

Novel DOPO-based epoxy curing agents

Synthesis and the structure–property relationships of the curing agents on the fire safety of epoxy resins

Xiaodong Qian¹ · Lei Song² · Yuan Hu² · Saihua Jiang³

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Abstract A series of DOPO-based curing agents with similar structures were prepared through Mannich-type reaction and characterized. The curing agents with weak electron-donating methylene groups, strong electron-withdrawing sulfonyl groups and strong electron-donating ether groups were then incorporated into epoxy resins, and the structure–property relationships of the curing agents on the fire safety of epoxy resins were investigated. Thermal and flame-retardant properties of the resins were investigated by thermogravimetric analysis, cone calorimeter, micro-scale combustion calorimeter, UL-94 and limiting oxygen index. The results showed that the curing agents with proper structure could impart epoxy resins with high thermal stabilities and low flammability. The curing agents containing ether groups exhibited better flame-retardant efficiency compared with other curing agents. In order to further investigate the mechanism, the char residues of the resins were studied by scanning electron microscopy, Fourier transform infrared and Raman spectroscopy. Char residues of the resins containing ether groups exhibited a

condense char morphology, associated with a high degree of graphitization. This work not only provides novel epoxy resins with good thermal stability, but also will trigger more scientific interest in the development and investigation of the structure–property relationships of the DOPO-based flame retardants.

Keywords Fire safety · Curing agents · Epoxy resins · Structure–property

Introduction

Among the common engineering polymers, epoxy resins (EP) have already occupied a dominant position in the development of high-performance polymeric materials. Epoxy resins are widely used as coatings, adhesives, laminates, semiconductor encapsulation and matrices for advanced composites owing to their good toughness, mechanical stiffness, chemical resistance and superior adhesion [1–3]. However, flammability is one of the main disadvantages of epoxy resins and strict flame-retardant performances are often required [4, 5]. Among various flame retardants for epoxy resins, reactive flame retardants have practical value and are usually introduced to epoxy resins through the reaction between epoxy groups and curing agents. The epoxy groups on the main chains of epoxy resins could react with the amidogen or hydroxy of curing agents; thus, the flame-retardant agents could be introduced to the epoxy resins through ring-opening reactions. Generally, introducing curing agents containing flame-retardant elements into epoxy matrix is a practical way to improve the fire safety of epoxy resins.

Recently, worldwide interests in halogen-free flame retardants (FRs) have been increasing due to their good health and environmental properties [6, 7]. Among the

✉ Xiaodong Qian
wjxyqxd@hotmail.com

✉ Yuan Hu
yuanhu@ustc.edu.cn

¹ Key Lab Firefighting and Rescuing Technology, Ministry of Public Security, Chinese People's Armed Police Force Academy, Xichang Road 220, Langfang City 065000, Hebei Province, People's Republic of China

² State Key Laboratory of Fire Science, University of Science and Technology of China, Jinzhai Road 96, Hefei 230027, Anhui, People's Republic of China

³ School of Mechanical and Automotive Engineering, South China University of Technology, Wushan Road 381, Guangzhou 510641, People's Republic of China

various halogen-free flame retardants, phosphorus-containing compounds are promising, because phosphorus-containing compounds release less toxic gases and smoke during the combustion [8–10]. Among phosphorus-containing flame retardants, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) has attracted extensive attentions due to its good flame-retardant efficiency in epoxy resins [11–13]. In addition to phosphorus-based flame retardants, incorporation of aromatic groups is also advantageous to improve the thermal property of polymeric materials [14]. Thus, epoxy resins containing phosphorus and aromatic groups will be expected to provide not only excellent flame-retardant properties but also favorable thermal properties.

Compared with phosphorus-containing flame retardants, the flame retardants containing P-N or P-S usually have synergistic effects on the flame retardancy of polymeric materials [15–17]. Despite this advantage, many flame retardants reported are additive flame retardants, and those additive flame retardants usually result in weak water resistance of the polymer materials. The general advantage of aromatic groups on the flame retardancy of polymeric materials is high thermal stable, but the relationship between the structure of the aromatic groups and the flame-retardant efficiency is not clear. Thus, exploring novel flame retardants containing aromatic groups and studying the relationship between the structures and the efficiency of the flame retardants have important scientific significance.

In this study, a series of curing agents, containing weak electron-donating methylene groups, strong electron-withdrawing sulfonyl groups or strong electron-donating ether groups, were prepared and characterized. To study the flame-retardant efficiency, the curing agents were incorporated into the epoxy resins, and the fire safety and the degradation mechanisms and especially the relationship of the structure–property were investigated. In the interest of applying such epoxy resins in a more effective manner, significant study and progress in this regard are required.

Experimental

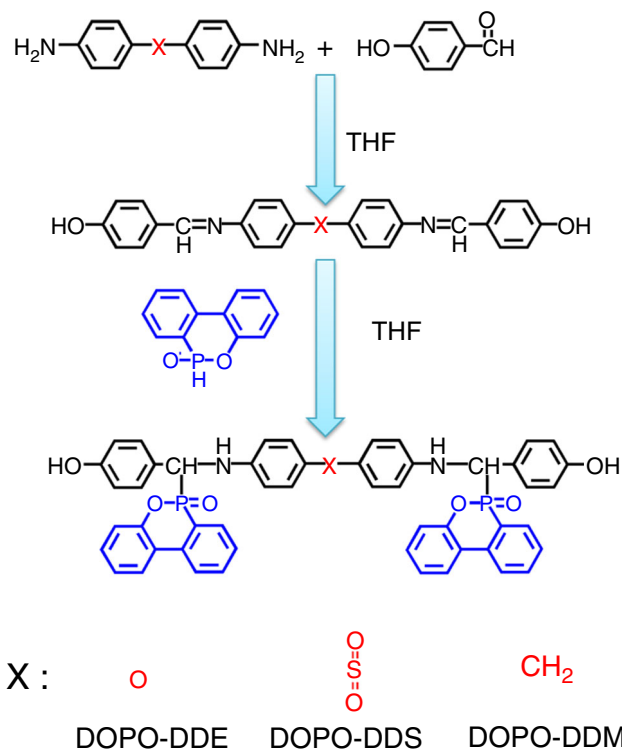
Raw materials

Epoxy resins (DGEBA, commercial name: E-44, epoxy value: 0.44) were supplied by Hefei Jiangfeng Chemical Industry Co. Ltd. (Anhui, China). 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was supplied by Shandong Mingshan Fine Chemical Industry Co. Ltd (Shandong, China). 4-Hydroxybenzaldehyde, 4,4-diaminodiphenyl methane (DDM), 4,4-diaminodiphenyl sulfone (DDS), 4,4'-diaminodiphenyl ether (DDE) and tetrahydrofuran (THF) were all reagent grade

and provided by China Medicine (Group) Shanghai Chemical Reagent Corporation.

Preparation of DOPO-containing curing agents

4,4-Diaminodiphenyl sulfone (DDS) (41.6 g, 0.1 mol), 4-hydroxybenzaldehyde (24.4 g, 0.2 mol) and THF (200 mL) were added into a three-necked flask equipped with a mechanical stirrer, flux condenser, dropping funnel and nitrogen inlet. After the mixtures were saturated with nitrogen atmosphere under vigorous mechanical stirring, the mixture was heated to 50 °C and stirred for 5 h. Then, the mixtures were heated to 60 °C and stirred for 12 h. DOPO (43.2 g, 0.2 mol), which was predissolved in a proper quantity of THF, was then slowly dropped into the above reactants and kept stirring for another 5 h. The resulting solutions were then poured into 1000 mL deionized water, and the precipitates were filtered and washed several times with deionized water; then, the powders were dried under vacuum. Finally, the yellow powders were labeled as DOPO-DDS. The synthesis routes of the curing agents are illustrated in Scheme 1. The other flame-retardant curing agents (DOPO-DDM, DOPO-DDE) are synthesized under the same condition.



Scheme 1 Synthesis route of the curing agents (DOPO-DDM, DOPO-DDE and DOPO-DDS)

Preparation of the FRs/EP resins

The cured epoxy resins were obtained via thermal curing of DOPO-DDM, DOPO-DDS and DOPO-DDE with epoxy resins (EP). In order to get the full comparison of the flame retardants, the mass ratios of the flame-retardant curing agents in epoxy resins are 10 mass%. The other epoxy groups are cured by DDM, and the loading is according to the epoxy value of EP. The mixtures of epoxy resins, flame-retardant curing agents and DDM were stirred fully at 50 °C temperature for 2 h. Then, the mixtures were cured at 100 °C for 2 h (h) and 150 °C for 2 h. After curing, the samples were cooled to room temperature and the flame-retardant resins were obtained according to Table 1.

Characterization

The FTIR spectroscopy was recorded with Nicolet 6700 FTIR spectrophotometer, and the wavelength ranges were set from 4000 to 500 cm^{-1} .

^1H NMR measurement was taken on Avance 400 Bruker spectrometer at room temperature, and the solvent is CDCl_3 .

The dimension of the specimens used for vertical burning test is $100 \times 13 \times 3 \text{ mm}^3$, and the test was carried out on a CFZ-2-type instrument (Jiangning Analysis Instrument Company, China) for three times.

The flammability of the samples was also characterized by the cone calorimeter (Fire Testing Technology, UK) according to ISO 5660. Each specimen (dimensions of $100 \times 100 \times 3 \text{ mm}^3$) was mounted on aluminum foil and placed on a holder filled with the mineral fiber blanket, and only the upper face was exposed to the radiant heater.

The thermogravimetric analysis (TG) was carried out on a TGA Q5000 IR thermalgravimetric analyzer (TA instruments). About 4–10 mg of samples was heated from 30 to 800 °C at a heating rate of 20 °C min^{-1} under air purge, respectively.

GOVMARK MCC-2 microscale combustion calorimeter (MCC) was used to investigate the combustion of the polymeric materials. In this system, about 5 mg of the samples was heated to 900 °C at a heating rate of 1 K s^{-1} and in a stream of nitrogen flowing at 80 $\text{cm}^3 \text{ min}^{-1}$.

Microstructure of the char layers is investigated by the scanning electron microscopy (SEM). The samples were sputter-coated with a conductive layer. The tests were performed with a scanning electron microscope AMRAY1000B.

Laser Raman spectroscopy measurements were taken at room temperature with a SPEX-1403 laser Raman spectrometer (SPEX Co., USA).

Results and discussion

Synthesis and characterization of the curing agents

The reactive rigid heterocyclic ring structures containing phosphorus (DOPO-DDS, DOPO-DDM and DOPO-DDE) were synthesized through the Mannich-type reaction according to Scheme 1. The chemical structure of the as-obtained flame-retardant curing agents (DOPO-DDS, DOPO-DDM and DOPO-DDE) was identified by FTIR and ^1H -NMR. FTIR spectrums of DOPO-DDS, DOPO-DDM and DOPO-DDE are shown in Fig. 1. The phosphorus structures in the monomers observed at 1263 cm^{-1} are assigned to stretching vibrations of P=O, and the peaks at 910 and 1590 cm^{-1} correspond to the vibrations of P–O–Ph and P–Ph, respectively [18, 19]. Moreover, the –OH appears at 3300 cm^{-1} . Those characteristic peaks indicate that the curing agents are synthesized. The structures of those flame-retardant curing agents were further characterized by ^1H -NMR, as shown in Fig. 2. As for the primary structure (a), the character peaks of H in the –N = CH– structure can be found at 8.5 PPM (a), and the character peaks of H in the –OH structure are obvious at 10.2 PPM. However, when the DOPO is added into the mixtures, the Mannich-type reaction occurred and the characteristic peaks of H in the –OH structures are shifted to 9.5 PPM. The characteristic peaks of H in the –N=CH– structures at around 8.5 PPM disappeared. Those results indicate that the DOPO structures are connected with the curing agents and the flame-retardant curing agents are synthesized according to Scheme 1.

The flame-retardant properties and the thermal stability of EP and FRs/EP resins

According to ASTM D2863, LOI is used to rank the flammability of polymeric materials and is a quantitative

Table 1 The composition and LOI values of FRs/EP resins with different curing agents

Sample	FRs content/mass%	LOI/%	UL-94	$T_1/T_2/\text{s}$
EP	0	23.0	NR	–
DOPO-DDM/EP	10	29.5	V1	$5.6/6.2 \pm 1.4$
DOPO-DDE/EP	10	31.5	V0	$1.7/4.1 \pm 1.3$
DOPO-DDS/EP	10	31.0	V0	$1.5/3.1 \pm 1.2$

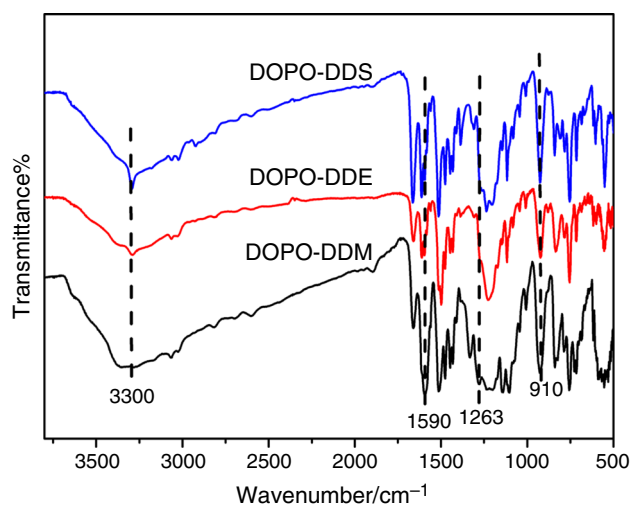


Fig. 1 FTIR spectrum of curing agents (DOPO-DDM, DOPO-DDE and DOPO-DDS)

method. LOI values of EP and FRs/EP resins are shown in Table 1. The LOI values of the materials increased from 23.0 % for pure EP to 29.5 % when DOPO-DDM was incorporated into the epoxy resins. However, as for DOPO-DDS, LOI value of flame-retardant epoxy resins decreased slightly compared with DOPO-DDM/EP resins, indicating that DOPO-DDS with the sulfur elements had good flame-retardant effect. Moreover, compared with DOPO-DDS and DOPO-DDM, the DOPO-DDE resulted in higher LOI value, which was due to the existence of Ph–O–Ph structures. As for the UL-94 of the resins, it can be found that when the total amount of flame-retardant curing agents is 10 mass%, DOPO-DDE/EP and DOPO-DDS/EP resins could reach the UL-94 V-0 rating, while DOPO-DDM/EP resins could only exhibit a V-1 rating. The electronic pictures of char residues after UL-94 test are shown in Fig. 3. As for the pure epoxy resins, it would burn out without

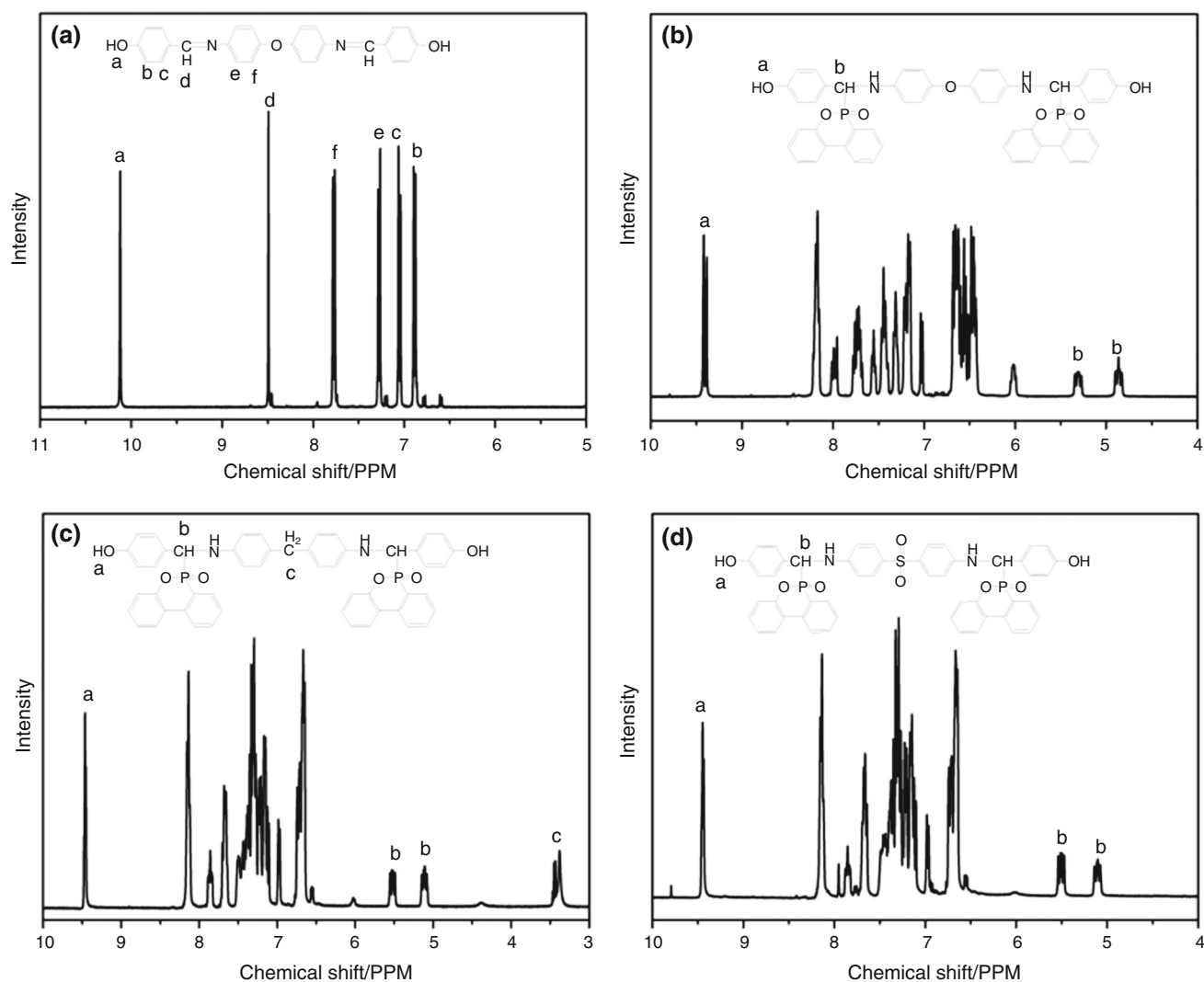


Fig. 2 ^1H NMR of the curing agents (DOPO-DDM, DOPO-DDE and DOPO-DDS)

extinguishing the fire. Compared with the char residues of DOPO-DDM/EP resins, the char residues of both DOPO-DDE/EP and DOPO-DDS/EP resins after UL-94 test are less, but the DOPO-DDE/EP and DOPO-DDS/EP resins had higher LOI values and could reach UL-94 V0 rating. It can be concluded that a significant flame-retardant effect existed when the curing agents contained the sulfur or Ph-O-Ph, and it seems that the DOPO-DDE and DOPO-DDS played flame-retardant roles in the initial heating stages. That phenomenon may be due to the gas-phase flame-retardant principle of DOPO-DDS or the easily catalyzing charring effect of the DOPO-DDE.

The thermal degradation behaviors of EP and flame-retardant EP are investigated by TG under both air and nitrogen atmospheres. Figure 4 shows TG results of the flame-retardant EP in air atmosphere at the heating rate of 20 °C min⁻¹. Epoxy resins have a very small amount of volatiles when the temperature is increased to around 320 °C. As the temperature increased, mass loss increases remarkably and a large quantity of volatiles are produced until almost no residues are left at around 700 °C. The FRs/EP resins are not thermally stable compared with pure EP before 320 °C. This can be explained as follows: The phosphorus in DOPO structures will degrade and form the Lewis acid at high temperature, and the Lewis acid could catalyze the thermal degradation of EP at low temperature, generating more small molecules such as water, alkene and alkane [20]. In the temperature range of 550–700 °C, the DOPO-DDE/EP resins have the highest char residues. It is obvious that the flame-retardant materials with the curing agents containing ether group are more thermally stable at the high temperature than those curing agents containing methylene or sulfone groups. The reason may be attributed to the difference of the char morphologies and compositions among the curing agents. As for the DOPO-DDS/EP resins, the loading of char residues is almost the same with the DOPO-DDM/EP resins, which indicates that the sulfur could play flame-retardant role in the gases phase. The high char residues are very important for the flame retardancy of

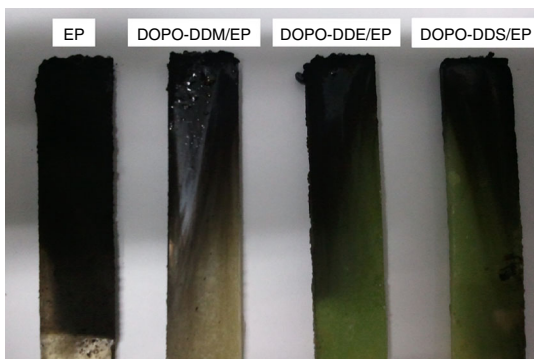


Fig. 3 The char residues of the resins after UL-94 test

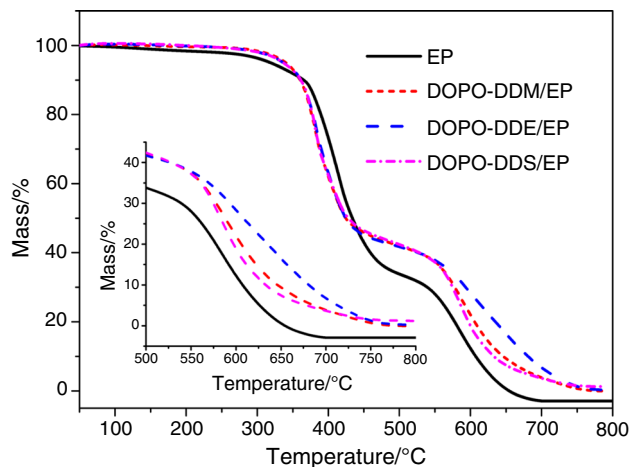


Fig. 4 TG curves of EP and FRs/EP resins under air atmosphere

epoxy resins because it could protect the underlying materials from oxygen and heat, which will result in high flame-retardant efficiency.

Figure 5 shows the resins heated in nitrogen condition at the heating rate of 20 °C min⁻¹. It can be found that the degradation processes of all samples are very different from those under air atmosphere. The thermal degradation process of EP and FRs/EP resins has only one stage, and approximately 78 mass% of the total mass loses occurs at the temperature range between 300 and 450 °C. The char yield increases from 13 mass% to almost 20 mass% at 700 °C when the curing agents are incorporated into the epoxy matrix, which are much higher than the values obtained under air atmosphere. Those results indicate that the incorporation of the flame-retardant curing agents can increase the char yield which can protect the underlying materials from further decomposition. However, compared

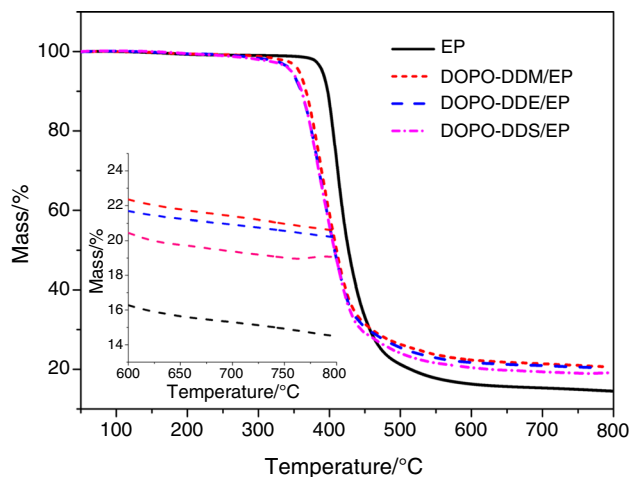


Fig. 5 TG curves of EP and FRs/EP resins under nitrogen atmosphere

with the DOPO-DDE/EP and DOPO-DDM/EP resins, the char residues of the DOPO-DDS/EP resins are less, that may be attributed to the gas-phase flame-retardant mechanism of the sulfur elements.

Generally, the flame-retardant materials with the curing agents containing ether group are more thermally stable at the high-temperature region than the other synthesized curing agents in oxidative conditions [14]. The high char residues in air atmosphere usually result in the high LOI values and UL-94 V0 rating. Because the char yield in air atmosphere contributes great to the flame-retardant efficiency, those curing agents are expected to possess high flame-retardant properties. The high char yield could decrease the production of combustible gases, limit the exothermicity of the pyrolysis reactions and inhibit the thermal conductivity of the burning resins. Those key points may contribute to good flame-retardant properties such as LOI, UL-94, cone calorimeter and MCC results.

The combustion performance of EP and FRs/EP resins

Cone calorimeter can reflect the combustion of polymeric materials in air atmosphere. The fire safety properties, including heat release rate (HRR) and total heat release (THR) of the resins, are shown in Figs. 6 and 7. From HRR of the resins, it can be seen that the decreased peak HRR (pHRR) is actually greater for the FRs/EP resins than for pure EP (1730 kW m^{-2}). Therefore, it can be assumed that the flame-retardant curing agents exhibit good flame-retardant properties when they are incorporated into epoxy resins. The maximum decreases (1190 kW m^{-2}) for DOPO-DDS/EP resins are 30 % in pHRR. As compared to DOPO-DDS/EP resins, DOPO-DDM/EP (1480 kW m^{-2}) and DOPO-DDE/EP resins (1370 kW m^{-2}) had higher

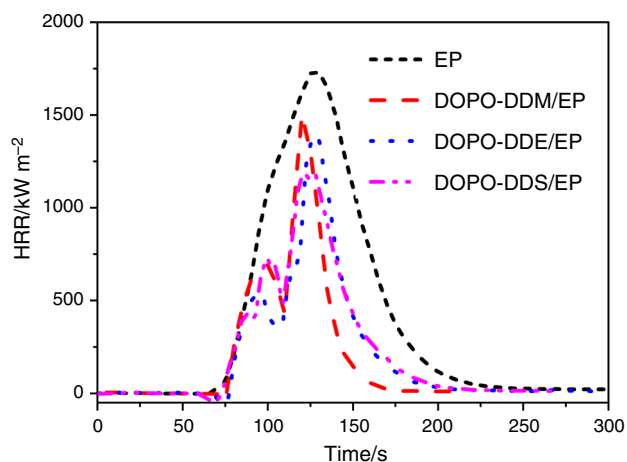


Fig. 6 HRR curves of EP and FRs/EP resins by the cone calorimeter

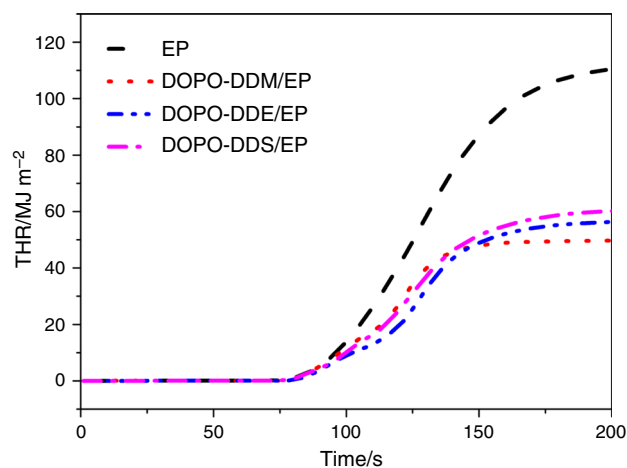


Fig. 7 THR curves of EP and FRs/EP resins obtained from the cone calorimeter

pHRR. That may be ascribed to the combination of condensed flame-retardant mechanism and gases flame-retardant mechanism of the flame-retardant curing agents. Physical barrier effect of the char layers and the gases flame-retardant effect of sulfur result in the decreased pHRR of DOPO-DDS/EP resins. Besides, it can be found that there are two heat release stages during the combustion process of the flame-retardant resins, but as for pure epoxy resins, there is only one heat release stage during the combustion process. That is because the formed char layers of pure epoxy resins could not delay the degradation of EP under drastic measuring thermal radiation, but the flame-retardant resins could form condensed char layers which could delay the degradation of the resins. As a result, the flame retardants will result in the two degradation stages. As shown in Fig. 7, the THR results are in accordance with the pHRR results. Generally, when incorporated into the epoxy matrix, DOPO-DDS has significant effects on reducing pHRR and THR. Pure EP has the highest THR values, while DOPO-DDS/EP resins have the lowest THR values. It seems that enough char layers are formed during the combustion and the sulfur in the gases phase leads to the improved flame-retardant properties.

GOVMARK MCC-2 microscale combustion calorimeter (MCC) is a good and rapid method to evaluate the flammability of polymeric materials in nitrogen atmosphere. Different from cone calorimeter, the MCC results of the samples are related to the thermal degradation in nitrogen atmosphere. The MCC results of the resins are shown in Fig. 8. Similar to the calorimeter cone results, the incorporation of flame-retardant curing agents into epoxy resins can reduce the pHRR of epoxy resins, and the DOPO-DDS/EP resins have the lowest pHRR. Therefore, it can be assumed that the flame-retardant curing agents

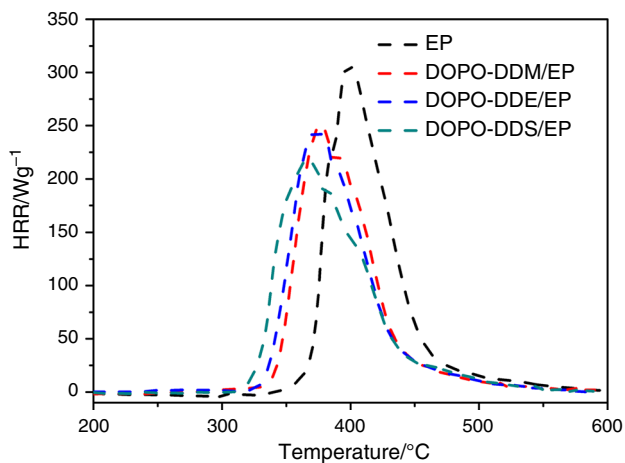


Fig. 8 HRR curves of EP and FRs/EP resins by the microscale combustion calorimeter

exhibit good flame-retardant efficiency at the loading of 10 mass%. However, there is only one degradation peak during the MCC test, which is very different from those during the cone test. The single degradation peak of pHRR during the MCC test is generally relative to the principles of MCC (ASTM D7309-07). There is only one degradation stage in the TG curve of EP resins in nitrogen atmosphere. As a result, the degradation process of EP during the MCC test is in the nitrogen atmosphere and the heat release has only one peak, which are in accordance with the TG results.

To summarize, the introduction of heteroatoms such as O and S into the structures of curing agents can reduce the flammability of epoxy resins and the pHRR and THR of epoxy resins are significantly reduced. It seems that the curing agents with the O and S exhibit better flame-retardant efficiency when they are incorporated into the epoxy resins.

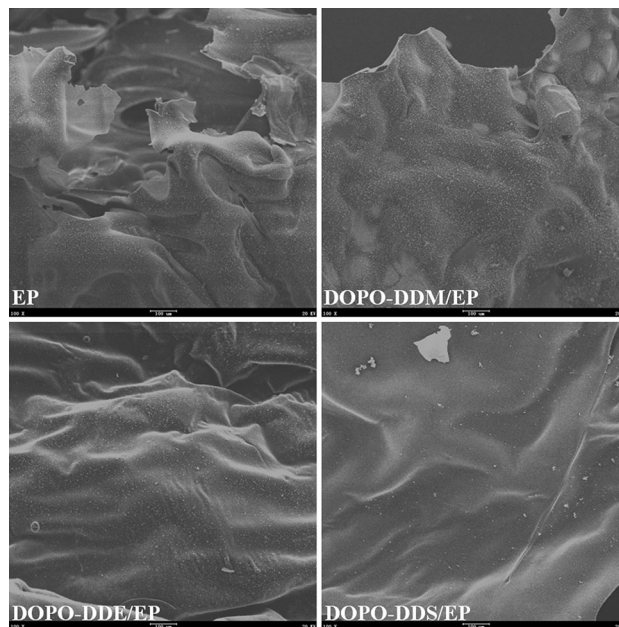


Fig. 10 SEM of the char residues after the cone calorimeter test (a EP, b DOPO-DDM/EP resins, c DOPO-DDS/EP resins and d DOPO-DDE/EP resins)

The residual chars of EP and FRs/EP resins

In order to investigate the relationships between the flame-retardant materials and char formation, the char residues of the polymeric materials after the cone calorimeter are obtained and evaluated, as shown in Figs. 9 and 10. As for the char residues of pure EP in Fig. 9, it is found that the char layer is so wizened that most char layers are caved in and distributed with pores. However, the char layers of flame-retardant resins expanded distinctly, which indicated that condensed char layers were formed during the combustion. As for the char layers of DOPO-DDE/EP resins, large quantities of chars are formed and the char layers

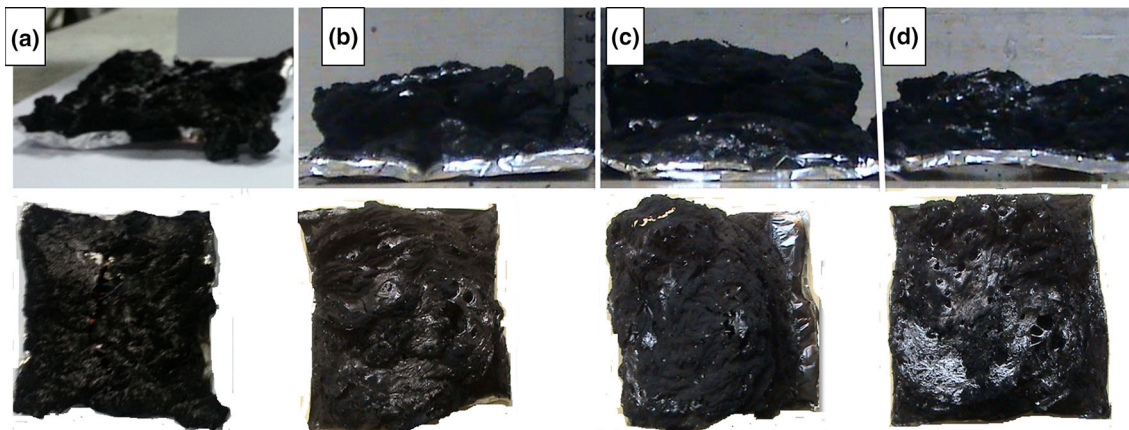


Fig. 9 Electronic picture of char residues after the cone calorimeter

have expanded greatly during the combustion. However, there is no difference between the char layer of DOPO-DDS/EP and DOPO-DDM/EP resins, indicating that the catalyzing charring effect of DOPO-DDS and DOPO-DDM structures is weaker than those of DOPO-DDE. As for the DOPO-DDS/EP resins, the sulfur elements in the curing agent are released into the gases phase, resulting in expanded char layers. The surface morphology of the char layer is a very important criterion to define the efficacy of the flame-retardant curing agents, and the scanning electron microscope (SEM) is adopted, as shown in Fig. 10. Compared with the other char layers, the char layer of EP is easily broken and there are some holes. That is because the phosphorus in the flame-retardant resins could not only catalyze the char formation but also play the roles of cross-linking effect, which have been discussed in the previous work [21–23]. Compared with DOPO-DDM, the DOPO-DDE could catalyze the formation of huge amounts of char layers at around 600 °C effectively, and the DOPO-DDS/EP resins could play its flame-retardant roles in both the condensed and gases phases.

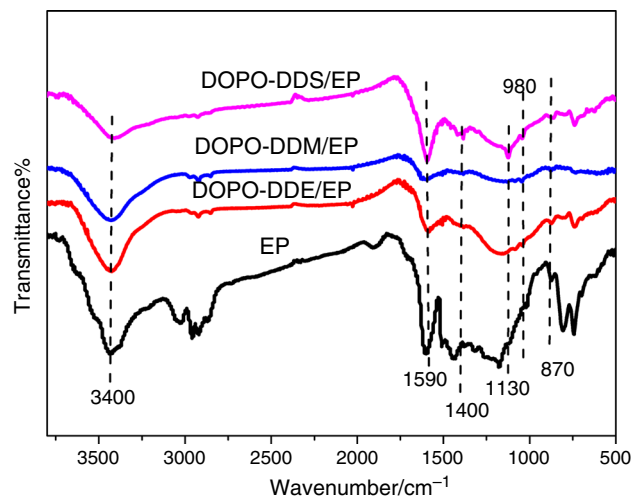


Fig. 12 FTIR of the char residues after the cone calorimeter test

Raman spectroscopy, which is sensitive not only to crystal structures but also to molecular structures, is a powerful tool to analyze carbonaceous materials. The

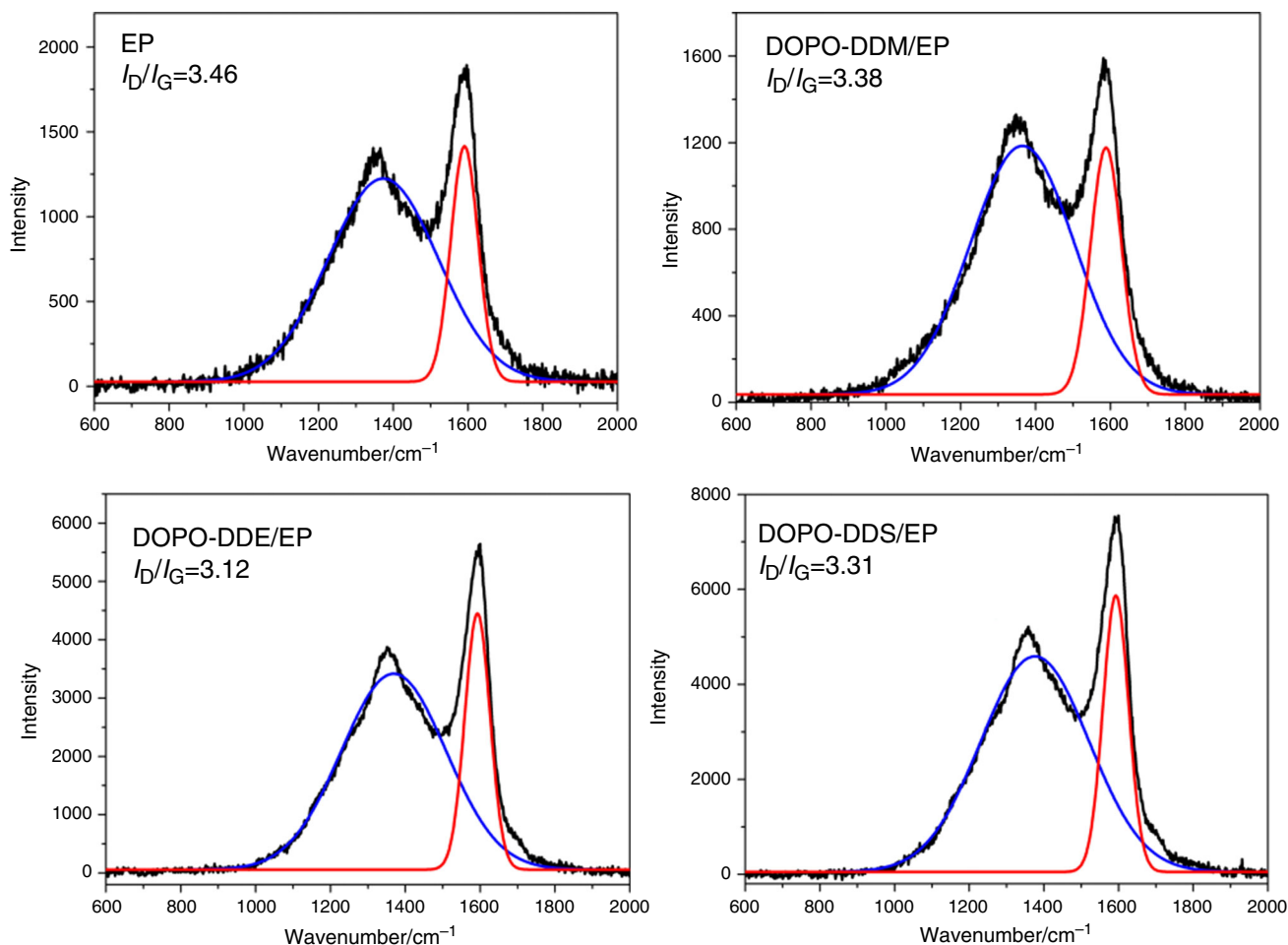
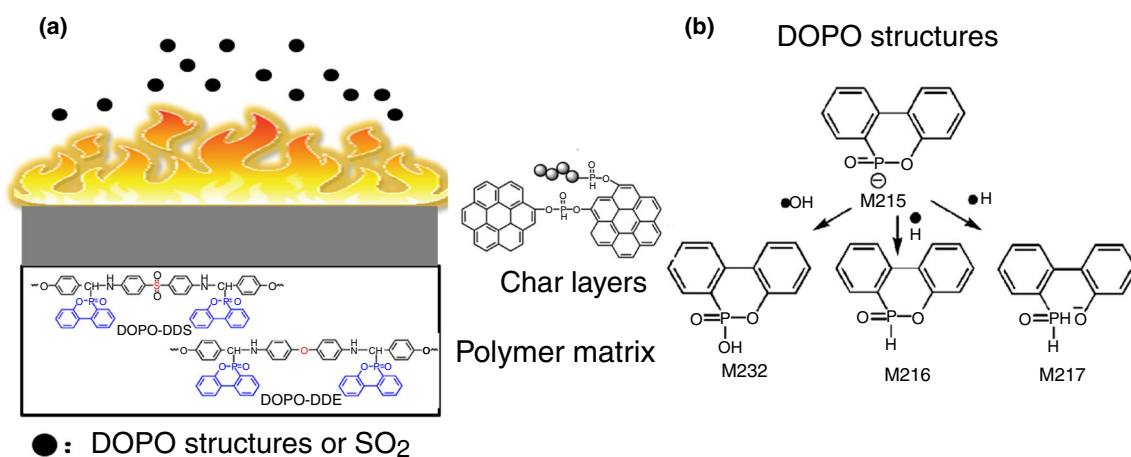


Fig. 11 Raman spectroscopy of the char residues after the cone calorimeter test



Scheme 2 The possible route of the flame-retardant mechanism, **a** thermal degradation of the flame-retardant resins and **b** the thermal degradation of the DOPO structures

Raman spectroscopy of the char residues after the cone calorimeter test is shown in Fig. 11. The spectra usually exhibit two strongly overlapping peaks with intensity maxima at around 1585 and 1360 cm^{-1} . The former band (G band) corresponds to the stretching vibration mode with E_{2g} symmetry in the aromatic layers of the graphite crystalline, and the latter one (D band) is disordered graphite or glassy carbons [24, 25]. The graphitization degree of the char layers is estimated by the ratio of the intensity of the D and G bands (I_D/I_G), where I_D and I_G are the integrated intensities of the D and G bands, respectively. Basically, the lower the ratios of I_D/I_G , the higher the graphitization degree of the char is [14, 24]. According to Fig. 11, the I_D/I_G ratios follow the sequence of DOPO-DDE/EP < DOPO-DDS/EP < DOPO-DDM/EP < EP, indicating that the highest graphitization degree is DOPO-DDE/EP resins. Moreover, the TG results indicated that the incorporation of DOPO-DDE/EP resins could improve the char residue significantly. Thus, based on the Raman spectroscopy, the sample containing an ether group exhibited more condensed char morphologies, associated with a high degree of graphitization. Owing to the special structure of DOPO-DDE, the char strengthen effect of phosphorus and the gases flame-retardant effect of phosphorus, the as-fabricated resins exhibited significant improvements in the flame retardancy. The FTIR spectra of the char residues after the cone test are shown in Fig. 12. Compared with the char residues of pure EP, the broad vibration bands at 980 and 870 cm^{-1} are due to the superposition of stretching vibrations of P–O–P bonds. And the broad peak at around 1130 cm^{-1} is due to the stretching vibration of P=O, which are different from those of pure EP [11, 26]. The intensity of peaks at around 1130 cm^{-1} (DOPO-DDS/EP) is higher than those of DOPO-DDM/EP and DOPO-DDE/EP. Those indicate that the sulfur in the DOPO-DDS structures could

prevent the DOPO from escaping into the air during the combustion process. Meanwhile, sharp absorption peaks at 1590 cm^{-1} are assigned to the stretching vibrations of C=C in the aromatic compounds, but the peak at 1590 cm^{-1} for the EP and DOPO-DDM/EP shifts to higher wave numbers, indicating the incorporations of DOPO-DDS and DOPO-DDE have impact on the formation of phosphorus-based carbons. Those indicate that phosphorus in the curing agent play its flame-retardant roles in the condensed phase, which is in accordance with the previous reports. Moreover, the peak at 1400 cm^{-1} indicates the existence of bands of C–N or –COOH structures. In our previous research, it is found that the DOPO radicals were released into the gas phase during the thermal degradation process of the DOPO-based flame-retardant materials [27] and the DOPO radicals can interact with H or OH radicals in the gas phase, resulting in good flame-retardant efficiency. Moreover, the sulfur in the DDS may release sulfur dioxide during the thermal degradation process. On the basis of the results for volatile pyrolysis products of DOPO structures and the FTIR results of the condensed products, a possible route of the flame-retardant mechanism, as shown in Scheme 2, has been postulated and summarized.

Conclusions

Three DOPO-containing curing agents with weak electron-donating methylene groups, strong electron-withdrawing sulfonyl groups or strong electron-donating ether groups were prepared and incorporated into epoxy resins (EP). The flame-retardant efficiency of the FRs/EP resins is compared, and the mechanism is discussed. Compared with DOPO-DDS/EP and DOPO-DDM/EP resins, the

DOPO-DDE/EP resins present higher LOI values and exhibit better flame-retardant efficiency. The TG results indicate that DOPO-DDE/EP resins have the highest char residues and the high char residues could reduce the pHRR of the resins and impart epoxy resins with high flame-retardant efficiency. Moreover, the DOPO-DDS/EP resins also exhibit good flame-retardant efficiency, which are due to the both condensed and gases flame-retardant mechanisms. The electronic pictures and SEM results of char residues indicated that the flame-retardant EP has more complete char layers. Raman spectroscopy of the resins shows that DOPO-DDE/EP resins create more graphitization carbon as it thermally decompose, which are the main reasons for the high flame-retardant efficiency. This work not only provides novel epoxy resins with good thermal stability, but also will trigger more scientific interest in the development and investigation of the structure–property relationships of the DOPO-based flame retardants.

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References

- Sandler J, Shaffer MSP, Prasse T, Bauhofer W, Schulte K, Windle AH. Development of a dispersion process for carbon nanotubes in an epoxy matrix and the resulting electrical properties. *Polymer*. 1999;40:5967–71.
- Fu SY, Feng XQ, Lauke B, Mai YW. Effects of particle size, particle/matrix interface adhesion and particle loading on mechanical properties of particulate-polymer composites. *Compos Part B Eng*. 2008;39:933–61.
- Jiao CM, Zhou JL, Chen XL, Li SX, Wang H. Flame retardant epoxy resin based on bisphenol A epoxy resin modified by phosphoric acid. *J Therm Anal Calorim*. 2013;114:253–9.
- Morgan AB. Flame retarded polymer layered silicate nanocomposites: a review of commercial and open literature systems. *Polym Adv Technol*. 2006;17:206–17.
- Levchik S, Piotrowski A, Weil E, Yao Q. New developments in flame retardancy of epoxy resins. *Polym Degrad Stab*. 2005;88:57–62.
- Lu SY, Hamerton I. Recent developments in the chemistry of halogen-free flame retardant polymers. *Prog Polym Sci*. 2002;27:1661–712.
- Gao F, Tong LF, Fang ZP. Effect of a novel phosphorous-nitrogen containing intumescent flame retardant on the fire retardancy and the thermal behaviour of poly(butylene terephthalate). *Polym Degrad Stab*. 2006;91:1295–9.
- Du LC, Qu BJ, Xu ZJ. Flammability characteristics and synergistic effect of hydrotalcite with microencapsulated red phosphorus in halogen-free flame retardant EVA composite. *Polym Degrad Stab*. 2006;91:995–1001.
- Nie SB, Zhang MX, Yuan SJ, Dai GL, Hong NN, Song L, Hu Y. Thermal and flame retardant properties of novel intumescent flame retardant low-density polyethylene (LDPE) composites. *J Therm Anal Calorim*. 2012;109:999–1004.
- Nie SB, Qi SH, He MS, Li BX. Synergistic effects of zeolites on a novel intumescent flame-retardant low-density polyethylene (LDPE) system. *J Therm Anal Calorim*. 2013;114:581–7.
- Wang X, Hu Y, Song L, Xing WY, Lu HDA, Lv P, Jie GX. Flame retardancy and thermal degradation mechanism of epoxy resin composites based on a DOPO substituted organophosphorus oligomer. *Polymer*. 2010;51:2435–45.
- Gaan S, Liang SY, Mispreuve H, Perler H, Naescher R, Neisius M. Flame retardant flexible polyurethane foams from novel DOPO-phosphoramidate additives. *Polym Degrad Stab*. 2015;113:180–8.
- Vasiljevic J, Jerman I, Jaksa G, Alongi J, Malucelli G, Zorko M, Simoncic B. Functionalization of cellulose fibres with DOPO-polysilsesquioxane flame retardant nanocoating. *Cellulose*. 2015;22:1893–910.
- Tai QL, Hu Y, Yuen RKK, Song L, Lu HD. Synthesis, structure–property relationships of polyphosphoramides with high char residues. *J Mater Chem*. 2011;21:6621–7.
- Jiang P, Gu XY, Zhang S, Wu SD, Zhao Q, Hu ZW. Synthesis, characterization, and utilization of a novel phosphorus/nitrogen-containing flame retardant. *Ind Eng Chem Res*. 2015;54:2974–82.
- Dai K, Song L, Yuen RKK, Jiang SH, Pan HF, Hu Y. Enhanced properties of the incorporation of a novel reactive phosphorus- and sulfur-containing flame-retardant monomer into unsaturated polyester resin. *Ind Eng Chem Res*. 2012;51:15918–26.
- Chao PJ, Li YJ, Gu XY, Han DD, Jia XQ, Wang MQ, Wang T. Novel phosphorus–nitrogen–silicon flame retardants and their application in cycloaliphatic epoxy systems. *Polym Chem UK*. 2015;6:2977–85.
- Liu YL. Flame-retardant epoxy resins from novel phosphorus-containing novolac. *Polymer*. 2001;42:3445–54.
- Lin CH. Synthesis of novel phosphorus-containing cyanate esters and their curing reaction with epoxy resin. *Polymer*. 2004;45:7911–26.
- Liu YL, Hsiue GH, Chiu YS. Synthesis, characterization, thermal, and flame retardant properties of phosphate-based epoxy resins. *J Polym Sci Polym Chem*. 1997;35:565–74.
- Hsiue GH, Shiao SJ, Wei HF, Kuo WJ, Sha YA. Novel phosphorus-containing dicyclopentadiene-modified phenolic resins for flame-retardancy applications. *J Appl Polym Sci*. 2001;79:342–9.
- Bugajny M, Bourbigot S, Le Bras M, Delobel R. The origin and nature of flame retardance in ethylene-vinyl acetate copolymers containing hostaflam AP 750. *Polym Int*. 1999;48:264–70.
- Qian XD, Song L, Hu Y, Yuen RKK. Preparation and thermal properties of novel organic/inorganic network hybrid materials containing silicon and phosphate. *J Polym Res*. 2012;19:1–10.
- Sadezky A, Muckenhuber H, Grothe H, Niessner R, Poschl U. Raman micro spectroscopy of soot and related carbonaceous materials: spectral analysis and structural information. *Carbon*. 2005;43:1731–42.
- LeBras M, Bourbigot S, LeTallec Y, Laureyns J. Synergy in intumescence—application to beta-cyclodextrin carbonisation agent intumescent additives for fire retardant polyethylene formulations. *Polym Degrad Stab*. 1997;56:11–21.
- Qian XD, Song L, Hu Y, Yuen RKK, Chen LJ, Guo YQ, Hong NN, Jiang SH. Combustion and thermal degradation mechanism of a novel intumescent flame retardant for epoxy acrylate containing phosphorus and nitrogen. *Ind Eng Chem Res*. 2011;50:1881–92.
- Qian XD, Song L, Hu Y, Yuen RKK. Thermal degradation and flammability of novel organic/inorganic epoxy hybrids containing organophosphorus-modified oligosiloxane. *Thermochim Acta*. 2013;552:87–97.