

A Furan-based Phosphaphenanthrene-containing Derivative as a Highly Efficient Flame-retardant Agent for Epoxy Thermosets without Deteriorating Thermomechanical Performances

Hao-Xin Niu, Hong-Liang Ding, Jia-Li Huang, Xin Wang*, Lei Song, and Yuan Hu

State Key Laboratory of Fire Science, University of Science and Technology of China, Hefei 230026, China

Electronic Supplementary Information

Abstract In order to reduce greenhouse gas emissions, developing flame retardants from bio-based resources has aroused extensive interest in recent years. In this work, we utilized furfural (biomass) and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) to synthesize a bio-based co-curing agent (FGD) to combine with 4,4'-diaminodiphenyl methane (DDM) for obtaining a low-phosphorus loading flame-retardant epoxy thermosets. The introduction of FGD decreased the activation energy of the curing progress, enhanced the mechanical properties of the epoxy thermosets, and did not affect the glass transition temperature of the epoxy thermosets. EP-5.0 had a lower thermal degradation rate and a doubled char yield compared with EP-0. The phosphorus content of EP-5.0 was only 0.45 wt%, while EP-5.0 reached the UL-94 V-0 rating with a high LOI value of 32%. Compared with EP-0, the PHRR of EP-2.5 and EP-5.0 decreased by 22.3% and 31.3%, respectively. The SEM results showed that the addition of FGD made the char residues more uniform and denser, which could effectively prevent combustible volatiles from escaping from the degradation area to the flame area and isolate the heat transfer so that the epoxy thermosets had an excellent flame-retardant performance.

Keywords Furfural; DOPO; Bio-based co-curing agent; Flame-retardant performance

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INTRODUCTION

In recent decades, with the development of industrialization and urbanization, the massive use of fossil energy has led to a large amount of greenhouse gas emissions, which has caused global warming and severely endangered the global ecological balance.^[1–4] People began to devote themselves to developing polymers from bio-based resources to reduce environmental pollution. Furfural is an important bio-based platform molecule, which can be obtained from the hemicellulose of lignocellulosic biomass on a large scale.^[5–7] As a platform molecule, furfural can realize the synthesis of multi-purpose functional molecules through a variety of elementary reactions for being applied in a variety of fields.^[8–10]

As a thermosetting polymer composite material, epoxy thermoset has excellent mechanical properties, electrical insulation properties, adhesion and corrosion resistance, etc., so that it is widely used in machinery manufacturing, aerospace, shipbuilding, and other fields.^[3,11] However, epoxy thermoset is a flammable material. Once ignited, epoxy thermosets will

burn violently, accompanied by droplets, posing a great burning hazard.^[12–14] Therefore, it is necessary to endow the epoxy thermosets with outstanding flame-retardant performance. It is a very common method for adding flame retardants to modify epoxy thermosets. Current flame retardants include metal hydroxide flame retardants,^[15,16] nitrogen flame retardants,^[17] boron flame retardants,^[18,19] phosphorus flame retardants,^[20–22] silicon flame retardants,^[19,23] intumescent flame retardants,^[24] halogen flame retardants,^[25] etc.

Halogen flame retardants have high flame-retardant efficiency, but polymer with halogen flame retardants will produce harmful hydrogen halide gas and toxic compounds, such as polybrominated dibenzoxane and polybrominated dibenzofurans, during combustion.^[19] With the improvement of people's environmental protection awareness, many famous companies are actively researching and developing halogen-free flame retardants for producing halogen-free products.

DOPO and its derivatives are widely used as halogen-free phosphorus flame retardants.^[21,26–28] Ionela *et al.* synthesized a new DOPO oligomer as the flame retardant and utilized DDM as the curing agent to obtain the epoxy thermosets (PFR-EP/DDM).^[26] The PHRR of PFR-EP/DDM is reduced up to

* Corresponding author, E-mail: wxcmx@ustc.edu.cn

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45% compared with that of the pure epoxy thermosets, but the thermal stability is reduced. Wang *et al.* prepared lots of epoxy thermosets with different contents of phosphorus flame retardants.^[21] Flame-retardant epoxy thermosets have extraordinary flame-retardant performance and thermal stability, but the mechanical properties are reduced. The high loading of phosphorus makes the polymer have excellent flame-retardant performance, but at the same time, it will also affect the thermal stability and mechanical properties.^[20,21,26] Thus, it is very important to develop high-efficiency and low-phosphorus-loading flame retardants to modify epoxy thermosets so as not to affect the performance of epoxy thermosets.

In this work, we utilized furfural and DOPO to synthesize a bio-based co-curing agent, FGD, through a one-pot method for enhancing the mechanical properties and flame-retardant performance of epoxy thermosets. The chemical structure of FGD was characterized by the ^1H - and ^{31}P -NMR. The effect of FGD on the curing kinetics, thermomechanical properties, flame-retardant performance, mechanical properties, and thermal stability of epoxy thermosets was investigated.

EXPERIMENTAL

Materials

The electronic supplementary information (ESI) provides a detailed list of the chemicals utilized in this work.

Synthesis of Bio-based Curing Agent (FGD)

The bio-based co-curing agent (FGD) was synthesized by using furfural and DOPO, as shown in Scheme S1 (in ESI). In a 250 mL three-necked glass flask equipped with a magnetic stirrer, a reflux condenser, and a nitrogen inlet, furfural (4.81 g, 0.05 mol) and 3,5-diamino-1,2,4-triazole (2.48 g, 0.025 mol) were dissolved in 110 mL of 1,4-dioxane. The reaction system was stirred at 80 °C for 4 h, then cooled to 55 °C, in which 50 mL of 1,4-dioxane solution containing DOPO (10.80 g, 0.05 mol) was added and stirred for 12 h. The resulting mixed solution is rotated to remove most of the solvent and then poured into ethanol to precipitate a large number of crude products. The crude products were washed with ethanol for five times and then

dried in the vacuum oven at 70 °C for 36 h to obtain the bio-based curing agent (FGD). FGD is the white powder with a yield of 73%.

Preparation of the Cured Epoxy Thermosets

In the light of the formulations listed in Table S1 (in ESI), a certain amount of FGD was added into DGEBA and mixed at 160 °C for 2 h. Then, the mixed epoxy was cooled to 100 °C and the corresponding amount of DDM was added into the mixed epoxy for 3 min (N—H/epoxy group molar ratio: 1/1). The mixture was finally mixed and poured into the PTFE mold, and then cured at 100 °C for 2 h and 150 °C for 2 h.

Characterization

The ESI provides detailed information about the characterization methods and experimental instruments utilized in this work.

RESULTS AND DISCUSSION

Structural Characterization

The chemical structure of FGD was confirmed by the ^1H -NMR and ^{31}P -NMR spectra, which are shown in Fig. 1. As it can be seen in the ^1H -NMR spectrum of FGD, the signal peaks at 6.32 and 6.38 ppm are attributed to the two protons of the furan ring. The multiple peaks between 7.00 and 8.15 ppm are attributed to the protons of the benzene ring of DOPO, the proton near the oxygen atom on the furan ring, and the proton of the N—H structure. The peak at 5.15 ppm is ascribed to the proton of the P—CH structure. The peak at 10.63 ppm is ascribed to the proton of the N—H in the five-membered ring of guanazole. The characteristic P—H peak of DOPO, the characteristic amino peak of guanazole, and the characteristic aldehyde group peak of furfural all disappeared. In the ^{31}P -NMR spectrum of FGD, it is found that there is only one peak at 27.72 ppm. The above analysis results demonstrated that the FGD has been successfully synthesized by a one-pot method.

Curing Behavior

For studying the influence of FGD on the curing progress of uncured epoxy thermosets, the curing progress of EP-0 and EP-5.0 was studied by non-isothermal differential scanning

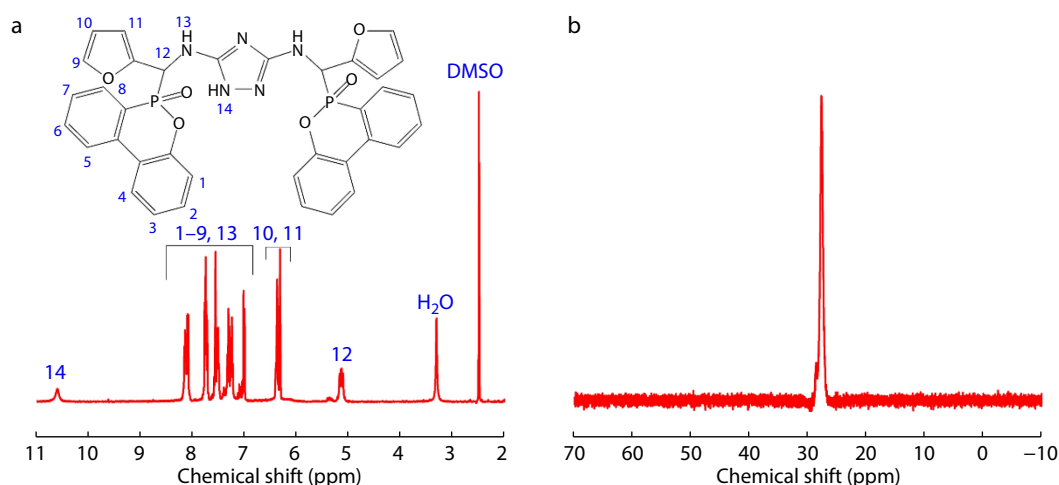


Fig. 1 (a) ^1H -NMR and (b) ^{31}P -NMR spectra of FGD.

calorimetry (DSC) at various heating rates (20, 15, 10, 5 °C/min), as shown in Fig. 2. The exothermic peaks of EP-0 and EP-5.0 are both single peaks, and DSC curves move to a higher temperature when the heating rate is increased, which is for that with the higher β , the residence time of curing at a certain temperature would be shorter, and the accumulation to the higher temperature to continue curing, resulting in the exothermic curve moving to a higher temperature. By comparing the data of EP-0 and EP-5.0 in Table S2 (in ESI), it is found that the starting temperature (T_{onset}) and the peak temperature (T_p) of EP-5.0 are less than those of EP-0, which is because of the ring-opening reaction of the partial epoxy group with secondary amine group in FGD. The apparent curing activation energy (E_a) of uncured epoxy thermosets systems is calculated by Kissinger's and Ozawa's methods,^[4,29] as shown in Fig. 2. It is observed that whether it is by Kissinger's method or Ozawa's method, the E_a of EP-5.0 (41.13 kJ/mol for Kissinger, 45.85 kJ/mol for Ozawa) is lower than that of EP-0 (50.63 kJ/mol for Kissinger, 54.86 kJ/mol for Ozawa), which indicates that the addition of FGD promotes the cross-linking reaction.

Mechanical Property

The thermo-mechanical properties of epoxy thermosets were studied by DMA. As shown in Fig. 3, the loss factor ($\tan\delta$) and storage modulus (E') of EP-0 and EP-5.0 are given as a function of temperature. Table S3 (in ESI) summarizes the glass transition temperature (T_g), storage modulus, and crosslinking

density (ν_e) of EP-0 and EP-5.0. The E' of EP-5.0 is 1710 MPa at 30 °C, while the E' of EP-0 is 1605 MPa. This indicates that the stiffness of epoxy thermosets is improved by the introduction of FGD, which may be due to the rigid structure of FGD (furan quinary ring and phosphaphenanthrene structure of DOPO) and more hydrogen bonding. The T_g corresponds to the peak temperature of the α -transition of the $\tan\delta$ versus temperature curve. In Fig. 3, the T_g of EP-5.0 (165 °C) is only 3 °C lower than that of EP-0 (168 °C). The ν_e of epoxy thermosets are calculated by the formula given in the literature:^[30]

$$\nu_e = E' / 3RT \quad (1)$$

where R represents the gas constant, E' represents the cured epoxy resins' storage modulus in the rubbery plateau region, and T denotes the absolute temperature. The ν_e of EP-5.0 is lower than that of EP-0, which may be attributed to the steric hindrance that inhibited the movement of polymer chains, FGD has a rigid structure and occupies a larger volume, and that FGD has three active —NH while DDM has four active —NH. All in all, EP-5.0 has the same excellent thermos-mechanical properties as EP-0.

For studying the effect of FGD as a co-curing agent on the mechanical properties of the cured epoxy thermosets, the impact strength and tensile strength were studied, which are shown in Fig. 4. With the increase of FGD, the tensile strength of epoxy thermosets increased by 18% from 40.22 MPa (EP-0) to 47.66 MPa (EP-5.0), which is due to the rich rigid structure

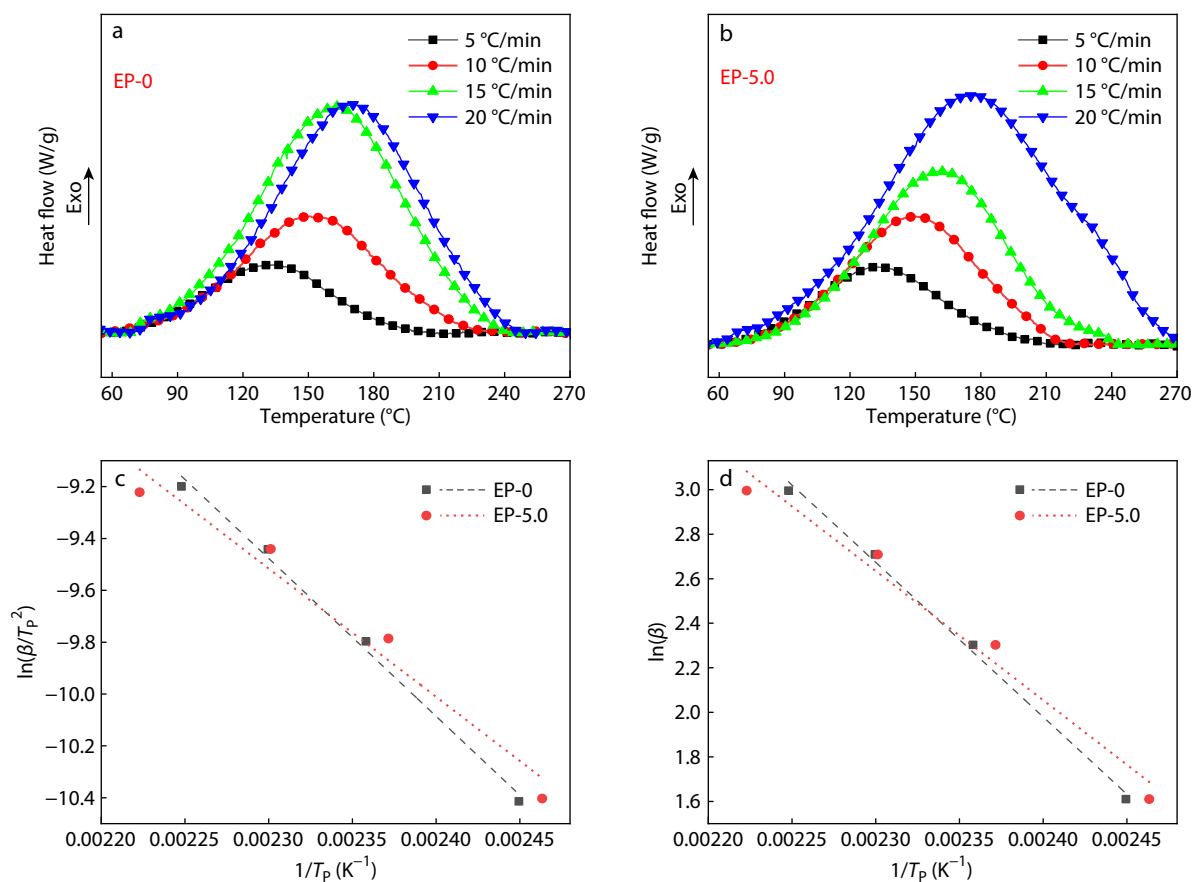


Fig. 2 The non-isothermal DSC curves of (a) EP-0 and (b) EP-5.0; The linear fitting curves of the uncured EP-0 and EP-5.0 systems according to (c) Kissinger and (d) Ozawa methods.

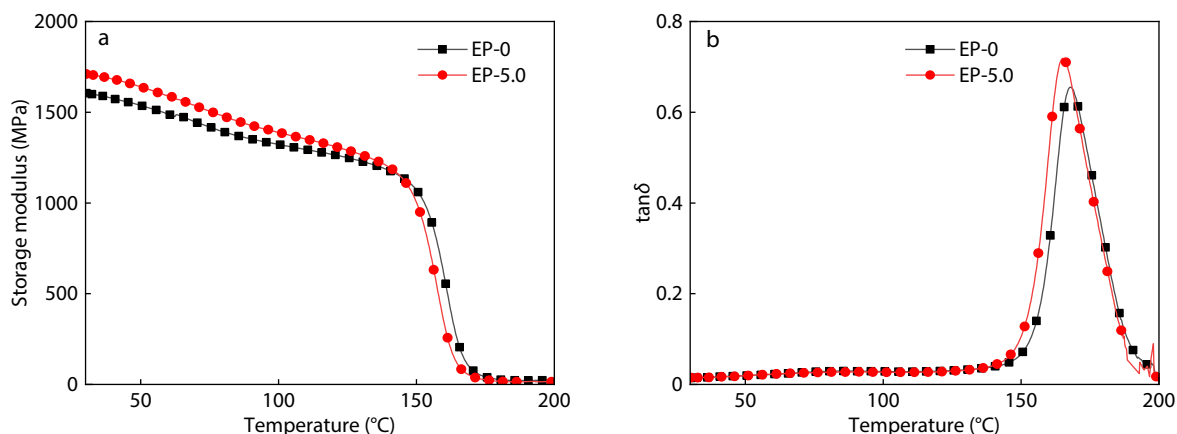


Fig. 3 (a) E' and (b) $\tan\delta$ curves of EP-0 and EP-5.0.

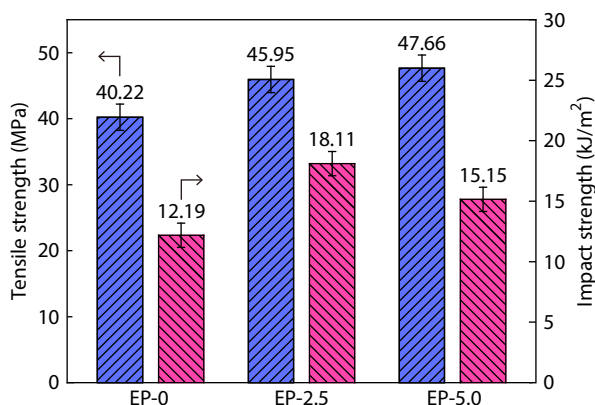


Fig. 4 Tensile strength and impact strength of epoxy thermostets.

of FGD such as furan five-membered ring and phosphaphenanthrene structure, which requires more energy to destroy. Moreover, FGD contains more nitrogen and oxygen atoms, which strengthens the intermolecular hydrogen bonding and enhances the interaction between the substrates. Compared with EP-0 (12.19 kJ/m²), the impact strength of EP-2.5 (18.11 kJ/m²) and EP-5.0 (15.15 kJ/m²), increase by 48.6% and 24.3%, respectively. Visibly, the introduction of FGD can enhance the toughness of epoxy thermostets, but the toughening effect will decrease when the content exceeds a certain

amount. This phenomenon may be due to the fact that the introduction of FGD reduces the crosslinking density of the epoxy networks, and improves the freedom of movement of the epoxy cross-linked network. Moreover, the complex rigid aromatic ring structure of FGD and its interaction with the epoxy crosslinking network will also affect the toughness of epoxy thermostets. In general, the introduction of FGD can improve the mechanical properties of epoxy thermostets.

Thermal Degradation Behavior

The thermal degradation behavior of epoxy thermostets in nitrogen was studied by TGA. As shown in Fig. 5, the curves of TGA and DTG are given, and the TGA data are listed in Table S4 (in ESI). It can be seen from Fig. 5 that the three epoxy thermostet systems have a similar thermal degradation process, which mainly occurs between 310–550 °C, corresponding to the fracture and degradation of crosslinking epoxy network. With the increase of FGD content, $T_{-10\%}$ decreases from 383.6 °C to 364.0 °C, and $T_{\max}$ also decreases from 391.9 °C to 389.0 °C, which indicates that FGD would promote the premature degradation of epoxy thermostets, which might be due to the early catalytic degradation of phosphorus-containing compounds. At 700 °C, the char yield of EP-0 was only 12.9%. With the introduction of FGD, the char yield of EP-2.5 and EP-5.0 increased to 17.6% and 25.5%, respectively. The maximum thermal degradation rate of epoxy thermostets decreased from

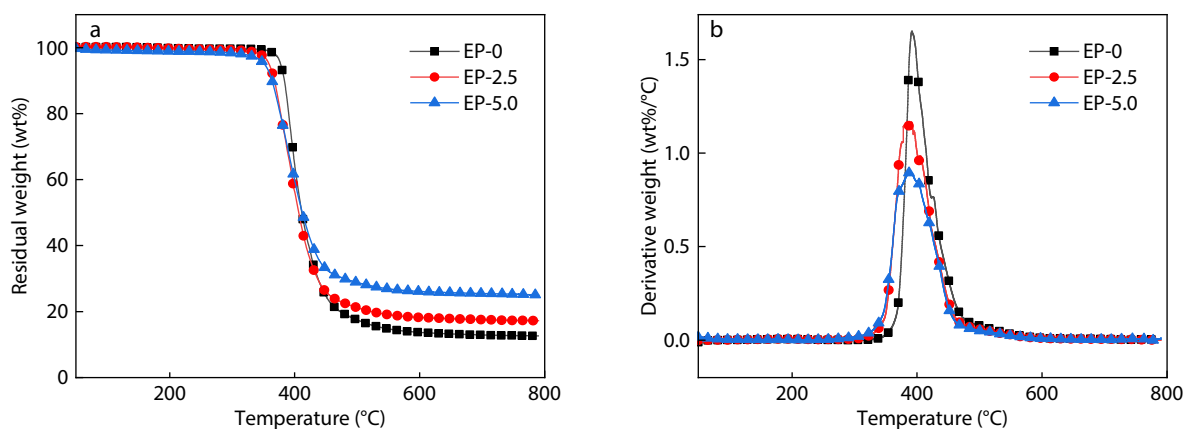


Fig. 5 (a) TGA and (b) DTG curves of EP-0, EP-2.5, and EP-5.0.

1.6 wt%/°C to 0.9 wt%/°C. This indicates that FGD can cut down the thermal degradation rate, promote the formation of char, and enhance the flame-retardant performance of epoxy thermosets.

Flame-retardant Performance

For the sake of studying the influence of FGD on the flame-retardant performance of epoxy thermosets, LOI and UL-94 vertical-burning tests were carried out, and the relevant data are displayed in Table 1. It can be found that the LOI of EP-0 is only 23.5% and EP-0 has no rating in UL-94 vertical-burning test. Fig. S1 (in ESI) shows that once the pure epoxy thermoset is ignited, it will burn violently until burning out, accompanied by dripping. The LOI of EP-2.5 increased to 29%. Generally, polymer materials with an LOI of more than 26% are considered to have excellent flame-retardant performance. The LOI of EP-5.0 was further increased to 32%, and EP-5.0 reached the UL-94 V-0 rating. The results show that FGD as a co-curing agent can stupendously ameliorate the flame-retardant performance of epoxy thermosets, which may be ascribed to the improved charring capacity by the presence of nitrogen, phosphorus, and the aromatic structures of FGD.

The combustion behavior of epoxy thermosets was further

Table 1 The UL-94 and LOI data of epoxy thermosets.

Sample	LOI (%)	UL-94		
		t_1+t_2	Dripping	Rating
EP-0	23.5	BC	Yes	No
EP-2.5	29.0	11+7	No	V-1
EP-5.0	32.0	4+5	No	V-0

studied for evaluating the flame-retardant performance by cone calorimeter.^[31] As shown in Fig. 6, the heat release rate (HRR) and residual mass (RM) curves of epoxy thermosets are given as a function of temperature. It can be seen from Table 2 that the time to ignition (TTI) of EP-2.5 and EP-5.0 are lower than that of EP-0. As indicated by the results of TGA, the introduction of FGD can make the epoxy thermosets degrade in advance, which is the reason for the decrease in TTI. The HRR curve of EP-0 rises sharply and reaches the strongest peak of 1194.7 kW/m², indicating that the combustion process is extremely violent. With the increase of FGD, the peak HRR (PHRR) of epoxy thermosets decreased gradually, indicating that the intensity of combustion decreases greatly. Compared with EP-0, the PHRR of EP-2.5 and EP-5.0 decreased by 22.3% and 31.3%, respectively. Moreover, an obvious shoulder peak is observed in the HRR curves of EP-2.5 and EP-5.0, indicating that they degrade into charcoal in advance during the combustion process and that the introduction of FGD makes the epoxy thermosets from a typical non-carbonized material transfer to a carbonized material. In order to evaluate the potential fire hazard of materials, divide PHRR by

the time to PHRR value (T_{PHRR}) to obtain the fire growth index (FIGRA). Compared with EP-0, the FIGRA of EP-2.5 and EP-5.0 decrease by about 20%, which indicated that the introduction of FGD could endow epoxy thermosets with better flame-retardant ability. With the increase of FGD, the residual yield of epoxy thermosets increased gradually. Compared with EP-0, the residual yield of EP-2.5 increased by 81%, and the residual yield of EP-5.0 increased by 101%, indicating that the introduction of FGD could promote the carbonization of the epoxy matrix, prevent the thermal degradation of epoxy crosslinking network, reduce the intensity of combustion, and substantially enhance the flame-retardant performance of epoxy thermosets.

Analysis of the Char Residues

SEM was utilized to characterize the microstructure of char residues. Fig. S2 (in ESI) shows the SEM micrographs of the char residues after full combustion in the muffle furnace at 500 °C. It can be seen that after combustion, the char residues of EP-0 are broken and discontinuous, which cannot prevent the flammable gas compounds from escaping from the

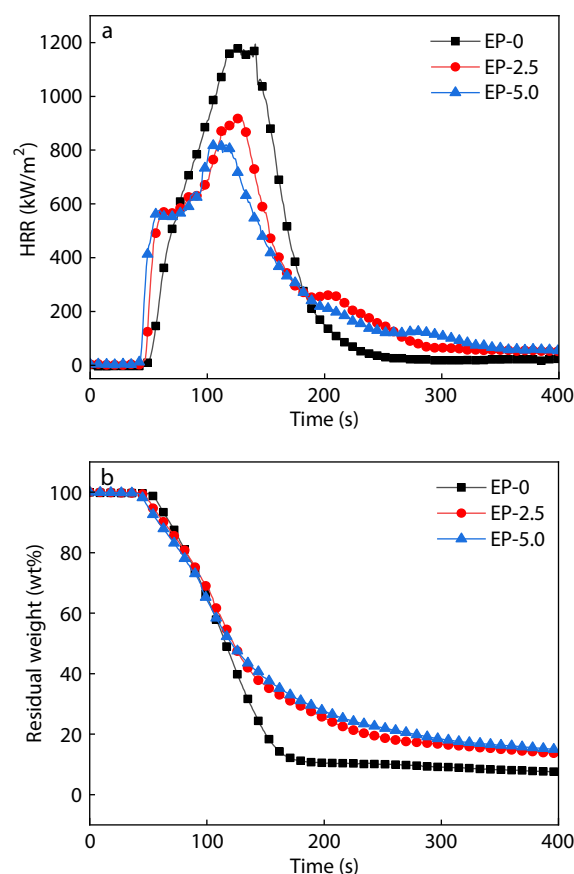


Fig. 6 (a) HRR and (b) residual mass curves of epoxy thermosets.

Table 2 The cone calorimeter data of the epoxy thermosets.

Sample	TTI (s)	PHRR (kW/m ²)	Reduction in PHRR (%)	THR (MJ/m ²)	T_{PHRR} (s)	FIGRA (kW·m ⁻² ·s ⁻¹)	Residual yield (%)
EP-0	52±2	1194.7±17.3	—	123.9±3.1	126±4	9.5	7.4
EP-2.5	43±3	928.7±17.0	22.3	117.5±4.3	127±5	7.3	13.5
EP-5.0	40±3	820.3±16.0	31.3	113.8±3.9	105±5	7.8	14.9

degradation area to the flame area. In addition, oxygen and heat can easily pass through these cracks and holes, so that EP-0 is easy to burn. The char residues of EP-2.5 have better integrity, but there are still some cracks and holes. The char residues of EP-5.0 are more uniform and denser, which can effectively prevent the combustible volatiles from escaping from the degradation area to the flame area and isolate the heat transfer so that it has excellent flame-retardant behaviors.

The graphitization degree of the char residue was studied by Raman spectroscopy. The Raman spectra are shown in Fig. 7(a), exhibiting two characteristic bands at 1359 and 1599 cm^{-1} , corresponding to D-band and G-band, respectively. The graphitization degree of the char residue is evaluated by the intensity ratio (I_D/I_G) between D-band and G-band. The I_D/I_G of the EP-5.0's char residues is smaller than that of EP-0's char residues, indicating that the char residue of EP-5.0 has a higher graphitization degree and is more compact, endowing EP-5.0 with higher thermal stability.

The char residues were further studied by X-ray photoelectron spectroscopy (XPS). The XPS spectra of the EP-0 and EP-5.0's char residues are shown in Figs. 7(b)–7(d), indicating that the char residues are composed of C, H, and O elements. The additional P element appears in the char residues of EP-5.0, which represents the presence of phosphorus oxides. For the char residues of EP-5.0 and EP-0, the C1s XPS spectrum is splitted to three sub-peaks at 288.4 eV (C=O), 286.4 eV (C–O), and 284.8 eV (C–C/C=C). For the char residues of EP-

5.0, the P2p XPS spectrum is splitted to four sub-peaks at 132.7 eV (P–O–P), 133.4 eV (O=P–O), 134.05 eV (P–C) and 134.8 eV (P_2O_5). The XPS fitting results of the appeal show that the introduction of FGD makes the epoxy thermosets cross-linked with phosphorus oxide during the degradation process, accelerates the formation of the char residues, and makes char residues more compact.

Analysis of the Gaseous Products Emitted

The formation of gaseous thermal decomposition products of epoxy thermosets was studied by TG-FTIR during the thermal degradation progress of epoxy thermosets. The FTIR spectra of the gas-phase compounds of epoxy thermosets at the maximum decomposition rate are shown in Fig. 8. The main characteristic absorption bands of EP-0 and EP-5.0 are almost the same, mainly including 1175–1258 cm^{-1} (ethers), 1300–1400 cm^{-1} (C–H), 1450–1630 cm^{-1} (aromatic compounds), 2360 cm^{-1} (carbon dioxide), 2850–3050 cm^{-1} (C–H). The characteristic absorption band of CO_2 of EP-5.0 is very weak, indicating that the degradation degree of epoxy thermosets decreases, and that the carbon oxide products also decrease. The changing trend of the absorption band intensity of some representativeness gas-phase compounds for the epoxy thermosets is shown in Fig. S3 (in ESI). The absorption band intensities of both samples have been processed by mass normalization. Compared with EP-0, the characteristic absorption band intensity of typical gas compounds (including ethers, aromatic compounds, saturated alkanes, unsaturated

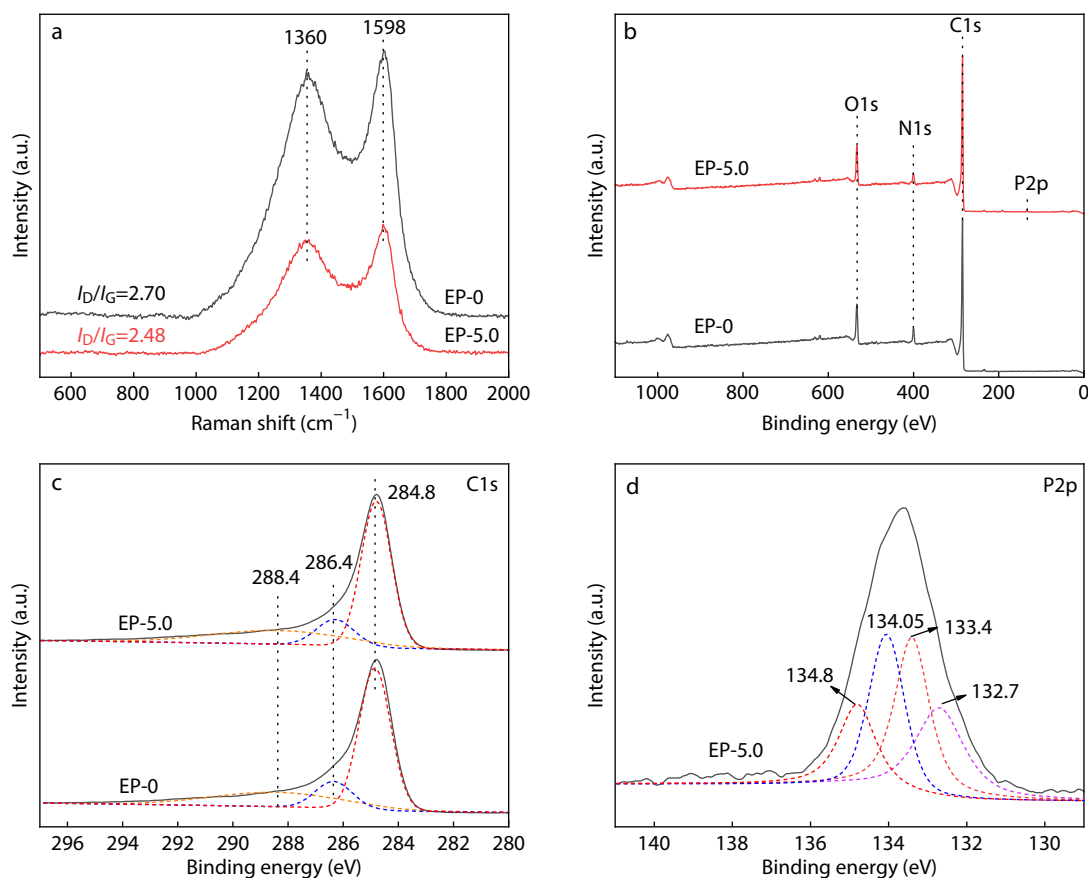


Fig. 7 (a) Raman, (b) full-scan, (c) high-resolution C1s XPS and (d) high-resolution P2p XPS spectra of epoxy thermosets.

alkanes, and carbon monoxide) of EP-5.0 is significantly lower, which is mainly due to that the denser char residues block the volatilization of combustible gaseous products, reduces the smoke generation and heat release, and improves the flame-retardant performance.

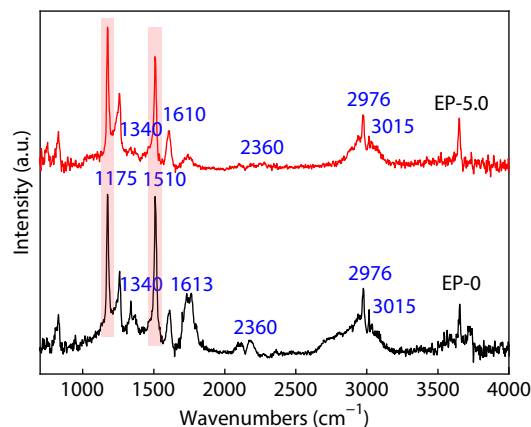


Fig. 8 FTIR spectra of the gas products of the epoxy thermosets at the maximum decomposition rate.

CONCLUSIONS

To summarize, a bio-based co-curing agent was synthesized by using furfural and DOPO. EP-5.0 had a high LOI value of 32% and reached the UL-94 V-0 rating when the phosphorus content of EP-5.0 is only 0.45 wt%. The TGA results indicated that the introduction of FGD would accelerate the early degradation of the epoxy thermosets into char, and the char yield had reached 25.5%, which is twice as much as EP-0. According to the results of the SEM and Raman, the char residues of EP-5.0 were more uniform and denser, while the char residues of EP-0 were broken and discontinuous. The TG-FTIR results showed that the introduction of FGD greatly reduced the release of gaseous thermal decomposition products. In addition, the introduction of FGD enhanced the mechanical properties of epoxy thermosets, but only slightly reduces the glass transition temperature. All in all, the introduction of FGD would greatly enhance the flame-retardant performance and the mechanical properties of epoxy thermosets.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-022-2655-y>.

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