5\%}$), 10 wt% mass loss temperature ($T_{10\%}$), temperature at the maximum mass loss rate (T_{max}), and char yield at 600 °C, among others.

Table 2 Thermal properties of the epoxy thermosets.

Samples	T_g[a] (°C) ±2.0	$T_{5\%}$ (°C) ±3.0	$T_{10\%}$ (°C) ±3.0	T_{max} (°C) ±3.0	Char yield at 600 °C (wt%) ±0.2
EP/P-0	144.0	388.3	395.5	415.9	19.1
EP/DPO–PHE–P-0.3	155.6	379.3.	391.3	413.2	21.5
EP/DPO–PHE–P-0.5	154.0	369.7	384.7	408.6	22.7
EP/DPO–PHE–P-0.7	151.6	366.3	379.7	404.2	24.8
EP/DPO–PHE–P-0.9	154.4	353.7	375.0	405.9	25.3
EP/DOPO–PHE–P-0.3	148.5	371.3	384.3	405.2	25.3
EP/DOPO–PHE–P-0.5	152.2	362.7	376.7	400.9	26.1
EP/DOPO–PHE–P-0.7	153.7	349.7	369.7	400.5	27.2
EP/DOPO–PHE–P-0.9	147.0	344.7	364.0	397.6	27.8

[a] The T_g value was obtained by DMA testing.

As shown in **Figs. 5(a)** and 5**(c)**, all thermosets showed a similar single decomposition process with a shoulder in the mass loss rate after main decomposition. The flame retardants of DPO–PHE and DOPO–PHE influenced the decomposition temperature of the DGEBA/DDS thermoset when each of them was used as a co-curing agent with DDS. All flame-retarded thermosets showed lower $T_{5\%}$, $T_{10\%}$, and T_{max} than those of EP/P-0. The influence increased with an increase in P content. In addition, given the same P content, thermosets modified using DPO–PHE exhibited higher thermal stability than those modified using DPO–PHE. The $T_{5\%}$, $T_{10\%}$, and T_{max} of the EP/DPO–PHE–P-0.5 thermoset were 18.6 °C, 10.8 °C, and 7.3 °C lower, respectively, than those of EP/P-0. Meanwhile, the $T_{5\%}$, $T_{10\%}$, and $T_{\max}$ of the EP/DOPO–PHE–P-0.5 thermosets were 25.6 °C, 18.8 °C, and 15.0 °C lower, respectively, than those of EP/P-0. With an increase in P content from 0.3 wt% to 0.9 wt%, the $T_{5\%}$ of the thermosets modified using DPO–PHE decreased from 379.3 °C to 353.7 °C, and the thermosets modified using DOPO–PHE decreased from 371.3 °C to 344.7 °C. With the same P content, the thermosets modified using DPO–PHE showed higher stability than that of the thermosets modified using DOPO–PHE. This occurrence could be attributed to the difference between the DPO and DOPO skeletons. In the DPO skeleton, the three P-C bonds were stable, whereas in the DOPO skeleton, the P-O-C bond was unstable [37,41].

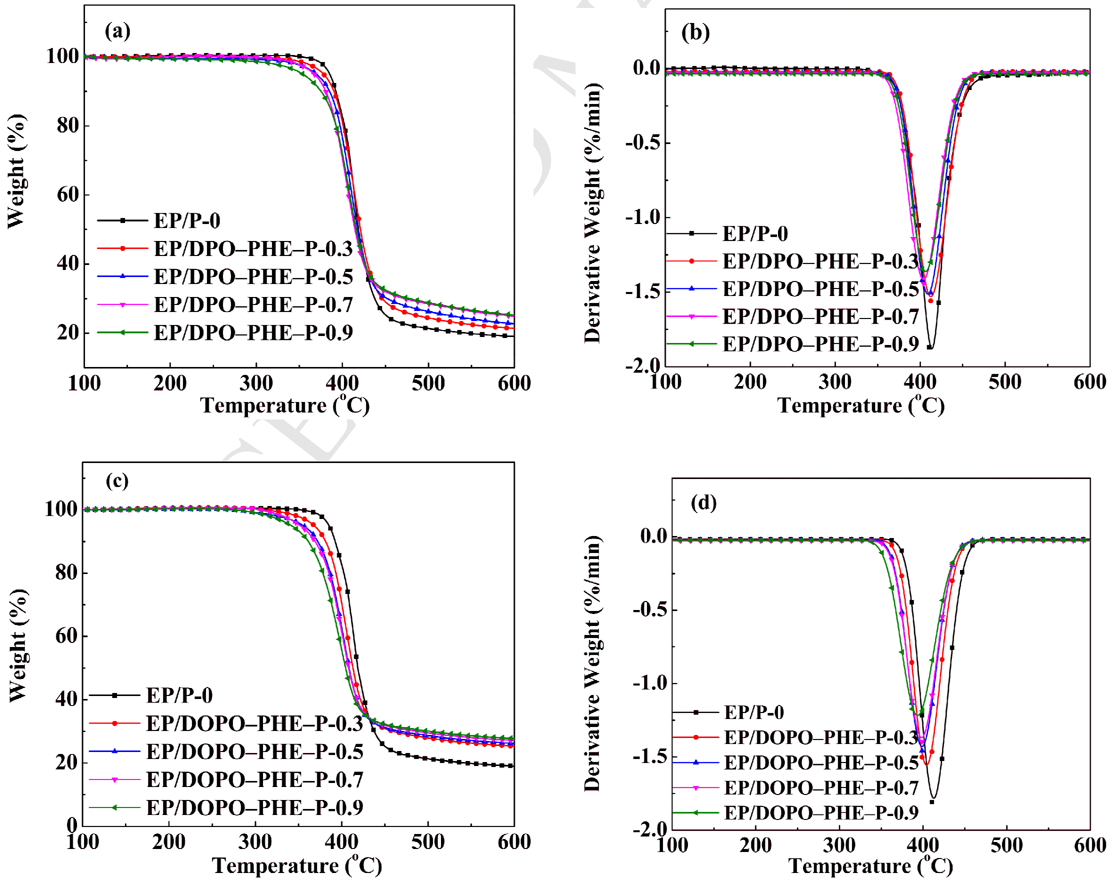


Fig. 5 TG (a, c) and DTG (b, d) curves of thermosets under nitrogen atmosphere; (a), (b) thermosets cured with DPO–PHE and DDS; (c), (d) thermosets cured with DOPO–PHE and DDS

The data in **Table 2** indicate that the introduction of the two phosphorus-containing flame retardants into the DGEBA/DDS thermosets led to an increase in char yield at 600 °C. The char yield of the EP/P-0 thermoset at 600 °C was 19.1 wt%, and those of the EP/DPO–PHE–P-0.3 and EP/DOPO–PHE–P-0.3 thermosets were 21.5 wt% and 25.3 wt%, respectively. However, the char yield of the flame-retardant epoxy thermosets increased slowly as the phosphorus content increased. This findings were consistent with the results reported in many studies [2,46–48]: the introduction of phosphorus into epoxy resins can improve the char yield and benefit the flame-retardant property. Notably, DPO–PHE and DOPO–PHE exerted different effects on the char yield of the corresponding thermosets. The thermosets modified using DOPO–PHE exhibited a slightly higher char yield than those of the thermosets modified using DPO–PHE if the phosphorus content was kept at the same level. The different char forming behaviors of the thermosets modified using DPO–PHE and DOPO–PHE could be attributed to the different structures of the two flame retardants. The DPO skeleton in DPO–PHE was attributed to phosphine oxide, which was characterized by high thermal stability and high water resistance because of the three P-C bonds in the structure [37,41,49]. Meanwhile, the DOPO skeleton in DOPO–PHE was determined by low thermal stability and poor water resistance, mainly caused by the P-O and C-O bonds in the heterocyclic structure [26,50–51]. According to the detailed study by Schartel et al. on the charring mechanism, the DOPO skeleton contains an additional P-O-C_{ar} bond in its heterocycle. This linkage is sensitive to hydrolysis, and the P-O-C_{ar} bond in DOPO breaks during thermal decomposition. The resulting P-OH can help form char in the condensed phase [38].

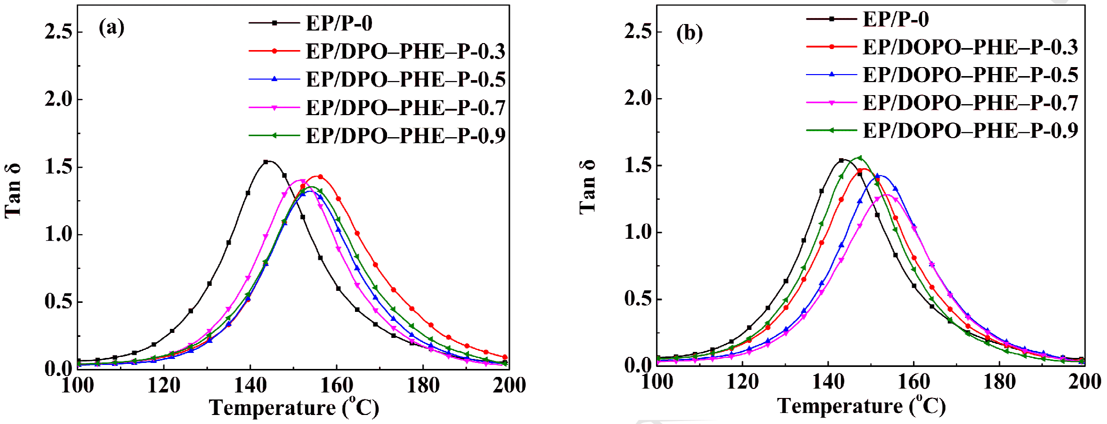


Fig. 6 DMA curves of thermosets in air atmosphere; (a) thermosets cured with DPO–PHE and DDS; (b) thermosets cured with DOPO–PHE and DDS

The T_g values of all thermosets were obtained by DMA in air atmosphere, with the temperature at maximum of tan δ at T_g [2,47,52–53]. The DMA curves of the thermosets modified using DPO–PHE and DOPO–PHE are presented in **Fig. 6**. All samples exhibited a single T_g, indicating homogeneous morphology of the epoxy systems [31,52]. **Table 2** shows that all flame-retardant thermosets have higher T_g values than those of the EP/P-0 thermoset. The T_g value of the EP/P-0 thermoset is 144.0 °C, and those of the thermosets modified using DPO–PHE and DOPO–PHE ranged from 147.0 °C to 155.6 °C. However, as P content increases from 0.3 wt% to 0.9 wt%, the T_g values of the thermosets modified using DPO–PHE are relatively stable despite the uncertainty of data. Meanwhile, the thermosets modified using DOPO–PHE exhibits fluctuant T_g with an increase in P content.

As concluded by a number of studies, the large steric effect of DOPO units may influence the curing reaction between curing agents and epoxy, which reduces the cross-linking density of epoxy thermosets [2,10], thereby decreasing T_g. Meanwhile, the bulky and rigid DOPO skeleton can inhibit the mobility of macromolecular chains and increase the T_g of epoxy resins [17,53]. Together, these two competing factors affect the T_g of the thermosets. Thus, the T_g values of the DOPO–PHE flame-retardant thermosets fluctuate as P content increases. Similarly, the two factors affect the T_g values of the thermosets modified using DPO–PHE. The DPO and DOPO skeletons vary, consequently exerts different effects on the two factors. Thus, the T_g values of the epoxy thermosets modified using the two flame retardants slightly vary.

3.3. Flame-retardant properties of epoxy thermosets

The flame-retardant properties of all epoxy thermosets were evaluated using LOI and UL-94 vertical burning tests. The results are summarized in **Table 3**.

The EP/P-0 sample exhibited an LOI of 23.7%, whereas all DPO–PHE or DOPO–PHE flame-retardant thermosets obtained higher LOI values. When P content was increased from 0.3 wt% to 0.9 wt%, the LOI increased from 27.1% to 32.1% for the DPO–PHE flame retardant thermosets and 26.7% to 30.5% for the DOPO–PHE flame retardant thermosets. Moreover, with the same P content, the DPO–PHE flame retardant thermosets exhibited relatively higher LOIs than those of the DOPO–PHE flame retardant thermosets (**Table 3**). This increase indicates that DPO–PHE was a more effective flame-retardant than DOPO–PHE.

Table 3 LOIs and UL-94 ratings of the epoxy thermosets.

Samples	LOI	UL-94		
	(%) ±0.5	$t_1{}^a$/s ±1	$t_2{}^b$/s ±1	Rating
EP/P-0	23.7	-	-	Unrated
EP/DPO–PHE–P-0.3	27.1	17.9	6.6	V-1
EP/DPO–PHE–P-0.5	30.1	9.1	5.1	V-0
EP/DPO–PHE–P-0.7	31.3	3.4	4.9	V-0
EP/DPO–PHE–P-0.9	32.1	2.7	2.8	V-0
EP/DOPO–PHE–P-0.3	26.7	20.4	11.4	V-1
EP/DOPO–PHE–P-0.5	27.9	10.6	11.0	V-1
EP/DOPO–PHE–P-0.7	28.9	5.2	6.1	V-0
EP/DOPO–PHE–P-0.9	30.5	4.9	3.2	V-0

[a] After-flame time of the first flame test.

[b] After-flame time of the second flame test.

The UL-94 vertical burning test data in **Table 3** show that the EP/P-0 sample sustained burning until the whole sample was burned out, leading to no rating, whereas most flame retardant thermoset samples were quenched after the removal of the ignition source. The EP/DPO–PHE–P-0.5 sample obtained a UL-94 V-0 rating, whereas the EP/DOPO–PHE–P-0.5 sample obtained a V-1 rating. For epoxy resin modified using DOPO–PHE, a higher phosphorus content of 0.7% was needed to achieve the V-0 rating. For the EP/DPO–PHE–P-0.7 sample, a relatively shorter burning time (t_1 and t_2) was observed. Thus, the UL-94 vertical burning test results also indicated that DPO–PHE was a more effective flame retardant than DOPO–PHE.

3.4. Cone Calorimetry Testing

To elucidate the burning behavior of the samples, the combustion of EP/P-0, EP/DPO–PHE–P-0.9, and EP/DOPO–PHE–P-0.9 thermosets was investigated by cone calorimetry testing. The time to ignition (TTI), peak of heat release rate (pk-HRR), average effective heat of combustion (av-EHC), total heat released (THR), and total smoke produced (TSP) are summarized in **Table 4**. **Fig. 7** presents the heat release rate, THR, and TSP curves. For epoxy resins, the phosphorus flame retardant performs flame retardancy via the gas-phase and condensed-phase mechanisms [55]. The amount of residue after combustion and the effective heat of combustion, which is the THR divided by the mass loss (THR/ML), were investigated to evaluate the condensed-phase activity mechanism and gas-phase activity mechanism, respectively, for the flame retardants.

TTI was used to determine the influence of flame retardants on ignitability. As presented in **Table 4**, compared with that of EP/P-0, the TTI of the two flame-retarded thermosets was delayed by about 10 s. This delay is quite significant for the enhancement of flame-retardant properties of epoxy resins [54]. The EP/P-0 thermoset burned uniformly with an intensive flame covering the entire sample.

leaving almost no residue at the end of combustion. **Table 4** and **Fig. 7** show that compared with that of EP/P-0, the reductions in pk-HRR for EP/DPO–PHE–P-0.9 and EP/DOPO–PHE–P-0.9 are 38.4% and 10.5%, respectively. The reductions in av-EHC of the two flame-retarded samples are comparable. The av-EHC of EP/P-0 is 25 MJ/kg and those of EP/DPO–PHE–P-0.9 and EP/DOPO–PHE–P-0.9 are both 18 MJ/kg. The reductions in THR are nearly the same for the two flame-retarded samples and the THR decreased from 76 MJ/m^2 for EP/P-0 to 59 MJ/m^2 for EP/DPO–PHE–P-0.9 and 57 MJ/m^2 for EP/DOPO–PHE–P-0.9. The reductions in pk-HRR, av-EHC, and THR indicate that both flame retardants act via the gas-phase activity mechanism. As presented in **Fig. 7(c)**, the TSP of the two flame-retarded thermoset samples were lower than that of EP/P-0. This difference indicates that the flame retardants can help reduce smoke during combustion.

Table 4 Cone calorimetry data of the epoxy thermosets.

Samples	TTI (s) ±3	pk-HRR (kW/m^2) ±100	av-EHC (MJ/kg) ±5	THR (MJ/m^2) ±5	Residue (wt%) ±0.5	THR/ML (MJ/(m^2*g)) ±0.5	TSP (m^2) ±5
EP/P-0	31	1068	25	76	1.8	2.5	28.4
EP/DPO–PHE–P-0.9	41	657	18	59	0.9	2.2	21.3
EP/DOPO–PHE–P-0.9	39	956	18	57	4.2	2.6	14.9

Compared with EP/P-0, EP/DOPO–PHE–P-0.9 showed a negligible increase in residue. Despite the uncertainty of the data, the residue of EP/DPO–PHE–P-0.9 is almost equal to that of EP/P-0. The higher residue of EP/DOPO–PHE-P-0.9 than that of EP/DPO–PHE-P-0.9, which is similar to their TGA data, can also be attributed to the unstable and water-sensitive characteristic of the DOPO group. Thus, for the epoxy thermoset system, both flame retardants mainly act via the gas-phase activity mechanism. In addition, no condensed-phase activity was observed in DPO–PHE, whereas negligible or slight condensed-phase activity occurred in DOPO–PHE.

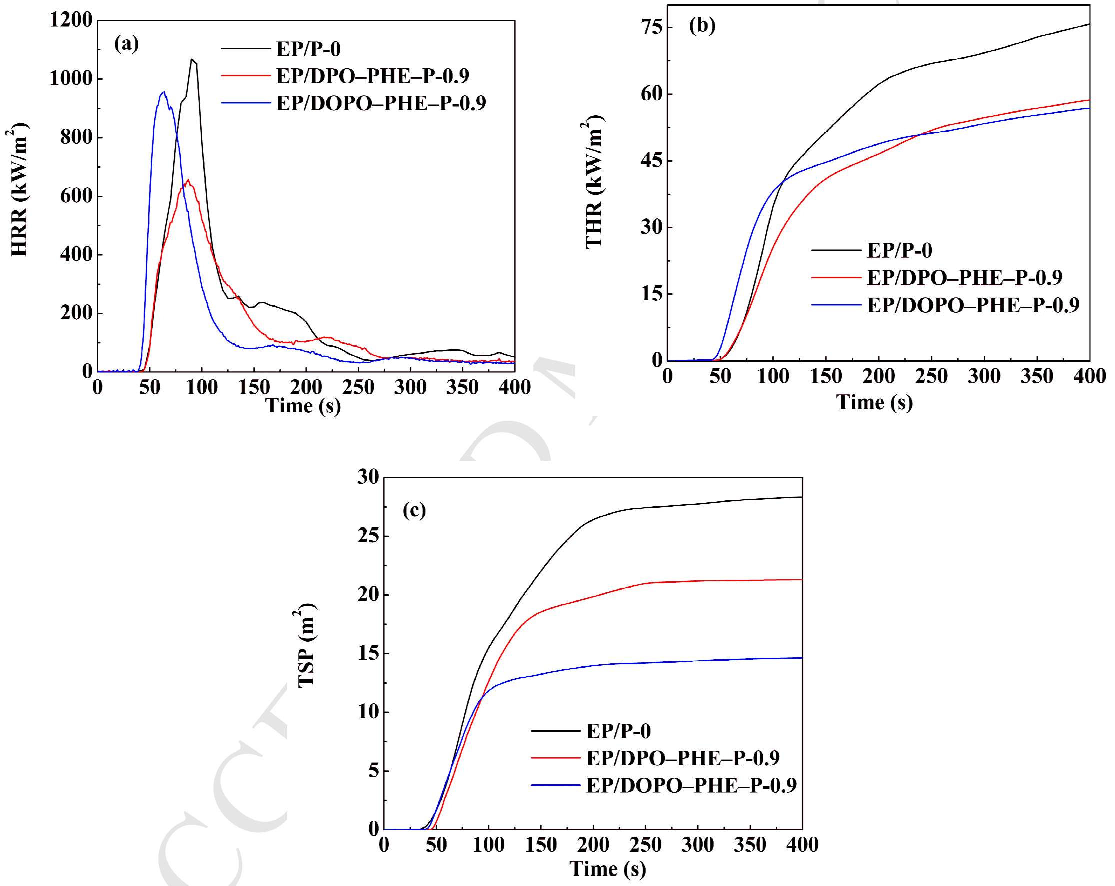


Fig. 7 Curves of EP/DDS, EP/DPO–PHE-P-0.9, and EP/DOPO–PHE-P-0.9 from CCT. (a) HRR, (b) THR, (c) TSP

3.5. Morphological characterization of char residue

The morphologies of the residues after CCT were analyzed by SEM. Images of the exterior and the interior are shown in **Fig. 8**. A small amount of residue with a fragmentary structure, which could not act as a protective layer, was found in the char of EP/P-0. The exterior char layer of the EP/DPO–PHE–P-0.9 and EP/DOPO–PHE–P-0.9 samples were similar, showing a continuous and compact structure with no holes. The interior char of EP/P-0 showed large and continuous bubbles. The interior char residues of the EP/DPO–PHE–P-0.9 and EP/DOPO–PHE–P-0.9 samples also presented similar structures, with numerous bubbles separated by thin layers. During combustion, the compact surface and the multi-hole inner structure can prevent oxygen and heat transfer and then protect the matrix from high temperatures [2,55].

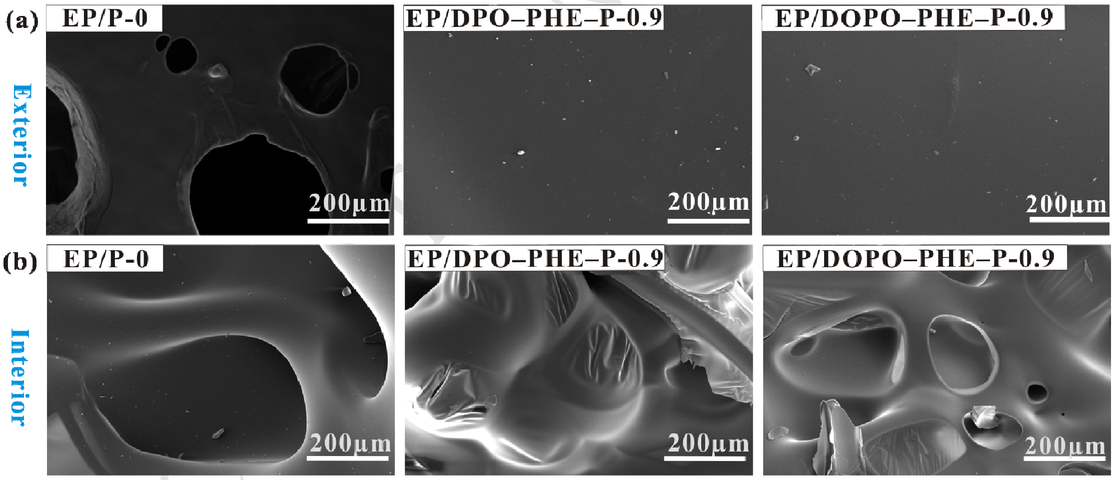


Fig. 8 SEM images of char residues after cone calorimetry testing.

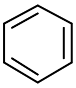
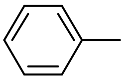
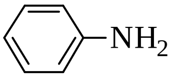
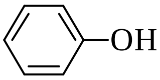
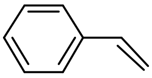
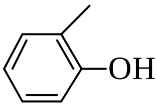
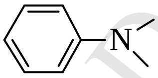
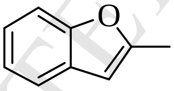
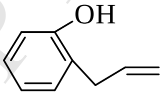
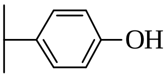
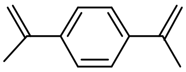
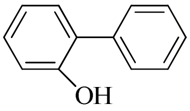
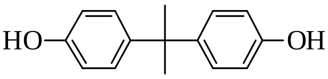
3.6. Pyrolysis–gas chromatography–mass spectrometry of the epoxy thermosets

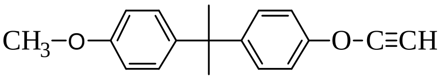
To obtain more information on the flame-retardancy mechanism of the thermosets in gas phase, the EP/DPO–PHE–P-0.9 and EP/DOPO–PHE–P-0.9 samples were investigated by Py–GC/MS, and the assigned products are collected in **Table 5**.

The pyrolytic products of EP/DPO–PHE–P-0.9 and EP/DOPO–PHE–P-0.9 are similar, but the relative areas of the pyrolytic products are fairly different. As shown in **Table 5**, the main pyrolytic products of EP/DPO–PHE-P-0.9 and EP/DOPO–PHE–P-0.9 include benzene, toluene, phenol, 4-methylphenol, benzofuran, 4-methylbenzofuran, 4-isopropenylphenol, and 4-isopropylphenol.

The volatiles of *o*-phenylphenol were observed in the pyrolytic products of EP/DOPO–PHE–P-0.9, and the considerably larger area of benzene in the pyrolytic products of EP/DPO–PHE–P-0.9 could be attributed to the two phosphorus flame retardants. This result indicated the existence of phosphorus-containing fragments in the gas phase. These phosphorus-containing fragments, such as PO· and PO_2·, together with phenol radicals, can scavenge ·H and ·OH in the flame and inhibit the free radical chain reaction of combustion. Alternatively, both samples containing nitrogen and the corresponding pyrolytic products included nitrogen-containing compounds, which could be further decomposed to nonflammable gases during combustion. These nonflammable nitrogen-containing gases, combined with CO_2, dilute ignitable gases and stop the supply of oxygen, thereby exerting a flame-retardant effect in the gas phase. Thus, as reported in other studies, the free radical quenching effect of phosphorus and phenol radicals and the diluting effect of nonflammable gases play important roles in the gas phase flame-retardant mechanism. [2,56–57]

Table 5 Pyrolytic products identified in the EP/DPO–PHE–P-0.9 and EP/DOPO–PHE–P-0.9 programs.

No.	*m/z*	Assigned structure	Relative area (%)	
			EP/DPO–P-0.9	EP/DOPO–P-0.9
a	78		16.93	2.10
b	92		5.6	2.10
c	93		0.58	-
d	94		23.92	27.60
e	104		0.58	-
f	108		3.83	2.79
g	121		0.35	1.28
h	132		4.58	3.36
i	134		3.07	9.92
j	136		2.14	9.32
k	158		0.83	2.07
l	170		-	0.80
m	228		0.06	4.01

n	266		0.02	0.85

3.7. Water Absorption Property

The water absorption properties of the epoxy resins were evaluated, given their close association with the electrical insulation characteristics, corrosion resistance, and mechanical properties of epoxy resins [30,58]. **Fig. 9** presents the relationship between water absorption (all samples were immersed for 48 h) and phosphorus content in the epoxy resins modified using DPO–PHE and DOPO–PHE. **Fig. 10** presents the water absorption curves vs. immersion times of the epoxy resins modified using neat and flame retardant (0.5 wt% phosphorus content).

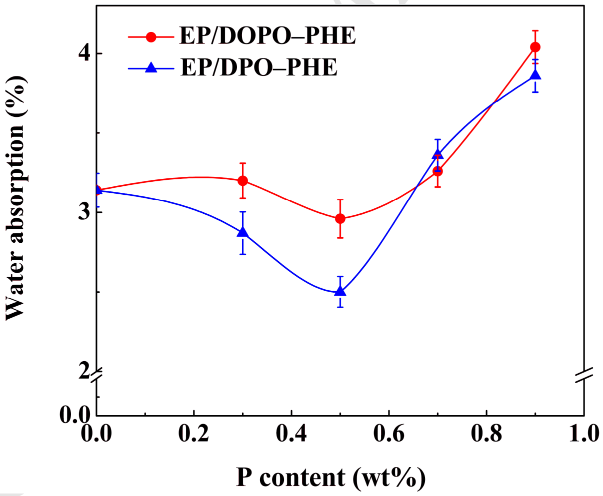


Fig. 9 Relationship between water absorption and P content in epoxy resins

Note: The samples were immersed in water for 48 h

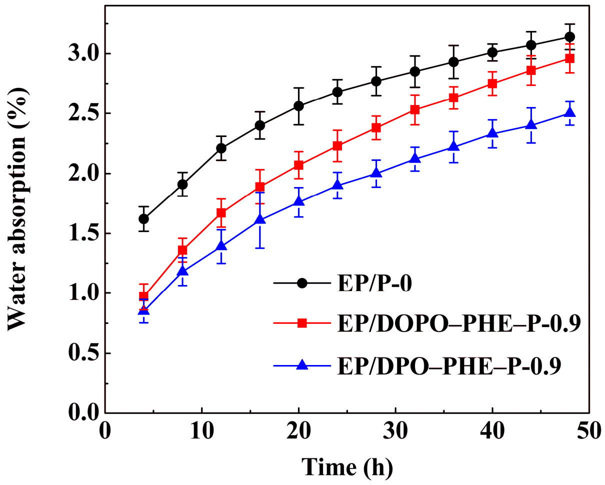


Fig. 10 Water absorption of epoxy thermosets vs. immersion time

A V-type profile was observed in the EP/DPO–PHE and EP/DOPO–PHE samples (**Fig. 9**). This profile suggests that the minimum water absorptivity be obtained with a change in phosphorous content. However, the trend also slightly varied. With an increase in phosphorus content from 0 wt% to 0.5 wt%, a reduction in water absorptivity indicated delay for the EP/DOPO–PHE samples; meanwhile, the EP/DPO–PHE samples sharply decreased. The sharp decrease of EP/DPO–PHE resulted in a lower bottom for the “V-type” profile in EP/DPO–PHE (2.5%) than that for the “V-type” profile in EP/DOPO–PHE (2.96%). A further increase in phosphorus content from 0.5 wt% to 0.9 wt% led to a relatively quick increase in water absorptivity. Notably, if the phosphorus content was kept below 0.65 wt%, the water absorptivity of the EP/DPO–PHE samples would be lower than that of the corresponding EP/DOPO–PHE samples under the current experimental conditions. Such occurrence could be verified by the results in **Fig. 10**. Both EP/DPO–PHE-P-0.5 and EP/DOPO–PHE-P-0.5 samples exhibited lower water absorptivity than that of EP/P-0. In addition, the EP/DPO–PHE–P-0.5 sample showed relatively lower water absorptivity than that of EP/DOPO–PHE–P-0.5. This property renders DPO–PHE more suitable for the modification of epoxy resins in electronics.

The behavior of the water absorptivity of the samples can be attributed to several factors. First, the hydrophilicity of the epoxy resins largely contributes to water absorption. Second, the cross-linking density and reticular formation in the epoxy resins can affect the water absorptivity. This factor would be more complicated by the introduction of flame retardants because of the different steric hindrance effects of the skeletons. Third, the structure of the flame retardant would cause the water absorptivity. Comparing with the structure of DPO， besides the P=O bond, there exist a P-O-C bond in the DOPO skeleton. The P-O-C bond in the DOPO skeleton can easily form a hydrogen bond and facilitates the increase in water absorption. The combined aforementioned factors prompt the water absorptivity of the flame-retardant epoxy resins to fluctuate. Compared with the samples modified using DOPO–PHE, those modified using DPO–PHE exhibited a lower absorptivity. This difference can be attributed to the small steric hindrance effect, relatively flexible activity of the two phenyl rings, and the absence of the P-O-C bond in the structure.

4. Conclusions

DPO–PHE and DOPO–PHE were synthesized using a two-step method. Using DPO–PHE (or DOPO–PHE) as a flame retardant and a co-curing agent and DDS as a main curing agent, flame retardant DGEBA resins were prepared (denoted as EP/DPO–PHE and EP/DOPO–PHE). TGA and DMA results showed that the

EP/DPO–PHE and EP/DOPO–PHE samples exhibited higher T_g values than that of EP/P-0. The introduction of flame retardants reduced the decomposition temperature of the epoxy resins. Compared with EP/DOPO–PHE, EP/DPO–PHE showed a higher thermal stability and a lower char yield. A study on the flame-retardant property showed that the EP/DPO–PHE and EP/DOPO–PHE thermosets exhibited satisfactory flame-retardant performance. CCT and Py–GC/MS of the flame-retardant samples, SEM of the burned residues, and the evaluation of char yield indicated that both flame retardants mainly acted via the gas-phase activity mechanism. In addition, no condensed-phase activity mechanism was observed in EP/DPO–PHE, whereas negligible or slight condensed-phase activity was reported in EP/DOPO–PHE. The water absorption activities of the flame-retardant epoxy resins are fluctuated. However, the introduction of the flame retardant could improve the water absorptivity of epoxy resins. Among the flame-retardant systems, EP/DPO–PHE–P-0.5 and EP/DOPO–PHE–P-0.5 exhibited the lowest water absorptivity. Comparison of the two flame retardants showed that DPO–PHE was a more effective flame-retardant than DOPO–PHE. In addition, DPO–PHE exhibited better characteristics for improving T_g, thermal stability, and water absorption of modified resins.

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(Bis(4-hydroxyphenyl)methyl)diphenyl phosphine oxide (DPO-PHE) and 1-(bis(4-hydroxyphenyl)methyl)-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO-PHE) were used as a flame retardant and a co-curing agent of 4,4'-diaminodiphenylsulfone of bisphenol A diglycidyl ether to prepare flame-retardant epoxy resins. Study showed that both flame retardants can improve the flame retardancy of epoxy thermosets. Burning behavior study indicated that both of the flame retardants act mainly through gas-phase activity mechanism. Limited oxygen index measurement and UL-94 vertical burning testing showed that DPO-PHE have higher flame-retardant effectiveness than DOPO-PHE. Compared with DOPO–PHE, DPO–PHE exhibited better characteristics for improving the T_g, thermal stability, and water absorption of modified resins.