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The influence of the phosphorus-based flame retardant on the flame retardancy of the epoxy resins

Wenchao Zhang [a, b], Xiangdong He [a], Tinglu Song [a], Qingjie Jiao [b], Rongjie Yang [a, *]

[a] Beijing Institute of Technology, School of Materials, National Engineering Technology Research Center of Flame Retardant Materials, 5 South Zhongguancun Street, Haidian District, Beijing 100081, PR China
[b] Beijing Institute of Technology, School of Mechatronical Engineering, PR China

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ABSTRACT

A series of flame-retarded epoxy resins (EPs) have been prepared loaded with PEPA (1-oxo-4-hydroxymethyl-2,6,7-trioxa-l-phosphabicyclo[2.2.2] octane), APP (Ammonium polyphosphate), and DOPO (9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide), respectively with or without OPS (Octaphenyl polyhedral oligomeric silsesquioxane). The different influences of PEPA, APP, and DOPO due to their different chemical structures are detected by the HRR, p-HRR, TSR, and SEA results after cone calorimeter test. Coupled with TGA analysis, the PEPA shows more condensed phase flame retardancy and the DOPO shows a more gas phase flame retardancy action are detected. The gas phase and condensed phase of EP or EP/OPS composites with PEPA, APP, and DOPO are investigated by the TGA-FTIR, visual observation, and FTIR. It is considered that the kind of phosphorus-containing flame retardants decide the structure of char layer of epoxy resins, which could seriously affect their flame retardant performance. Furthermore, The flame retardancy of these EPs are tested by the LOI, UL-94, which indicates that the model of flame retardancy of samples are decided by the chemical structure of phosphorus flame retardants, the synergy of OPS could reinforce this kind of action.

1. Introduction

Epoxy resins show advantageous properties such as: ease of processing, low cost, good mechanical properties, and environmental advantages [1–4]. They are commonly used as advanced composites matrices in electronic/electric industries where a remarkable flame-retardant grade is required, but the fire risk is a major drawback of these materials [5]. Traditionally, halogenated compounds are widely used as co-monomers or additive with epoxy resins to obtain fire-retardant materials. However, flame-retardant epoxy resins containing bromine or chlorine can produce poisonous and corrosive smoke and may give super toxic halogenated dibenzodioxins and dibenzofurans [6–8]. Therefore, the preparation and application of halogen-free flame retardants is the subject of extensive investigation.

Phosphorus-containing compounds have shown promising application as halogen-free, flame retardants in epoxy resins [9–11]. On one hand, the PO• radical and HPO produced by the pyrolysis of phosphorus-containing flame retardant could react with the radicals of H• and •OH, thus reducing the energy of flame in the gas phase. On the other hand, they generally convert into polyphosphoric acid in the solid phase during decomposition, consequently catalyzing the formation of a protective carbonaceous layer, which is highly thermal stability and can retard further decomposition of polymer chains.

9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) is a type of cyclic phosphate with a diphenyl structure, which has high thermal stability, good oxidation resistance, and good water resistance [12–15]. The DOPO is popular phosphorus-containing FR which could react with epoxy monomer, using DOPO or its derivatives as flame retardant for epoxy resins have been reported [16–19]. Furthermore, the intumescent flame retardants (IFRs) have been considered to be a promising method, which is due to the fact that they are low-toxicity, low-smoke, halogen-free, and very efficient [20–22]. A typical intumescent system comprises an acid source, a carbon source, and a gas source [23]. The compounds used as an acid source are generally inorganic acids or precursor of the acids, for example ammonium polyphosphate (APP), which is a common IFR. In addition, among the organophosphorus flame retardants, caged bicyclic phosphates

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* Corresponding author. Tel.: +86 10 6891 2927.
E-mail address: yrj@bit.edu.cn (R. Yang).

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have attracted much interest, and many investigations have been reported [24]. It is found that caged bicyclic phosphates and their derivatives can serve as effective intumescent flame retardants or charring agent in some polymers [24,25]. One caged bicyclic phosphates PEPA (1-oxo-4-hydroxymethyl-2,6,7-trioxa-l-phosphabicyclo[2.2.2] octane), which also is a reactive phosphorus-containing FR was combined into epoxy resins to obtain halogen-free flame retardant systems.

In this study, the DOPO, APP, and PEPA (Fig. 1) used as flame retardants for the epoxy resins, with the purpose that studying the chemical environment of P element influence on the flame retardant efficiency for epoxy resins. Furthermore, in our previously study, an interesting phenomenon, termed the “blowing-out effect”, has been detected in flame-retarded epoxy resins with P/Si hybrid flame retardants loading [26,27]. So the DOPO, APP, or PEPA is coupled with OPS (octaphenyl silsesquioxane) to flame retard the epoxy resins that are used to reveal the chemical structures of phosphorus-based flame retardant influence on synergy of P/Si hybrid and blowing-out effect. Therefore, the details of fire behaviors of flame-retarded EP composites are investigated seriously in this paper.

2. Experimental

2.1. Materials

Diglycidyl ether of biphenol A (DGEBA, E-44, epoxy equivalent = 0.44 mol/100 g) was purchased from FeiCheng DeYuan Chemicals CO., LTD. The 4, 4′-diaminodiphenylsulphone (DDS) was purchased from TianJin GuangFu Fine Chemical Research Institute. 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was purchased from Eutec Trading (Shanghai) Co., Ltd. Octaphenyl polyhedral oligomeric silsesquioxane (OPS) (Fig. 1) was synthesized in our laboratory with perfect T_8 cage [28]. Ammonium polyphosphate (APP) was supplied by Shandong Saida Chemical Co., Ltd. PEPA (1-oxo-4-hydroxymethyl-2,6,7-trioxa-l-phosphabicyclo[2.2.2] octane) was purchased from Alfa–Aesar chemical industry company.

2.2. Preparation of the cured epoxy resins

The cured epoxy resins were obtained using a thermal curing process. At first, the flame retardants were dispersed in DGEBA by mechanical stirring at 140 °C for 1 h and it would disperse in DGEBA. The mixture is homogeneous liquid always. After that, the curing agent DDS was then added relative to the amount of DGEBA. The equivalent weight ratio of DGEBA to DDS was 9:2. The epoxy resins were cured at 180 °C for 4 h. The LOI and UL-94 test samples were strips. The contents of the flame retardant in the EP composites are listed in Table 1.

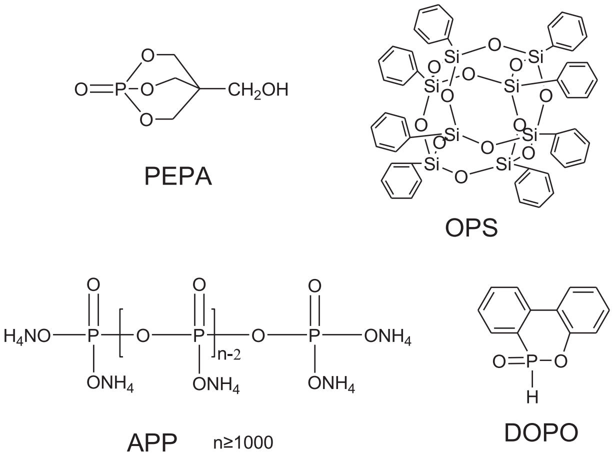

Fig. 1. Typical chemical structures of flame retardants.

Table 1
Composition of the investigated materials (wt.%).

Samples	Cured epoxy resins	OPS	PEPA	APP	DOPO	Si content	P Content
Pure EP	100.0	/	/	/	/	/	/
EP/PEPA	94.8	/	5.2	/	/	/	0.90
EP/APP	97.1	/	/	2.9	/	/	0.90
EP/DOPO	93.7	/	/	/	6.3	/	0.90
EP/OPS	95.9	4.1	/	/	/	0.90	/
EP/OPS/PEPA	95.3	2.1	2.6	/	/	0.45	0.45
EP/OPS/APP	96.5	2.1	/	1.4	/	0.45	0.45
EP/OPS/DOPO	94.8	2.1	/	/	3.1	0.45	0.45

2.3. Measurements

The limiting oxygen index (LOI) was obtained using the standard GB/T2406–93 procedure, which involves measuring the minimum oxygen concentration required to support candle-like combustion of plastics. An oxygen index instrument (Rheometric Scientific Ltd.) was used on barrel-shaped samples of dimensions 100 × 6.5 × 3 mm^3. Vertical burning tests were performed using the UL-94 standard on samples of dimensions 125 × 12.5 × 3.2 mm^3. In this test, the burning grade of a material was classified as V-0, V-1, V-2 or NR (unclassified), depending on its behavior (dripping and burning time).

Thermal gravimetric analysis (TGA) was performed with a Netzsch 209 F1 thermal analyzer, with the measurements carried out in a nitrogen atmosphere at a heating rate of 20 °C/min from 40 °C to 800 °C. 10 mg sample was used for each measurement, with a gas flow rate of 60 ml/min. The typical results from TGA were reproducible within ±1%, and the reported data are average value from three measurements.

Cone calorimeter measurements were performed according to ISO 5660 protocol at an incident radiant flux of 50 kW/m^2. The equipment is Fire Testing Technology apparatus with a truncated cone-shaped radiator. The specimen (100 × 100 × 3 mm^3) was measured horizontally without any grids. Typical results from the cone calorimeter tests were reproducible within ±10%, and the reported parameters are the average from three measurements.

For the SEM analysis, the exterior char is taken on the top part of char residues after cone test. Scanning electron microscopy (SEM) experiments were performed with a Hitachi S-4800 scanning electron microscope.

To investigate the condensed phase of the EP composites, all the cone calorimeter tests stopped at 500 s. The residue was cooled under room condition. The exterior char was grinded and analyzed by FTIR (Nicolet 6700) in mode of ATR.

3. Results and discussion

3.1. Cone calorimetry analysis of the cured epoxy resins

The cone calorimeter is one of the most effective bench-scale methods for studying the flammability of materials. The cone calorimeter could give many concerned combustion parameters include time to ignition (TTI), heat release rate (HRR), peak of heat release rate (p-HRR), total heat release (THR), total smoke release (TSR) and mean specific extinction area (mean SEA). These parameters are reported in Table 2 for different samples.

Table 2
Cone calorimeter data for the EP composites.

Samples	TTI (s)	p-HRR (kW/m^2)	THR (MJ/m^2)	TSR (m^2/m^2)	Mean SEA (m^2/kg)	Mean COY (kg/kg)	Mean CO$_2$Y (kg/kg)
Pure EP	50 ± 2	860 ± 22	112 ± 3	4182 ± 210	897 ± 30	0.07 ± 0.01	1.82 ± 0.01
EP/PEPA	53 ± 2	538 ± 24	78 ± 2	3196 ± 156	936 ± 34	0.11 ± 0.01	2.00 ± 0.01
EP/APP	61 ± 2	1087 ± 30	96 ± 2	3782 ± 190	974 ± 23	0.11 ± 0.01	2.16 ± 0.01
EP/DOPO	55 ± 1	684 ± 28	76 ± 1	3800 ± 186	1324 ± 39	0.13 ± 0.01	1.67 ± 0.01
EP/OPS	55 ± 1	626 ± 30	112 ± 2	3729 ± 188	899 ± 35	0.08 ± 0.01	2.00 ± 0.01
EP/OPS/PEPA	52 ± 2	524 ± 25	84 ± 2	3594 ± 193	961 ± 36	0.10 ± 0.01	1.96 ± 0.01
EP/OPS/APP	63 ± 2	584 ± 28	101 ± 3	3895 ± 212	943 ± 38	0.09 ± 0.01	2.05 ± 0.01
EP/OPS/DOPO	55 ± 1	548 ± 23	83 ± 2	3899 ± 160	1039 ± 43	0.13 ± 0.01	1.91 ± 0.01

TTI is used to determine the influence of flame retardant on ignitability. A clear increase of TTI is detected after loading with PEPA, APP, and DOPO in EP or EP/OPS composites. Especial for the epoxy composites with APP, their TTI increases from 50 s to 61 s and 63 s. These increases of TTI are very valuable for enhancement of the flame retardancy properties of epoxy resins.

The HRR curves and the p-HRR values for the different samples are presented in Fig. 2 and Table 2. Although the content of P element is same (0.9 wt.%), different chemical structure of PEPA, APP, and DOPO have leaded different combustion behaviors as shown in the HRR curves in Fig. 2. It was observed that the pure EP burns rapidly after ignition and HRR reaches a sharp peak with a peak heat release rate (p-HRR) of 860 kW/m^2. As shown in Fig. 2, to my surprise, when the EP loaded with 2.9wt.% APP (P content about 0.9wt.%), the peak of HRR curve of EP/APP is more higher and sharp. This result indicates that the EP/APP composite combust rapidly and reach flashover quickly after ignition. The inorganophosphorus flame retardants APP accelerate combustion of EP matrix rather than prevent it from fire. This result may be caused by that APP is just additive-type FR. For the organophosphorus flame retardants PEPA and DOPO, the p-HRR of flame-retarded EP is much lower than pure EP. The p-HRR of EP/PEPA and EP/DOPO are 538 kW/m^2 and 684 kW/m^2. The caged bicyclic phosphates PEPA could reduce the p-HRR of EP composites more effective than that of cyclic phosphate DOPO did. In the EP/OPS composites, APP, PEPA, and DOPO show a same trend as they did in the EP composites. The caged bicyclic phosphates PEPA has the best performance to reduce the p-HRR of EP/OPS composite, and that performance of the inorganophosphorus flame retardants APP is poor in Fig. 2.

As shown in Table 2, the THR of EP composites are lower than that of pure EP. The THR of EP/APP is 96 MJ/m^2, however, the THR of the EP/PEPA and EP/DOPO are 78 MJ/m^2 and 76 MJ/m^2. The organophosphorus flame retardants PEPA and DOPO perform better than that of inorganophosphorus flame retardants APP. When we compared performance of EP/PEPA and EP/DOPO, although they have similar THRs, the TSR and mean SEA of EP/PEPA are much lower than that of EP/DOPO. Furthermore, in Table 2, we find that the mean CO yield of EP/PEPA is 0.11 kg/kg which is lower than 0.13 kg/kg of EP/DOPO, at the same time, the mean CO$_2$ yield of EP/PEPA is 2.00 kg/kg which is higher than 1.67 kg/kg of EP/DOPO. Considering the results above, the higher smoke release and CO yield of EP/DOPO indicates that DOPO shows a more gas phase flame retardancy action than that of PEPA did. On the contrast, the PEPA shows a more condensed phase flame retardancy action than that of DOPO did. It was reported that flame retardants containing phosphorus can reduce polymer flammability by their ability to form gaseous intermediates which scavenge flame propagating free radicals (OH, H…) thereby inducing incomplete combustion. The incomplete-oxidation products are the main reasons for the CO and smoke emission [29,30], that is the gas phase flame retardancy mechanism of the phosphorus-containing flame retardant. The similar performance of DOPO and PEPA can be detected in the EP/OPS/PEPA and EP/OPS/DOPO composites.

Summarizing the conclusions above, we can find that the organophosphorus PEPA and DOPO shows better flame retardancy effective on the epoxy resins than that of inorganophosphorus flame retardant APP did. Furthermore, in this research, we find the DOPO perform better gas phase flame retardancy action, but the PEPA have better condensed phase flame retardancy action. Different chemical environment of P element in PEPA, APP, or DOPO make them showed different flame retardant efficiency for epoxy resins.

3.2. TGA analysis of the cured epoxy resins

In order to reveal the reasons of different flame retardant efficiency among the PEPA, APP, and DOPO, the thermal stability of the EP composites was investigated by TGA. The relevant thermal decomposition data, including the T_{onset}, defined as the temperature at which 5% weight loss occurs, the T_{max} defined as the temperatures at maximum weight loss rate, and the char residues at 800 °C, are given in Table 3.

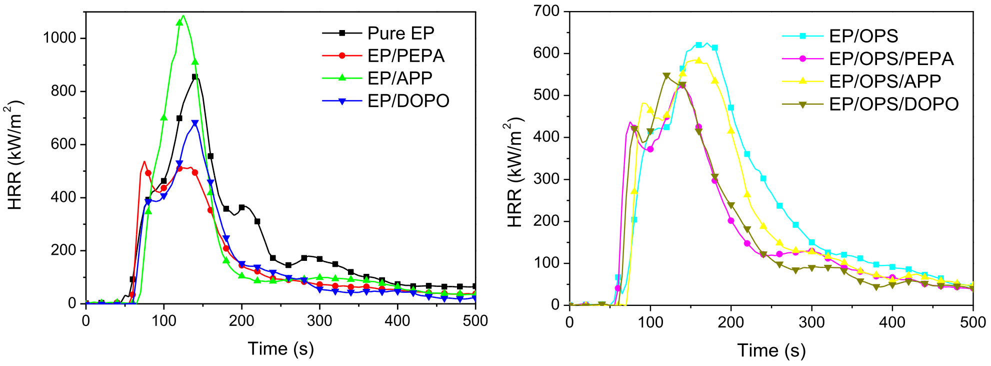

Fig. 2. Heat release rate curves of the flame-retarded EP composites.

Table 3
TGA data of EP composites in nitrogen.

Samples	T_{onset} (°C)	T_{max} (°C)	Residues at 800 °C (%)
Pure EP	395	431	12.0
EP/PEPA	349	390	26.1
EP/APP	376	410	20.2
EP/DOPO	365	394	16.8
EP/OPS	401	427	17.8
EP/OPS/PEPA	357	398	22.8
EP/OPS/APP	375	416	21.0
EP/OPS/DOPO	376	404	18.8

As shown in Table 3, with the PEPA, APP, or DOPO incorporation, the T_{onset} and T_{max} of EP and EP/OPS composites reduce obviously. Furthermore, in Table 3, we can detect that the T_{onset} and T_{max} of EP and EP/OPS composites with APP are clearly higher than that with PEPA and DOPO. This result indicates that the EP and EP/OPS composites with APP possess higher thermal stability under heat flux, which could explain the reason well that the TTI of EP and EP/OPS composites with APP are longer than other flame retarded samples. The TGA curves of EP composites are shown in Fig. 3, although the EP and EP/OPS composites with PEPA, APP, or DOPO have different thermal stability, their decomposition trend are similar. As shown in Table 3, the char residues of EP and EP/OPS composites with PEPA, APP, or DOPO at 800 °C are evidently higher than that of pure EP and EP/OPS. The char residue of EP/PEPA > EP/APP > EP/DOPO and the char residue of EP/OPS/PEPA > EP/OPS/APP > EP/OPS/DOPO. Although the EP composites with PEPA possess highest char residue and the EP composites with DOPO possess lowest char residue, they have almost same total heat release as shown in the cone calorimeter analysis section. The huge difference of char yield and same total heat release between EP/PEPA and EP/DOPO (EP/OPS/PEPA and EP/OPS/DOPO) composites proof again from another point of view that the PEPA shows the more condensed phase flame retardancy and the DOPO shows a more gas phase flame retardancy action. For the poor performance of APP on flame retarding EP in this research, it cannot be explained in this stage.

3.3. *Gas phase analysis of the cured epoxy resins*

In order to reveal the reasons that the chemical structures of phosphorus-based flame retardant influence on the flame retardant efficiency for epoxy resins, the pyrolytic gases produced by the epoxy resins composites in a nitrogen atmosphere have been investigated using TGA coupled with FTIR. The FTIR spectra of the pyrolytic gas products at T_{max} are shown in Fig. 4.

The major pyrolytic gases detected from the decomposition of EP composites and EP/OPS composites are phenol derivatives/water (3650 cm^{-1}), aromatic components (3036, 1604, 1510, and 1340 cm^{-1}), aliphatic components (3016, 2972, 2930 and 2869 cm^{-1}) and ester/ether components (1748, 1257, and 1181 cm^{-1}) [24,31]. As shown in Fig. 4, although the gas species from the EP composites and EP/OPS composites with or without PEPA, APP, and DOPO are almost same, the PEPA reduce the absorbance intensity of EP/PEPA and EP/OPS/PEPA clearly. In addition, it should be noted that no change of pyrolytic gases species is observed among the epoxy resins loaded with PEPA, APP, and DOPO. It is probable that some new absorbance bands, such as 1260 cm^{-1} (P=O), 1118 cm^{-1} (–P–O–P–O–), coincide with the characteristic peaks of the EP matrix [25].

Releases of aromatic and aliphatic components as a function of temperature for the epoxy composites are shown in Fig. 5 and Fig. 6. As shown in Figs. 5 and 6, the speeds of release of aliphatic and aromatic components of epoxy resins are decided by the kind of phosphorus-based flame retardants (DOPO > APP > PEPA). For the PEPA, it makes the absorbance intensity of gases released from the pure EP reduce more than 60%, which indicates that addition of PEPA could keep more aromatic and aliphatic structures in the char residues. This result corresponds well the conclusion that the PEPA shows the more condensed phase flame retardancy. For the DOPO, it makes the absorbance intensity of aliphatic and aromatic components higher than that of pure EP. The quick release of aliphatic and aromatic components means more fuel supplied in unit time. But as discussed in the cone analysis section, the EP/DOPO has same total heat release compared with EP/PEPA. This result proof again that the DOPO could play an important role of gas phase flame retardancy. For the APP, it makes EP/APP show middle release speed of aliphatic and aromatic components. However, the EP/APP has bad performance in cone test. This result indicates that the inorganophosphorus flame retardant APP neither plays a good condensed phase action like PEPA nor plays a good gas phase action like DOPO in the EP at low loading (P content 0.9 wt.%). In many researches, the APP could only play good flame retardancy in the EP when its content reach or exceed 10 wt.% (P content 3 wt.%) [32]. Gas phase analysis can only partly explain the reason that why the PEPA, APP, or DOPO has different flame retardant efficiency for epoxy resins. The different flame retardancy of PEPA, APP, or DOPO must have some relationship with their action in the condensed phase.

3.4. *Condensed phase analysis of the cured epoxy resins*

3.4.1. *Visual observation*

After the cone calorimeter tests, some valuable information was obtained by visual observation of the residues (Fig. 7). As shown in

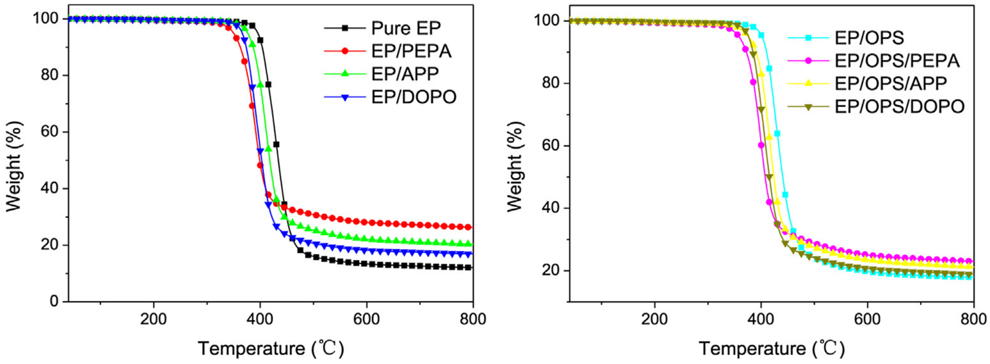

Fig. 3. TGA curves of EP composites in N_2.

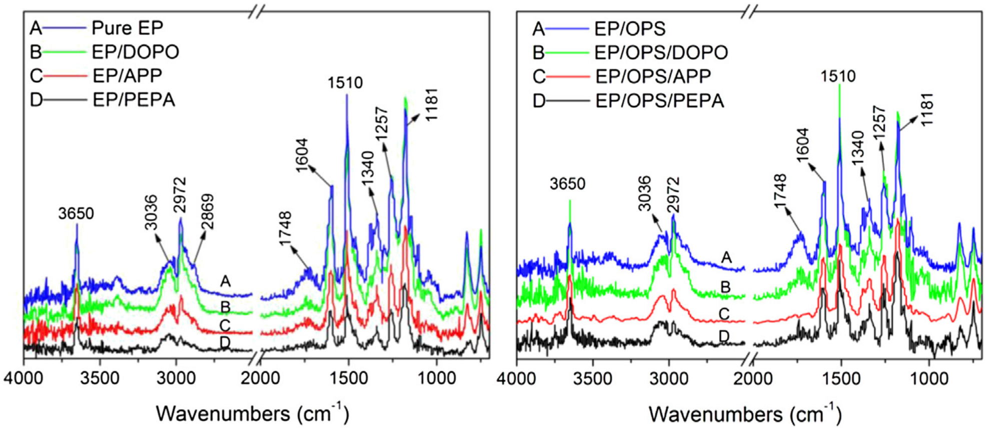

Fig. 4. FTIR spectra of pyrolytic products of EP composites and EP/OPS composites at T_{max}.

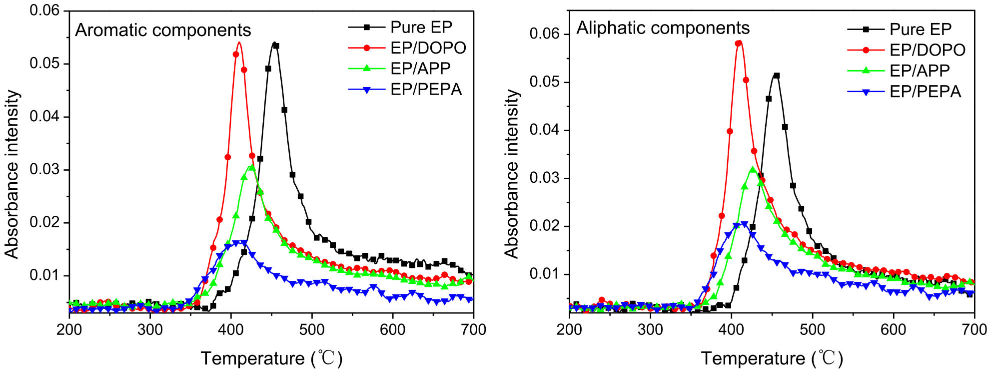

Fig. 5. The aromatic and aliphatic components release with temperature according to TG-FTIR spectra of EP composites.

Fig. 7, there is no obvious char for the pure EP, whereas the char layer for EP/OPS appeared distinctly intumescent and was covered with white silicon dioxide (SiO_2) of continuous construction, which was combined with the carbonaceous layer. Although the pure EP and EP/OPS showed different profiles, the EP composites and EP/OPS composites have almost same morphology after loaded with same phosphorus-containing flame retardants (PEPA, APP, or DOPO). However, it should be noticed that different phosphorus-containing flame retardants make structures of char layer changed a lot.

For the EP/PEPA and EP/OPS/PEPA, they have a highly crosslinked char layer, which is whole and strong. This char layer obviously holds the shape of the test sample, but just swells and arches slightly. This crosslinked and strong char layer could slow the decomposition and combustion of EP matrix. This is the reason that the PEPA could show good condensed phase flame retardancy.

In the case of EP/APP and EP/OPS/APP, they have obviously swell char layer, but many holes which interconnected from top to bottom can be detected on the surface these char layer, moreover, big cavities are created under these char layer. The interconnected holes could transport the decomposition products to the surface and supplied oxygen to interior. The big cavities under the char layer reveal that their char layer possess low crosslinking yield. The interconnected holes and big cavities just could explain the reason that why the EP/APP and EP/OPS/APP have poor flame retardancy.

For the EP/DOPO and EP/OPS/DOPO, they have obviously swell char layer also. The EP/DOPO shows a continuous and flawless lamellar char layer, and the EP/OPS/DOPO have more continuous

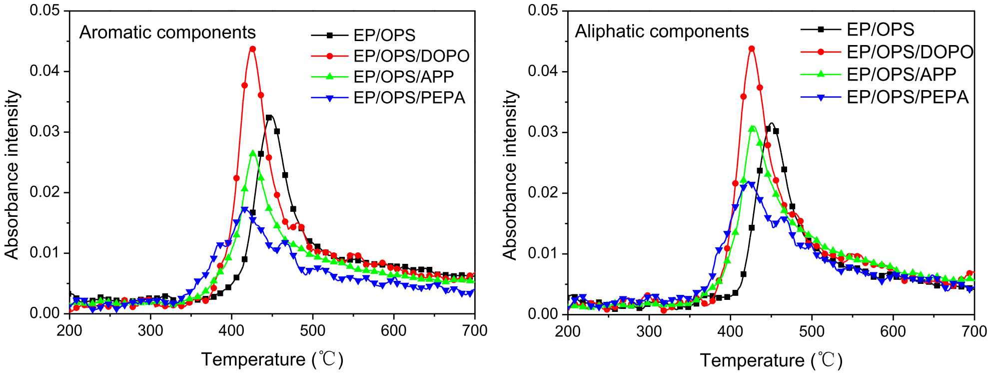

Fig. 6. The aromatic and aliphatic components release with temperature according to TG-FTIR spectra of EP/OPS composites.

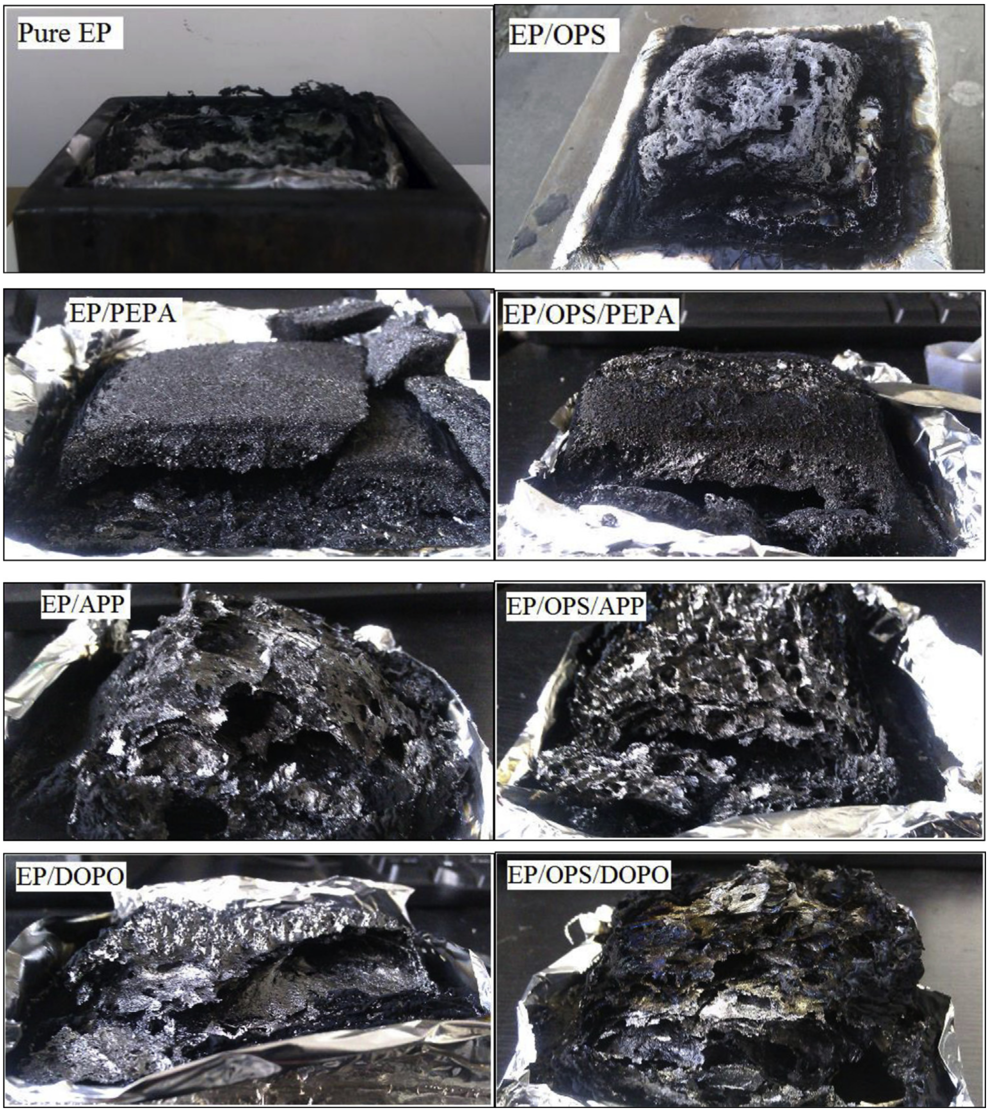

Fig. 7. Photographs of chars from EP composites after the cone calorimeter test.

lamellar char layer. The char layers of EP/DOPO and EP/OPS/DOPO have obviously better protection function than that of EP/APP and EP/OPS/APP.

From the visual observation analysis above, we can conclude that the kind of phosphorus-containing flame retardants decide the structure of char layer of epoxy resins, which could seriously affect their flame retardant performance.

3.4.2. SEM analysis

SEM images of the exterior chars from flame-retarded EPs are shown in Fig. 8. It can be seen that the chars of EP/PEPA and EP/OPS/PEPA exhibited a crosslinked structure, which corresponds well with the visual observation of the char of them. For the char of EP/APP, the obviously crack can be observed which is the channel for the transmit heat and fuel. However, the char of EP/OPS/APP shows a continual char layer, which could play a good protection for the EP matrix and reduce the p-HRR. For EP/OPS and EP/OPS/DOPO, their char layers exhibited a continuous membrane-like microscopic structure. Furthermore, we can observe that the OPS make the char layer more integrated.

From the SEM analysis above, we can proof again that the kind of phosphorus-containing flame retardants decide the microscopic structure of char layer of epoxy resins, and the OPS could improve them.

3.4.3. FTIR analysis

The FTIR analysis is used to reveal the influence of the kind of phosphorus-containing flame retardants on the chemical structure of char layer. The FTIR spectra of the char of the EP and EP/OPS composites after cone testing are shown in Fig. 9. In Fig. 9, for the EP composites the only absorbance of the pure EP is the broad peak at 1588 cm^{-1}, which indicates the formation of polyaromatic carbons. The similar FTIR spectrum is detected for EP/APP. The absorbance of P—O and P=O cannot be found in the FTIR spectrum EP/APP. This may be caused by that there are no interaction between APP and EP matrix, and the APP would decompose independent and quickly. For the EP/PEPA and EP/DOPO, except the broad peak at 1588 cm^{-1}, a new broad absorbance of P=O at 1220 cm^{-1} in the FTIR spectra of the exterior char can be recorded clearly, which means that some P=O structures are remain in the char. It was reported that after combustion of the phosphorus-containing flame retardancy system the carbon in the char is constituted mainly in stack of polyaromatic species, which bridged by polymer links via phosphate esters [33,34]. According to the analysis above, we summarized the main

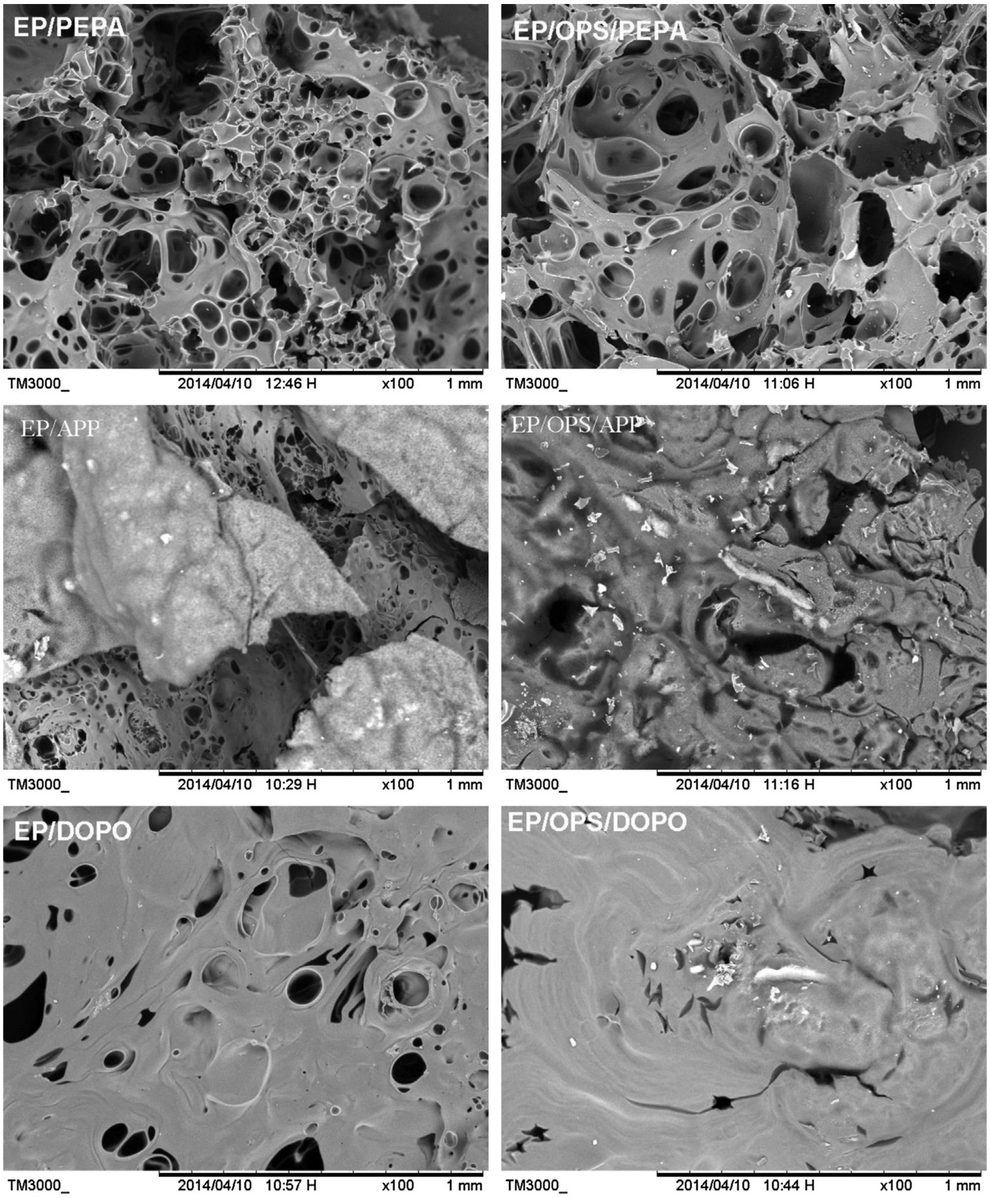

Fig. 8. SEM images of exterior chars from flame-retarded EP composites.

chemical structures in the char of EP/PEPA and EP/DOPO is the polyaromatic carbons and phosphate esters, but the main chemical structures in the char of EP/APP are the polyaromatic. The lower phosphorus-containing structure in the char of EP/APP reduces the thermal stability of this char layer and weakens its defensive function for the EP matrix as shown in Fig. 7.

In Fig. 9, for the EP/OPS composites, the only two absorbances are the intense peak at 1037 cm^{-1} due to the stretching vibrations of Si—O—Si structures and the small peak at 803 cm^{-1} caused by the deformation vibration of Si—O—C structures (and/or the stretching vibrations of Si—C structures). No other absorbance of C—C in the aliphatic or aromatic structures can be detected. That means most part of the white product is Si—O—Si— structures as shown in Fig. 7. In Fig. 9, some interesting results are noted in the FTIR spectra of the EP/OPS/APP, EP/OPS/PEPA, and EP/OPS/DOPO. On the one hand, the only stretching vibration of Si—O—Si structure at 1037 cm^{-1} in EP/OPS has transformed into two absorbance peaks between 1100 cm^{-1} and 998 cm^{-1} in EP/OPS composites with APP, PEPA, and DOPO. These changes are caused by that some interaction must have happened between the phosphate ester structure and the Si—O—Si—O structure. The most possible association is the formation of —P(═O)—O—Si— structure which is reported in previous paper [35]. On the another hand, compared the FTIR spectra of EP/OPS/APP with that of EP/OPS/PEPA and EP/OPS/DOPO, its absorbance peaks between 1100 cm^{-1} and 998 cm^{-1} are obviously weak, which means the —P(═O)—O—Si— structure and Si—O—Si—O structure in the char of EP/OPS/APP are lower than that of EP/OPS/PEPA and EP/OPS/DOPO. These results proof that the APP could rarely interact with OPS or EP matrix in the EP/OPS/APP and EP/APP composite, which corresponds well with its performance in the EP/APP composite. The interaction between phosphate ester and Si—O structure could enhance the thermal stability of the products in condensed phase during the combustion of the flame-retarded EP composites. The superior thermal stability of the char could explain the good flame retardancy of EP and EP/OPS composites with PEPA and DOPO in the cone calorimeter test. In contrast, due to lack the

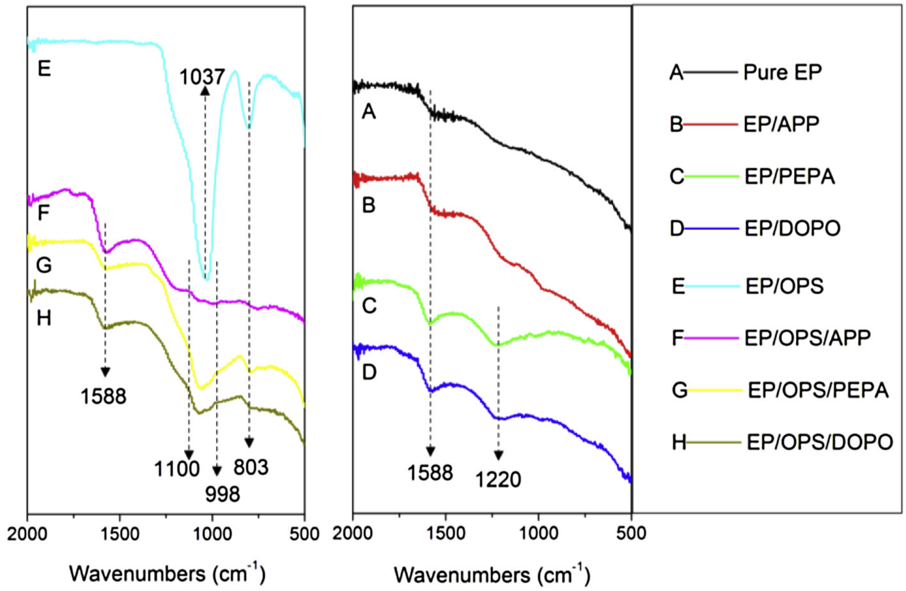

Fig. 9. The FTIR spectra of char residues of epoxy composites after cone calorimeter test.

interaction, the EP/APP and EP/OPS/APP show poor performance in the cone calorimeter test.

3.5. *Flame retardancy of the cured EP composites*

The effects of PEPA, APP and DOPO with or without OPS on the LOI values and UL-94 rating of epoxy resins are presented in Table 4. The chemical structures of phosphorus-based flame retardants could influence a lot on the condensed phase structure and gas phase release of epoxy resins as discussion above, so it should influence the flame retardancy of EP composites seriously.

UL-94 test reveals different behavior for the EP and EP/OPS composites with PEPA, APP or DOPO. In the case of the pure EP, no char layer forms at the end of the burnt samples. The thermal decomposing surface of the EP exposes in the fire directly and fire propagates quickly from igniting end. For the EP/PEPA, after the ignition, its char layer created slowly, the extinguishing does not happen until the t_1 is almost 82 s, and after second ignition, its t_2 is about 6 s. When the EP flame retarded by the PEPA and OPS, its extinguishing phenomenon is similar to that of EP/PEPA, but its t_1 and t_2 are 45 s and 1 s, respectively. The synergy of OPS and PEPA obviously accelerate the formation of the char layer. However, there is no gas jetting can be observed in the EP/PEPA and EP/OPS/PEPA, which is caused by that the lower gas release and highly crosslinked char layer are disadvantage for the formation of blowing-out effect.

For the EP/APP, after ignition, the fire would propagate upwards along the surface of the samples until the whole sample was burned. In the case of EP/OPS/APP, the loading of OPS improve its flame retardancy obviously. After first ignition, the extinguishing of EP/OPS/APP happens after about 60 s, however, no extinguishing can be observed after second ignition. The synergy of OPS and APP improve the flame retardancy of EP/OPS/APP, but due to its weak char layer, no gas jetting can be detected in EP/APP and EP/OPS/APP samples.

For the EP/DOPO, the char layer formed quickly and slowed the propagation of fire. Although gaseous jet is obvious, the extinguishing does not happen until the t_1 is almost 30 s. After second ignition, the fire would propagate upwards along the surface of the samples and extinguishing happens after about 60 s. Although obvious gaseous jet are detected for the EP composites with DOPO loading, the blowing-out effect need a long time to accomplish. In the case of EP/OPS/DOPO, char layers form in the initial several seconds after ignition and pyrolytic gases jet from the holes on the char layer. The flame hardly persists on the top of the airflow and extinguishing happens in several seconds. The synergy of OPS and DOPO makes the blowing-out effect remarkable in the UL-94 test.

Summarized the results above, we can find that the EP with different phosphorus-based flame retardant (PEPA, APP and DOPO) shows different combustion behaviors and flame retardancy. Their flame retardancy is obviously affected by the charring process and gas release of the epoxy resins. As discussed above, the charring process and gas release of the epoxy resins are decided by the phosphorus-based flame retardants rather than with or without OPS. So we conclude that the model of flame retardancy of samples are decided by the chemical structure of phosphorus flame retardants, the synergy of OPS could reinforce this kind of action.

Table 4
Flame retardancy of EP composites.

Samples	LOI (%)	UL-94 (3.2 mm)			
		t_1 (s)	t_2 (s)	Dripping	Rating
Pure EP	23.0	>120	/	Yes	NR
EP/PEPA	27.0	82	6	NO	NR
EP/APP	23.5	>120	/	NO	NR
EP/DOPO	32.0	30	60	NO	NR
EP/OPS	25.0	75	2	NO	NR
EP/OPS/PEPA	25.5	45	1	NO	NR
EP/OPS/APP	24.6	60	>120	NO	NR
EP/OPS/DOPO	30.8	9	3	NO	V-1

4. Conclusions

The epoxy resins flame retarded by the PEPA, APP, and DOPO with or without OPS are prepared. Different chemical structures of PEPA, APP, and DOPO have leaded different combustion behaviors of EP in the cone calorimeter test. According to the p-HRR, THR, CO yield, smoke emission results and the TGA analysis, we found that the organophosphorus PEPA and DOPO shows better flame retardancy effective on the epoxy resins than that of inorganophosphorus flame retardant APP did. Furthermore, in this research, the DOPO perform better gas phase flame retardancy action, but the PEPA have better condensed phase flame retardancy action. The pyrolysis gases of EP or EP/OPS composites with PEPA, APP, and DOPO are investigated by TGA-FTIR analysis which show that no change of pyrolytic gases species is observed among the epoxy resins loaded with low content PEPA, APP, and DOPO (P content 0.9 wt.%). But the structure of phosphorus-containing flame retardant would influence the release speed of pyrolysis gases. In the condensed phase analysis, we found the PEPA make EP have a crosslinked char layer, DOPO make EP have flawless lamellar char layer, but the APP make EP have a weak char layer. The kind of phosphorus-containing flame retardants decide the structure of char layer of epoxy resins, which could seriously affect their flame retardant performance. In the flame retardancy analysis by the LOI and UL-94 test show that the model of flame retardancy of samples are decided by the chemical structure of phosphorus flame retardants, the synergy of OPS could reinforce this kind of action.

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