Novel flame retardancy effects of DOPO-POSS on epoxy resins

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ABSTRACT

A series of flame retarded epoxy resins (EP) was prepared with a novel polyhedral oligomeric silsesquioxane containing 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO-POSS). The flame retardancy of these EPs was tested by the LOI, UL-94, which indicates that DOPO-POSS has meaningful effects on the flame retardancy of EP composites. 2.5 wt.% DOPO-POSS incorporation into epoxy resin (EP-2.5), results in a LOI value 30.2 and UL-94 V-1 ($t_1 = 8$ s and $t_2 = 3$ s) rating. Moreover, self-extinguishing effect through the pyrolytic gases spurt is observed in UL-94 test for the EP-2.5. The pyrolytic gases and thermal stability of epoxy resins with and without DOPO-POSS were detected by TGA-FTIR under air atmosphere. Releases of gaseous species are found to be similar for the pure EP and EP-2.5. The details of fire behaviour, such as TTI, HRR, p-HRR, TSR, SEA, COPR, CO_2PR, and TML, were tested by cone calorimeter. It is notable that 2.5 wt.% DOPO-POSS could make COPR and CO_2PR reach a maximum, which could explain the blowing-out extinguishing effect.

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1. Introduction

Epoxy resins are very important thermosetting material owing to their excellent mechanical and chemical properties [1–3]. They are widely used as advanced composite matrices in electronic/electrical industries where a remarkable flame-retardant grade is required, but the fire risk is a major drawback of these materials [4]. Halogen-containing flame retardants are reported to be effective flame retardants for epoxy resins. However, some of them are restricted to use due to their generating dense toxic smoke and corrosive products generated during combustion [5]. Therefore, the preparation and application of halogen-free flame retardants is the subject of extensive investigations.

Phosphorous compounds can impart flame retardancy through flame inhibition in the gas phase and char enhancement in the condensed phase [6–8]. Several either nonreactive or reactive phosphorus-containing flame retardants in epoxy resins have been investigated in recent research articles [9–12]. 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) is a cyclic phosphate with a diphenyl structure, which has high thermal stability, good oxidation and water resistance [13–16]. Using DOPO or its derivatives as flame retardant, significant improvement in the fire behaviour of epoxy resins has been reported [9–12].

Polyhedral oligomeric silsesquioxanes (POSS) are cage-like hybrid molecules composed of silicon and oxygen, ranging in size from approximately 1 to 3 nm. They have the chemical composition ($RSiO_{1.5}$), where R is hydrogen or any alkyl, alkylene, aryl, or arylene group, or organo-functional derivatives thereof, similar to the combination of both silica (SiO_2) and silicone (R_2SiO) [17,18]. POSS molecules with a nanosized, cage-shaped, three-dimensional structure can be incorporated into almost all kinds of thermoplastic or thermosetting polymers by blending, grafting, cross-linking or copolymerization, in order to improve their mechanical and thermal properties and oxidation resistance, and to reduce their flammability [19,20].

In our previous work [21], we described the successful synthesis of DOPO-containing polyhedral oligomeric silsesquioxane (DOPO-POSS) (Scheme 1). It is a novel phosphorus-containing POSS with high thermal stability. The subject of this work is to evaluate the effect of DOPO-POSS as a flame retardant in epoxy resins. An interesting phenomenon, which is tentatively named "blowing-out extinguishing effect", has been detected in UL-94 test for the epoxy resin with 2.5 wt.% DOPO-POSS loading. The "blowing-out extinguishing effect" is that: "After the sample was ignited, it showed an unstable flame for several seconds; with the pyrolytic gaseous products jetting outward from the condensed-phase surface, the flame was extinguished, it looks like that the gas blew out the flame". Therefore, the details of fire behaviours of DOPO-POSS/EP composites are investigated by TGA-FTIR and cone calorimeter.
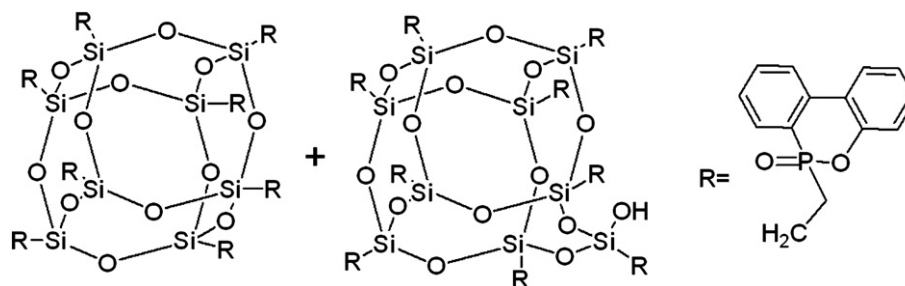
2. Experimental

2.1. Materials

Diglycidyl ether of bisphenol A (DGEBA, E-44, epoxy equivalent = 0.44 mol/100 g) was purchased from FeiCheng DeYuan

Scheme 1. Typical chemical structures of DOPO-POSS molecules.

Chemicals CO., Ltd. m-Phenylenediamine (m-PDA) was purchased from TianJin GuangFu Fine Chemical Research Institute. DOPO-POSS was synthesized in our laboratory [21]. DOPO-POSS was mixture of perfect T_8 cage and imperfect T_9 cage with one Si–OH group on it.

2.2. Epoxy resins cured by m-phenylenediamine (m-PDA)

The cured epoxy resins were obtained by thermally curing. At first the DOPO-POSS was dispersed in DGEBA by mechanical stirring at 140 °C for 1 h and it would dissolve in DGEBA. The mixture is homogeneous and transparent liquid always. The contents of the DOPO-POSS in the EP composites are listed in Table 1. After the mixture cooling to 80 °C, the curing agent (m-phenylenediamine) was then added relative to the amount of DGEBA. The equivalent weight ratio of DGEBA to m-PDA was 100:12. The mixtures were cured at 80 °C for 2 h and post-cured at 150 °C for 2 h. The LOI and UL-94 test samples were strips.

2.3. Measurements

Limiting oxygen index (LOI) was obtained according to the standard GB/T2406–93 through measuring the minimum oxygen concentration required to support candle-like combustion of plastics. An oxygen index instrument (Rheometric Scientific Ltd.) was used on barrels of dimensions of $100 \times 6.5 \times 3$ mm^3. Vertical burning tests were performed according to UL-94 standard with samples of dimensions of $125 \times 12.5 \times 3.2$ mm^3. In this test, burning grade of a material was classed as V-0, V-1, V-2 or unclassified, according to its behaviour (dripping and burning time).

Thermal gravimetric analysis (TGA) was performed with a Netzsch 209 F1 thermal analyzer, and the measurements were carried out under air atmosphere at a heating rate of 20 °C/min from 40 °C to 800 °C. The sample weight was 10 mg for each measurement at a gas flow rate of 60 ml/min. Typical results from TGA were reproducible within ±1%, and the reported data are average for three measurements. To detect gas species, the TGA was coupled with Fourier transform infrared spectrometry (TGA-FTIR, Nicolet 6700). The connection between TGA and FTIR was done by means of a quartz capillary at 200 °C.

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

3. Results and discussion

3.1. Flame retardancy of the cured epoxy resins

The effect of the content of DOPO-POSS on LOI values of epoxy resins are presented in Table 1. We can observe that the LOI values of epoxy resins cured with m-PDA increase obviously with the DOPO-POSS loading. When 2.5 wt.% DOPO-POSS incorporation, the LOI value of epoxy resin is levelled up from 25.0 to 30.2. However, the LOI values reduce obviously with 10 wt.% DOPO-POSS content. These results are different from the traditional notion. As many literatures reported [14–16,18,22], introducing phosphorous and silicon into epoxy resins would significantly enhance the resins' char formation, moreover, the epoxy resins' LOI values showed a linear relationship with contents of phosphorous and silicon in the epoxy resins. However, the flame retardancy of epoxy resins would worsen with the increase of DOPO-POSS loading according to Table 1.

The results of UL-94 test are show in Table 1 as well. It is clear that the epoxy resins with DOPO-POSS gain enhanced flame retardancy. The dripping are no longer observed for all the samples and the self-extinguishing is observed with 1.5–5.0 wt.% DOPO-POSS loading. The best UL-94 rating (V-1, $t_1 = 8$ s, $t_2 = 3$ s), which is very close to a V-0 rating, can be got when the content of DOPO-POSS is 2.5 wt.%.

Visual observation of the combustion experiments, in the UL-94 test, reveals different behaviour for the EP-2.5, compared to the EP-0 and EP-10, since beginning of the ignition. In the case of the EP-0 (Fig. 1A), no char layer forms at the end of the samples. The thermal decomposing surface of the EP-0 exposes in the fire directly and fire diffuses quickly from igniting end. However, an obvious char layer can be observed with DOPO-POSS loading. For the EP-10, the char layer formed quickly and the fire at the end of the sample diffuses upwards slowly. Char layer of the EP-10 obviously slow the diffusion of fire, however, the pyrolytic gases spurt and self-extinguishing could not be observed. The char layer of the EP-10 could not act as a perfect barrier to shield the unburned polymer matrix against heat as well as hindering the diffusion of pyrolytic gases. The picture of the intumescent char of the EP-10 after UL-94 test is shown in Fig. 1C and the small holes can be

Table 1
Flame retardancy of DOPO-POSS/EP composites.

Samples	Cured epoxy resin (wt.%)	Content of DOPO-POSS (wt.%)	LOI (%)	UL-94 (3.2 mm)	t_1 (s)	t_2 (s)	Dripping
EP-0	100.0	0.0	25.0	NR	>30	/	Yes
EP-1.5	98.5	1.5	29.0	V-1	21	8	No
EP-2.5	97.5	2.5	30.2	V-1	8	3	No
EP-3.5	96.5	3.5	29.1	V-1	11	12	No
EP-5.0	95.0	5.0	28.5	NR	35	20	No
EP-10	90.0	10.0	23.0	NR	>30	/	No

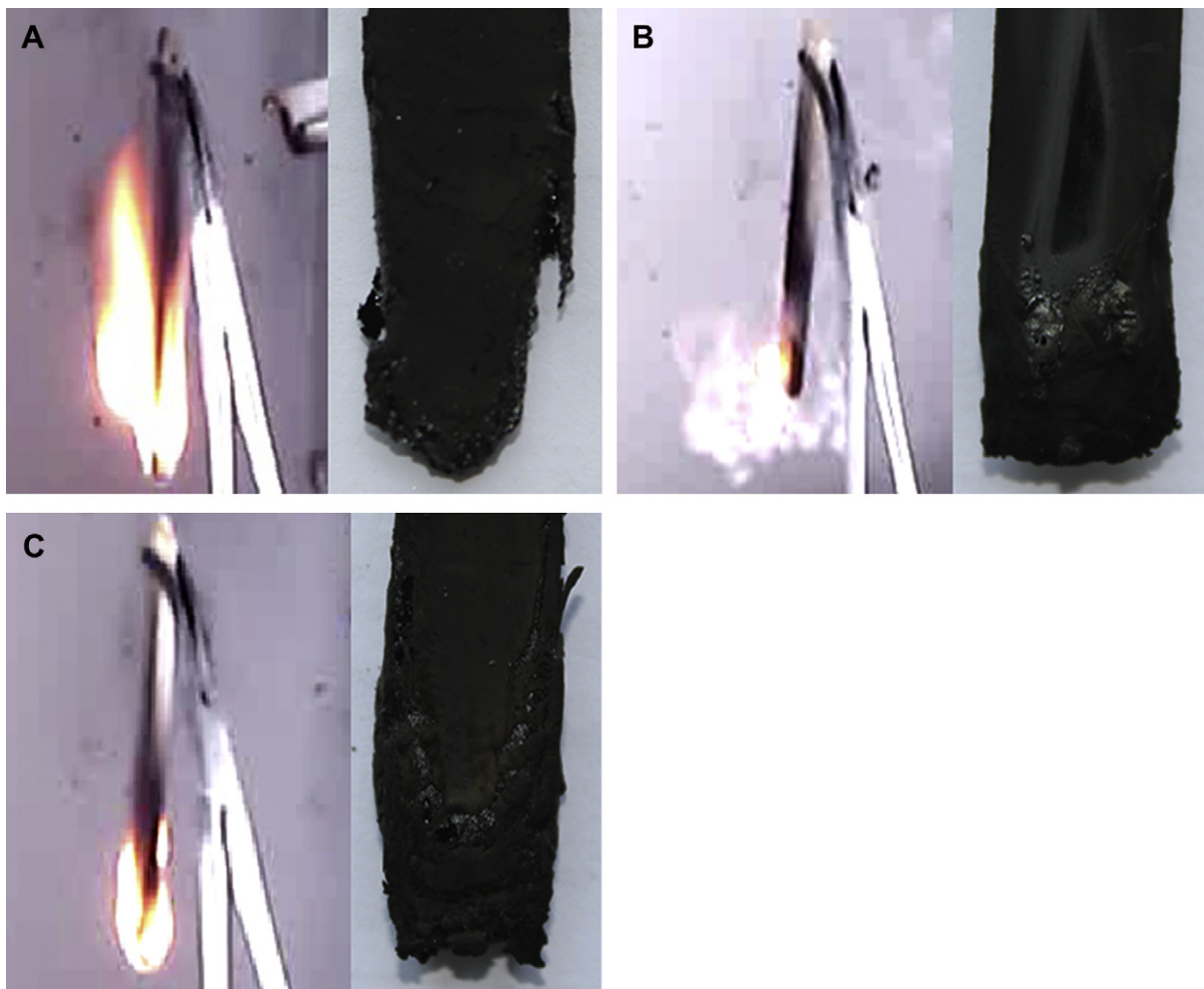t_1 and t_2 are mean values for 5 test samples.

Fig. 1. Videos screenshots and photo of bars after UL-94 test of EP-0 (A), EP-2.5 (B), and EP-10 (C).

observed directly with naked eye. In the case of the EP-2.5, an interesting blowing-out extinguishing effect can be observed. A char layer survives and grows in the initial several seconds after ignition, yielding a rigid char-brick with the same dimensions as the original sample (Fig. 1B). The most attractive phenomenon is that jet of the pyrolytic gases from the holes on the char layer and flame hardly persists on the top of the airflow, which has separated from the surface of char layer, this is so-called self-extinguishing effect through the pyrolytic gases spurt. Similar blowing-out extinguishing effect can be observed for the EP-1.5, EP-3.5, and EP-5.0 samples, however, the optimal result in Table 1 is the EP-2.5, which is very close to the V-0 rating.

3.2. TGA-FTIR analysis of the cured epoxy resins

In order to further understanding the blowing-out extinguishing effect of DOPO-POSS/EP composites, using TGA-FTIR to analyze the thermal stability and pyrolysis products is the suitable choice. TGA and DTG curves of the EP, DOPO-POSS/EP composites, and DOPO-POSS are presented in Fig. 2. The relevant thermal decomposition data, including the T_{onset}, defined as the temperature at 5% weight loss, the $T_{max}1$ and the $T_{max}2$, defined as the temperatures at maximum weight loss rate, and the char residues at 700 °C, are given in Table 2.

The mass loss temperature of DOPO-POSS is much higher than that of the EP-0. In comparison with degradation of EP-0, although

DOPO-POSS is blended with epoxy resin, the T_{onset} of DOPO-POSS/EP composites are similar to EP-0. As shown in Fig. 2, the first mass loss regions for the EP-0 and DOPO-POSS/EP composites are 350–450 °C. The improvements of thermal stability of DOPO-POSS/EP composites are negligible with increase of content of DOPO-POSS in this temperature region. The solid residues of the EP-0 and DOPO-POSS/EP composites at 500 °C show similar value, about 38%. Then a slower second degradation stage is in 525–625 °C, which is considered as the continuing thermo-oxidative degradation of the char. The char seems to possess higher thermal stability with higher content of DOPO-POSS. Considering the mass fraction of DOPO-POSS in the DOPO-POSS/EP composites, the char residues for the EP-1.5, EP-2.5, EP-3.5, EP-5.0, and EP-10 are a little higher than expected.

From the DTG curves of EP-0 and DOPO-POSS/EP composites in Fig. 2, a reduction of mass loss rate is detected with the increase of DOPO-POSS loading, and $T_{max}1$ exhibits an unexpected improvement with 10 wt.% DOPO-POSS loading in the first mass loss region. Moreover, the decrease of mass loss rate and the enhancement of $T_{max}2$ are observed with the increase of DOPO-POSS loading in the second degradation stage. Although all of the TGA and DTG results show that DOPO-POSS has a positive effect on the thermal stability of char of the DOPO-POSS/EP composites, flame retardancy of DOPO-POSS/EP composites are weakened seriously with increase (3.5–10 wt.%) of DOPO-POSS loading. It is speculated that improvement of thermal stability and yield of char residues with
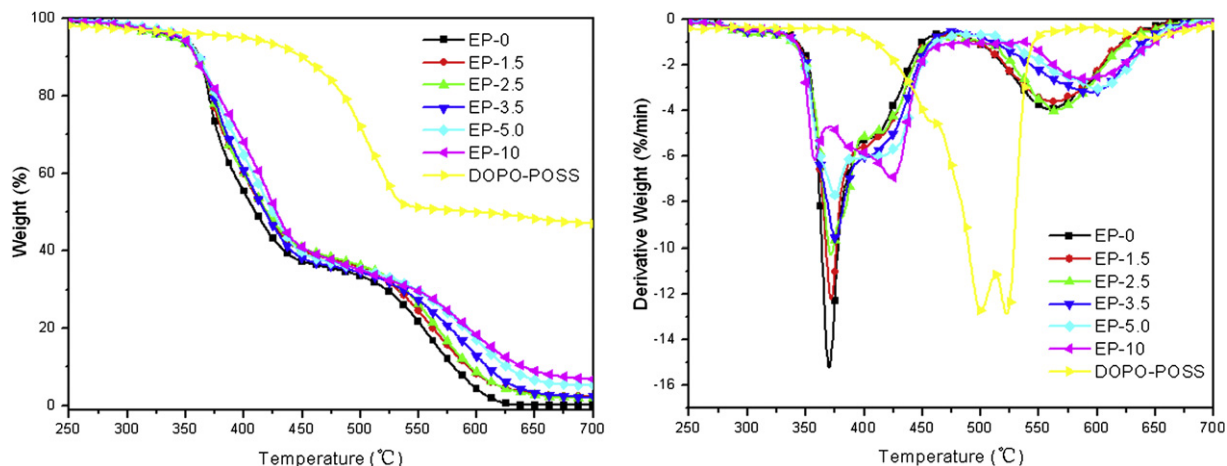
Fig. 2. TGA and DTG curves of DOPO-POSS/EP composites and DOPO-POSS in air.

DOPO-POSS loading is not the key point for outstanding flame retardancy of the EP-2.5.

FTIR spectra of EP-0, EP-2.5 and their solid products of collected in thermogravimetry at $T_{max}1$ and $T_{max}2$ are shown in Fig. 3. In the initial absorption of EP-0 and EP-2.5, it can be seen that peaks at 3200–3600, 3055, 2868–2962, 1602, 1504, 1226, 1178, 1103, 1025, and 825 cm^{-1} are the characteristic absorption of EP networks [1]. At $T_{max}1$, although most of the characteristic absorption of EP networks is kept, the decrease in the intensity of the aromatic component related bonds (1504 cm^{-1}) and ether bonds (1103 and 1025 cm^{-1}) are detected. At $T_{max}2$, the absorption of aliphatic components disappears totally. The aromatic ring C=C stretching vibration at 1504 cm^{-1} disappears and that at 1602 cm^{-1} becomes broader, indicating the formation of polyaromatic carbons. It should be indicated that the EP-0 and EP-2.5 show the same thermal decomposition process due to the analysis of the FTIR studies of the condensed-phase products.

To detect pyrolytic gas species of EP-0 and EP-2.5 in air atmosphere, the TGA was coupled with FTIR. The FTIR spectra of pyrolytic gas products at $T_{max}1$ and $T_{max}2$ are shown in Fig. 4. The assignment of the absorbance peaks is presented in Table 3.

As shown in Fig. 4, the evolving gas species of the EP-2.5 are similar to that of the EP-0. At $T_{max}1$ (Fig. 4A), the major pyrolytic gases detected from the decomposition of the EP-2.5 and EP-0 are phenol derivatives/water (3737 and 3650 cm^{-1}), aromatic components (3050, 1604, 1510, and 1340 cm^{-1}), aliphatic components (3016 and 2969 cm^{-1}) and ester/ether components (1257, 1181, and 1052 cm^{-1}), which is almost similar to that in N$_2$ atmosphere [23]. These are the characteristic absorbance bands of thermal decomposition products of EP matrix. At $T_{max}2$ (Fig. 4B), the major pyrolytic gases are CO$_2$ (2360 cm^{-1}) and CO (2180 and 2100 cm^{-1}). Furthermore, a spot of phenol derivatives/water, aromatic components, aliphatic components, and ester/ether components are also detected. These pyrolytic products are considered as the thermo-

oxidative decomposition of the char which formed in the first decomposition step. It should be noted that change of pyrolytic gases species is not observed with 2.5 wt.% DOPO-POSS loading.

3.3. Cone calorimetry analysis of the cured epoxy resins

The cone calorimeter, which can provide a wealth of information to simulate real fire conditions, is used to investigate the effects of DOPO-POSS on the fire behaviour of the epoxy resin. The concerned combustion parameters include time to ignition (TTI), heat release rate (HRR), peak of heat release rate (p-HRR), total mass loss (TML) and total heat release (THR). These parameters are reported in Table 4 for different samples.

TTI is used to determine the influence of flame retardant on ignitability, which can be measured from the onset on an HRR curve. Increase of TTI is detected clearly with increase of DOPO-POSS content. Ignition occurs when the volatiles are sufficient to be ignited by a spark. Ignition does not correspond to flammability measured by LOI and UL-94 in Table 1. However, DOPO-POSS slightly increase thermal stability of epoxy resins. When pyrolyzing, it may produce more inert gases (like CO$_2$) and less volatile products, which is advantageous of raising TTI. Fast formation of the char layer at the combustion surface should be helpful with addition of DOPO-POSS.

The HRR versus time curves for the different samples are presented in Fig. 5. It can be observed that the EP-0 burns rapidly after ignition and HRR reaches a sharp peak with a peak heat release rate (p-HRR) of 855 kW/m^2, which is typical for non-charring samples of intermediate thickness. The p-HRR of EP-5.0 and EP-10 reduced remarkably to 588 kW/m^2 and 483 kW/m^2, which are expected with DOPO-POSS loading. Furthermore, it is very surprising that the p-HRR of the EP-2.5 is 969 kW/m^2, which is a little higher than that of EP-0. It does not coincide with LOI and UL-94 results. However, as shown in Fig. 6, THR values of DOPO-POSS/EP composites decrease with enhancement of DOPO-POSS content. Considering the mass fraction of DOPO-POSS in the DOPO-POSS/EP composites, the calculated data of THR are shown in Table 4. It is noted that the experimental THR values for EP-2.5, EP-5, and EP-10 are lower than the calculated.

Based on the blowing-out extinguishing effect observed in the UL-94 test, the cone calorimeter data, such as CO production rate (COPR), CO$_2$ production rate (CO$_2$PR), total smoke released (TSR), and specific extinction area (SEA), are used to evaluate the effect of the DOPO-POSS on release of pyrolytic gases and smoke compared with the neat epoxy resin.

Table 2
TGA data of DOPO-POSS/EP composites and DOPO-POSS in air.

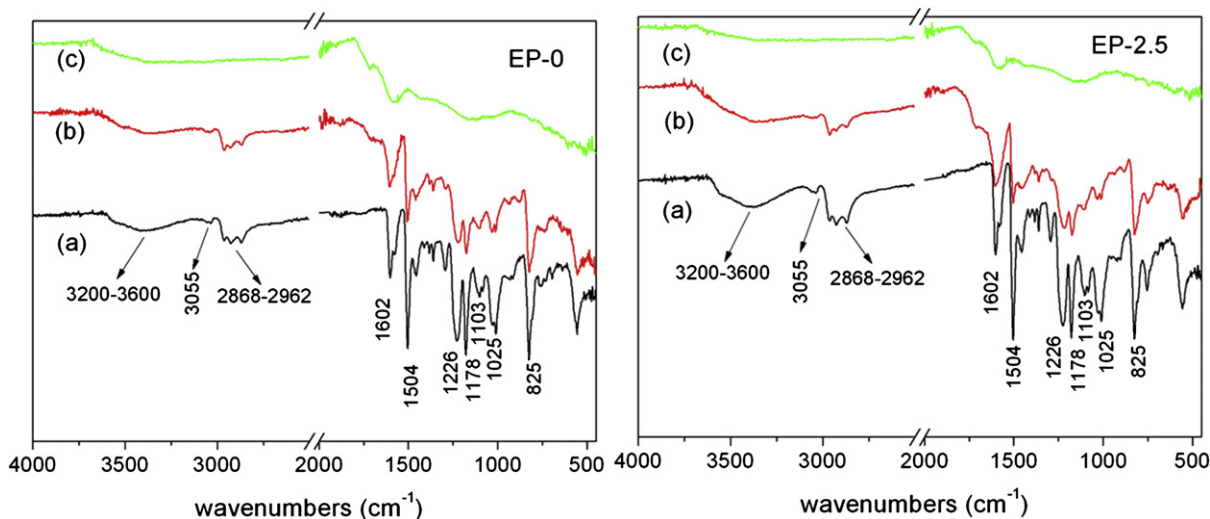| Samples	T_{onset} (°C)	$T_{max}1$ (°C)	$T_{max}2$ (°C)	Residues at 700 °C (%)
EP-0	345	370	559	0.1
EP-1.5	346	372	561	2.0
EP-2.5	345	371	562	2.8
EP-3.5	346	375	595	3.8
EP-5.0	349	375	599	5.2
EP-10	346	423	593	6.8
DOPO-POSS	398	522	/	46.9

Fig. 3. FTIR spectra of the condensed phase of EP-0 and EP-2.5: initial (a), at $T_{max}1$ (b), at $T_{max}2$ (c).
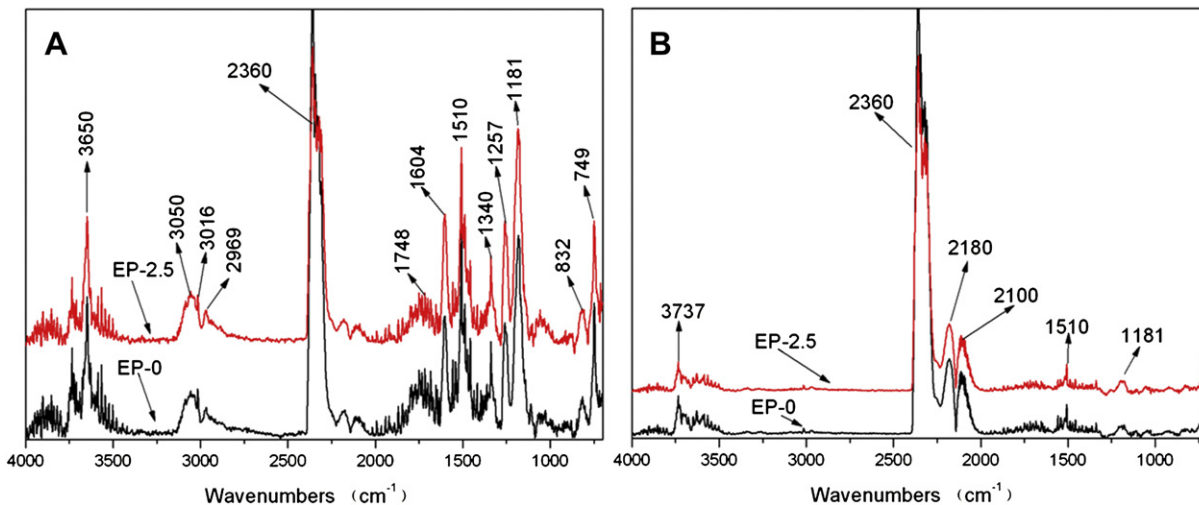

Fig. 4. The FTIR spectra of pyrolytic gases of EP-0 and EP-2.5 at $T_{max}1$ (A) and $T_{max}2$ (B).

We can notice that, as shown in Table 4, the mean CO yield (COY) of samples increase gradually with enlarging of DOPO-POSS content, and at the same time, the mean CO_2 yield (CO$_2$Y) of samples reduce with enhancement of DOPO-POSS loading in DOPO-POSS/EP composites. Increases of incomplete combustion products, typical CO, indicate the flame inhibition effects of the

DOPO-POSS. It is reported that the effective fire retardants, such as some halogen- and phosphorus-based systems, can reduce polymer flammability by their ability to form gaseous intermediates which scavenge flame propagating free radicals (OH, H…) thereby inhibiting complete combustion to CO_2 [25]. Furthermore, TSR and SEA of samples increase obviously in the EP-2.5, EP-5.0, and EP-10 samples with enlarging DOPO-POSS content. It is reported [24] that smoke emission is caused by evolution of the incomplete-oxidation

Table 3
Assignment of FTIR spectra of pyrolytic gases of EP-0 and EP-2.5.

Wavenumber (cm^{-1})	Assignment
3737, 3650	O–H stretching vibration of C_{Ar}–OH or water
3050	C_{Ar}–H stretching vibration of styrene derivatives
3016	Methane
2969	R–CH_2–R, R–CH_3 stretching vibration of aliphatic components
2360	CO_2
2180, 2100	CO
1748	C=O stretching vibration of compounds containing carbonyl
1604, 1510, 1340	Aromatic rings vibration
1257, 1181, 1052	C–O stretching vibration
832, 749	C_{Ar}–H deformation vibration

Table 4
Cone calorimeter data for the DOPO-POSS/EP composites.

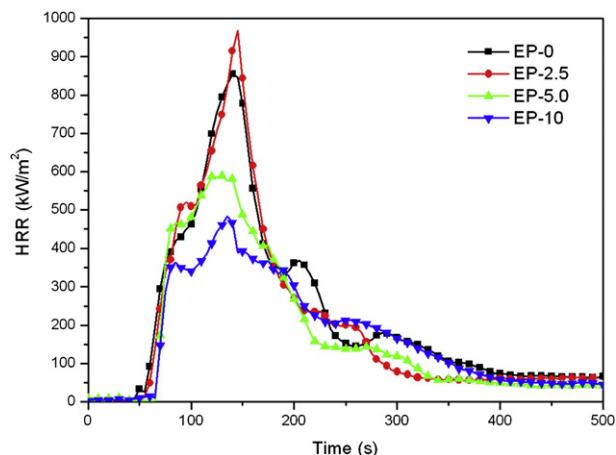| Samples	EP-0	EP-2.5	EP-5.0	EP-10
TTI (s)	45	48	58	61
p-HRR (kW/m^2)	855	969	588	483
THR (MJ/m^2)	112	103	92	85
Calculated THR (MJ/m^2)	112	109	106	100
TSR (m^2/m^2)	4182	3562	4452	5566
Mean SEA (m^2/kg)	897	878	1056	1343
Mean COY (kg/kg)	0.07	0.09	0.12	0.13
Mean CO$_2$Y (kg/kg)	1.82	1.86	1.68	1.63
TML (%)	89	88	86	84

Fig. 5. Heat release rate curves of DOPO-POSS/EP composites.

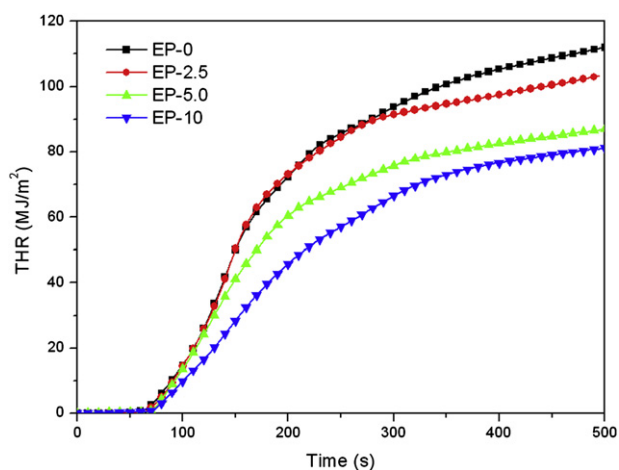**Fig. 8.** CO_2 production rate of samples with time.

Fig. 6. Total heat release curves of DOPO-POSS/EP composites.

The curves of CO production rate (COPR) of samples are shown in Fig. 7. The COPR (g/s) is obtained from the product of the CO yield (kg/kg) and the mass loss rate (g/s). The lower mass loss rates give higher COPR, during the combustion of the DOPO-POSS/EP composites, as compared to the EP-0. The most important is that the CO_2PR, as shown in Fig. 8, reaches a maximum when the content of DOPO-POSS in the composites is 2.5 wt.%. The maximal COPR and CO_2PR of the EP-2.5 could explain the pyrolytic gases spurt, which is the main reason of the self-extinguishing effect, during the UL-94 test. However, the COPR and CO_2PR of EP-10 slow down simultaneously in test of EP-10 sample, such as CO_2PR, which shows a reduction of 57%. This may be the reason that although more char is created in the EP-10, the pyrolytic gases spurt disappear, which leads to absence of self-extinguishing during UL-94 test. It is speculated that DOPO-POSS could accelerate the release of CO and CO_2; whereas the increased char of the epoxy resin with higher DOPO-POSS content induces the potential decrease of the CO_2PR, which are disadvantageous to the pyrolytic gases spurt.

4. Conclusions

Flame retardancy of epoxy resin can be improved by adding DOPO-POSS, but in different ranges of DOPO-POSS content in the resins, the composites show different flame-retardant behaviours. The LOI value and UL-94 rating of the epoxy resin with 2.5 wt.% DOPO-POSS loading are 30.2 and V-1 ($t_1 = 8$ s and $t_2 = 3$ s), respectively. Blowing-out extinguishing effect is observed in UL-94 test of the EP with 2.5 wt.% DOPO-POSS loading. However, the flame retardancy of epoxy resins weakens as the DOPO-POSS content increases from 3.5 wt.% to 10 wt.%. The TGA and DTG results show that increase of DOPO-POSS loading has a positive effect on the thermal stability and char yield of the DOPO-POSS/EP composites, which does not correspond with flame retardancy of DOPO-POSS/EP composites. It is speculated that thermal stability and yield of char residues of EP with 2.5 wt.% DOPO-POSS loading is not the key point for its outstanding flame retardancy. The TGA-FTIR results show that the 2.5 wt.% DOPO-POSS do not change the pyrolytic gases species. The studies of fire behaviour of DOPO-POSS/EP composites by cone calorimeter indicate that DOPO-POSS could enhance the flame retardancy of epoxy resins noticeably. The maximum COPR and CO_2PR of the EP with 2.5 wt.% DOPO-POSS loading could explain the pyrolytic gases spurt

products. It is noticeable that the mean COY and mean CO_2Y of the EP-2.5 are a little higher than that of the EP-0, which indicates that DOPO-POSS may catalyze the release of CO and CO_2. However, the CO_2 yields reduce gradually due to enhancement of char yields in EP-5.0 and EP-10 samples.
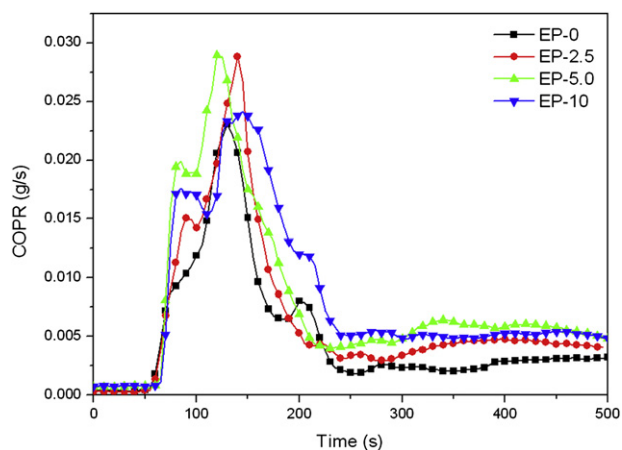

Fig. 7. CO production rate of samples with time.

phenomenon, which is the main reason of the self-extinguishing effect during the UL-94 test.

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