Polymer Degradation and Stability 98 (2013) 246–254

Contents lists available at SciVerse ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Investigations of epoxy resins flame-retarded by phenyl silsesquioxanes of cage and ladder structures

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ARTICLE INFO

Article history:
Received 11 July 2012
Received in revised form
24 September 2012
Accepted 4 October 2012
Available online 12 October 2012

Keywords:
Epoxy resin
Octaphenyl silsesquioxane
Ladder polyphenyl silsesquioxane
Blowing-out effect
Flame retardancy

ABSTRACT

Cage-type octaphenyl silsesquioxane (OPS) and ladder-type polyphenyl silsesquioxane (PPSQ) have been used as flame-retardants in epoxy resins (EPs) in the presence and absence of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO). The flame retardancy of these EPs have been tested by the LOI and UL-94 standard tests, and details of fire behaviors, such as TTI, HRR, p-HRR, THR, COPR, and CO_2PR, have been tested using a cone calorimeter. The results have shown that OPS has distinctly different effects on the flame retardancy of EPs compared to those of PPSQ. In the UL-94 test, the flame-retarded EP with OPS showed a weak blowing-out effect, but the flame-retarded EP with PPSQ did not; further, the flame-retarded EP with DOPO/OPS showed a significant blowing-out effect, but the flame-retarded EP with DOPO/PPSQ did not. According to the cone tests, addition of PPSQ to EPs, with or without DOPO, causes higher p-HRR; on the contrary, the addition of OPS to EPs leads to lower p-HRR compared to that of the neat EP. The thermal stability of these EPs has been investigated by TGA. The morphology of the chars after the cone tests has been investigated by visual observation, SEM, and XPS. Observation of the chars suggested that OPS can assist the EP, especially the EP with DOPO, to form stronger and denser chars than PPSQ, although PPSQ with a ladder structure has higher thermal stability than that of cage-type OPS. It was also observed that the Si concentration in the interior chars from the EPs with PPSQ was higher than that in those from the EPs with OPS. It is supposed that in the composites of EP or EP/DOPO, slow charring of PPSQ cannot match the intumescent and charring process of the EPs during combustion, but OPS can. This may explain why OPS exhibits significantly different flame retardancy on the EPs compared to PPSQ.

1. Introduction

Epoxy resins are commonly used as advanced composite matrices in the electronic and electrical industries, where a high-quality flame-retardant grade is required because the fire risk is a major drawback of these materials [1–5]. Traditionally, halogenated compounds have been widely used as co-monomers or additives 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 produce highly toxic halogenated dibenzodioxins and dibenzofurans [6–8]. Therefore, the development and application of halogen-free flame-retardants has been a subject of extensive investigation in relation to epoxy resins.

Silsesquioxanes are typical organic–inorganic hybrid composites, and are widely considered to be a new generation of high-performance materials [9–12]. Silsesquioxanes can be incorporated into almost any kind of thermoplastic or thermosetting polymer to improve their mechanical and thermal properties and oxidation resistance, and to reduce their flammability [13,14]. In recent years, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and its derivatives have received outstanding attention because of their high reactivity and applicability on flame retardancy [15–19]. Using DOPO or its derivatives as flame retardant for epoxy resins have been reported [20–25].

In our previous work, a DOPO-containing polyhedral oligomeric silsesquioxane (DOPO-POSS) was successfully synthesized [26]. An interesting phenomenon, termed the “blowing-out effect”, has been detected in flame-retarded epoxy resins with DOPO-POSS loading [27]. Moreover, the “blowing-out effect” can also be created in epoxy resins flame-retarded by a mixture of OPS (octaphenyl silsesquioxane) and DOPO [28]. The “blowing-out effect” has been described as follows: “after the sample was ignited, it showed an unstable flame for several seconds; with the pyrolytic gaseous products jetting outward from the condensed-phase

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http://dx.doi.org/10.1016/j.polymdegradstab.2012.10.005

surface, the flame was extinguished; it looks as though the gas blew out the flame". A model of the blowing-out effect is shown in Fig. 1. This concept reveals that the blowing-out effect is simultaneously determined by the rate of production of gases and the properties of the condensed char [29].

In this study, in order to further understand the "blowing-out effect", cage-type OPS (octaphenyl silsesquioxane) and ladder-type PPSQ (polyphenyl silsesquioxane), respectively, have been incorporated into pure EP or EP/DOPO composites to enhance their flame retardancy. The influences of phenyl silsesquioxanes of cage or ladder structures on the flame retardancy and blowing-out effect of epoxy resin are reported in detail.

2. Experimental

2.1. Materials

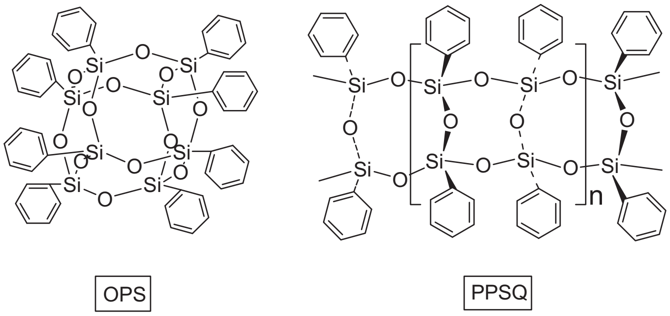
Diglycidyl ether of bisphenol A (DGEBA, E-44, epoxy equivalent = 0.44 mol/100 g) was purchased from FeiCheng DeYuan Chemicals Co., Ltd. *m*-Phenylenediamine (*m*-PDA) was purchased from TianJin GuangFu Fine Chemical Research Institute. 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was purchased from Eutec Trading (Shanghai) Co., Ltd.

2.2. Synthesis of the silsesquioxanes

Two kinds of silsesquioxanes are shown in Scheme 1. Octaphenyl silsesquioxane (OPS) was synthesized by the hydrolysis and condensation of phenyltrichlorosilane according to a previously reported procedure [30]. The OPS obtained in this way had a perfect T_8 cage structure. Polyphenyl silsesquioxane (PPSQ) was synthesized by the hydrolysis and condensation of phenyltrichlorosilane using a special catalyst under certain conditions. XRD and ^{29}Si NMR results indicated that the PPSQ was a ladder-type polymer [31].

2.3. Preparation of the EP composites

To prepare the pure EP and EP/silsesquioxane systems, OPS or PPSQ was dispersed in DGEBA by mechanical stirring at 140 °C for 1 h. After cooling the EP mixture to 80 °C, the curing agent *m*-PDA was added. The molar ratio of amino group to epoxy group is controlled at 1:1, correspondingly, the amounts of m-PDA and DGEBA are 12 g and 100 g, respectively. The liquid mixtures were poured into a mold, cured at 80 °C for 2 h, and post-cured at 150 °C for 2 h.



Scheme 1. Typical chemical structures of OPS and PPSQ.

To prepare the EP/DOPO and EP/DOPO/silsesquioxane systems, DOPO was added to DGEBA by mechanical stirring at 140 °C for 1 h, and then OPS or PPSQ was dispersed in the DGEBA/DOPO for a further 1 h. Thereafter, the same preparation processes as described above were followed.

The contents of OPS, PPSQ, and DOPO in the products are listed in Table 1. The samples were cut into strips to carry out the LOI and UL-94 tests.

2.4. 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 afterflame time). The t1 (t2) is afterflame time after the first (second) ignition of sample.

Thermal gravimetric analysis (TGA) was performed with a Netzsch 209 F1 thermal analyzer, with the measurements carried

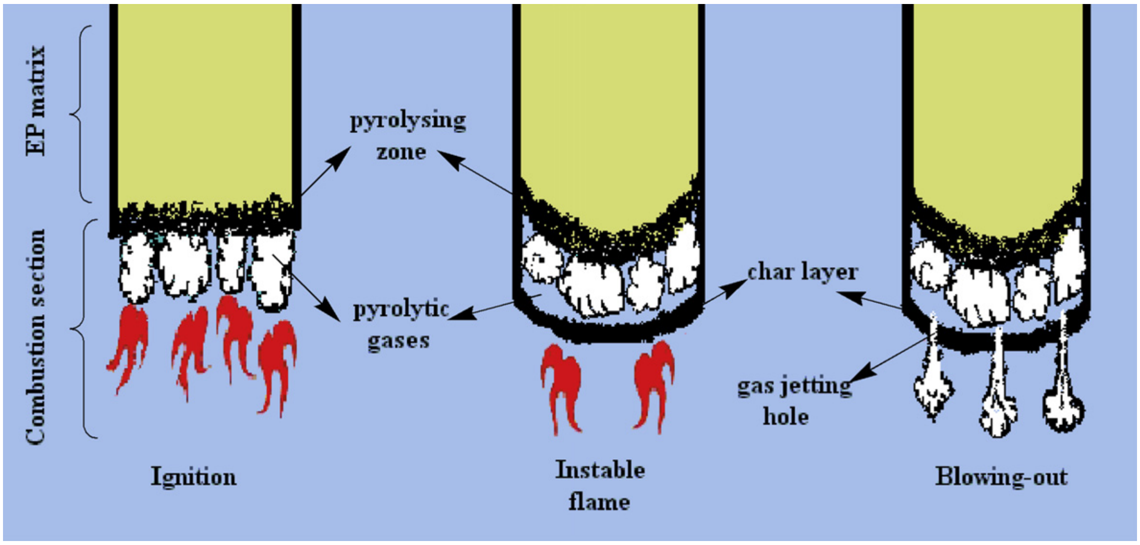


Fig. 1. Model of the blowing-out effect.

Table 1
Compositions of the investigated materials.

Samples	Cured epoxy resin (wt. %)	Content of flame retardant (wt.%)			
		Silsesquioxane	Si	DOPO	P
EP	100.0	/	/	/	/
EP/OPS	95.9	4.1	0.90	/	/
EP/PPSQ	95.9	4.1	0.90	/	/
EP/DOPO	93.7	/	/	6.3	0.90
EP/DOPO/OPS	94.8	2.1	0.45	3.1	0.45
EP/DOPO/PPSQ	94.8	2.1	0.45	3.1	0.45

out in the air atmosphere at a heating rate of 20 °C/min from 40 °C to 800 °C. Sample of 10 mg 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 based on 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.

To investigate the condensed phase of the EP composites in burning, all the cone calorimeter tests stopped at 500 s. The residue was cooled under room condition. For the SEM analysis, the exterior char is taken on the top part of char residues after cone test; the interior char is obtained at a depth 1 cm at least in the char layer. Moreover, the exterior and interior chars, respectively, were taken and were grinded for the XPS analysis.

Scanning electron microscopy (SEM) experiments were performed with a Hitachi S-4800 scanning electron microscope. The samples for SEM were sputtered on the surface with gold.

The X-ray photoelectron spectroscopy (XPS) measurements were achieved using a PHI Quantera II system (Ulvac-PHI) at 25 W, 15 kV under a vacuum better than 10^{-6} Pa. The sample was neutralized by both an ion-gun and an electronic-gun. Typical results from the XPS were reproducible within ±3%.

3. Results and discussion

3.1. Morphological properties of EP composites

The morphology of the fractured EP composites surface was observed by SEM. In Fig. 2, the big aggregation of OPS particles were observed in the epoxy resins, while the PPSQ particles show better dispersion than the OPS particles in the composites. The OPS particles are crystalline, its crystalline surface may be incompatible with DGEBA (diglycidyl ether of bisphenol A), but the PPSQ particles are amorphous, its side phenyl groups may be more compatible to DGEBA.

3.2. Flame retardancy of the cured EP composites

The effects of the silsesquioxanes on the LOI values of the epoxy resins are presented in Table 2. When OPS or PPSQ was incorporated into pure EP, the LOI values were increased from 25.0% to around 27.1%. Furthermore, when OPS or PPSQ was incorporated into the EP/DOPO composite, the LOI value was increased only marginally from 30.5% to around 31.1%. The increases in LOI values of the EP composites were thus negligible when OPS or PPSQ was added.

Table 2 shows the UL-94 results for these epoxy resins. When OPS or PPSQ was incorporated into EP alone, dripping was no longer observed. For the EP/OPS sample, a weak blowing-out effect, by which the sample self-extinguished after around 45 s, was

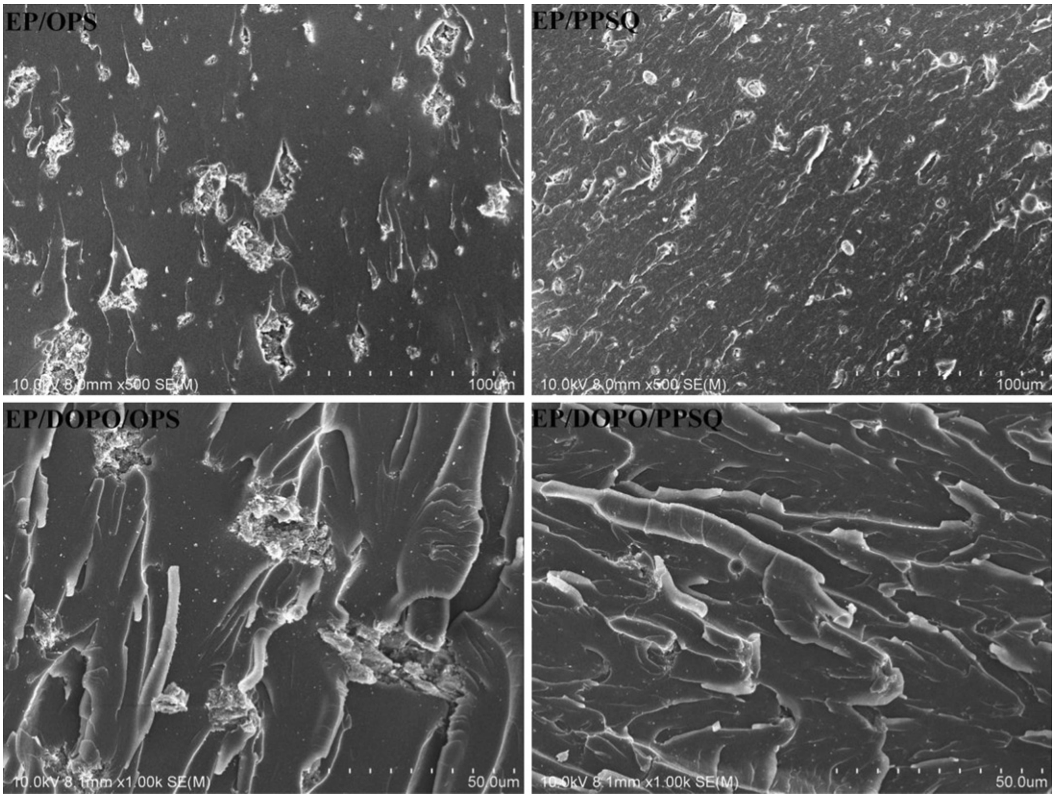


Fig. 2. SEM images of flame-retarded EP composites.

Table 2
Flame retardancy of EP composites.

Samples	LOI (%)	UL-94 (3.2 mm)	t_1 (s)	t_2 (s)	Dripping
EP	25.0	NR	>30	/	Yes
EP/OPS	27.2	NR	45	40	No
EP/PPSQ	27.1	NR	>30	/	No
EP/DOPO	30.5	NR	30	45	No
EP/DOPO/OPS	31.1	V-0	6	3	No
EP/DOPO/PPSQ	31.2	NR	36	15	No

observed (Fig. 3). For the EP/PPSQ sample, however, no such blowing-out effect was observed. OPS seemingly has a better flame retardancy than PPSQ for pure EP. A similar tendency was detected when OPS or PPSQ was incorporated into the EP/DOPO composites. From Table 2, it can be seen that the UL-94 rating of EP/DOPO composite is NR. When PPSQ was added to EP/DOPO, the UL-94 rating of the resulting EP/DOPO/PPSQ did not show any improvement. However, to our surprise, when OPS was added to this composite, the extinguishing times (t_1 and t_2) of the resulting EP/DOPO/OPS shortened remarkably, so that its UL-94 rating was raised to V-0. Moreover, another improvement was that an efficient blowing-out effect was observed in the UL-94 test on the EP/DOPO/OPS sample (Fig. 3). These improvements confirmed that OPS shows better flame retardancy than PPSQ for EP. Therefore, it seems that the respective structures of OPS and PPSQ play an important role in their flame retardancy and blowing-out effects in EPs.

3.3. *Thermogravimetric analysis of the cured epoxy resins*

The thermal stability of the EP composites was investigated by TGA. The relevant thermal decomposition data, including T_{onset}, defined as the temperature at which 5% weight loss occurs, $T_{\max}1$ and the $T_{\max}2$, defined as the temperatures at maximum weight loss rate, and the char residues at 800 °C, are given in Table 3.

The mass-loss curves of OPS and PPSQ are shown in Fig. 4, from which it is apparent that the thermal stability of PPSQ is much higher than that of OPS. As shown in Table 3, the values of T_{onset} for EP and EP/DOPO show small increases in the presence of silsesquioxanes (OPS and PPSQ). As can be seen in Fig. 5, in the first mass–loss region of 350–500 °C, the thermal stability of the EP composites is enhanced by the addition of silsesquioxanes. Besides, in this region, the EP composite with OPS shows better thermal stability than that with PPSQ. Thereafter, a slow second degradation stage appears at 500–700 °C, which is considered to correspond to the subsequent thermo-oxidative degradation of the char. In this second region, the improvements in thermal stability of the flame-retarded EP composites are negligible upon loading with silsesquioxanes. Moreover, as shown in Table 3, the char residues from EP/DOPO/silsesquioxane at 800 °C are evidently higher than those from the other EP composites. This enhancement is caused by the formation of a $-\mathrm{P}(=\mathrm{O})-\mathrm{O}-\mathrm{Si}-$ structure between DOPO and the silsesquioxanes, which serves to increase both the quantity and the thermal stability of the char [32]. TGA revealed that OPS and PPSQ have similar effects on the thermal stability of EP composites, though the ladder structure of PPSQ possesses higher thermal stability than the cage structure of OPS.

As shown in Table 3, the char residue of EP/OPS and EP/PPSQ are 0.6 wt.% and 0.4 wt.%, respectively, which are lower than the nominal Si content of the original composites (0.9 wt.%). To understand these needs deep research work. But it seems that under TGA conditions, the EP decomposition did not correlate with that of the OPS or PPSQ. The early and fast decomposition of the EP produced a large amount of pyrolytic gaseous products, while they may carry the molecules or fragments of OPS and PPSQ off the condensed phase. With increase of temperature, the OPS and PPSQ began to decompose, there were some interactions between the pyrolytic products of OPS and EP, and a little residue was left.

3.4. *Cone calorimeter analysis of the cured epoxy resins*

A cone calorimeter was used to investigate the fire behavior of the epoxy resins. The salient combustion parameters include time to ignition (TTI), heat release rate (HRR), peak of heat release rate

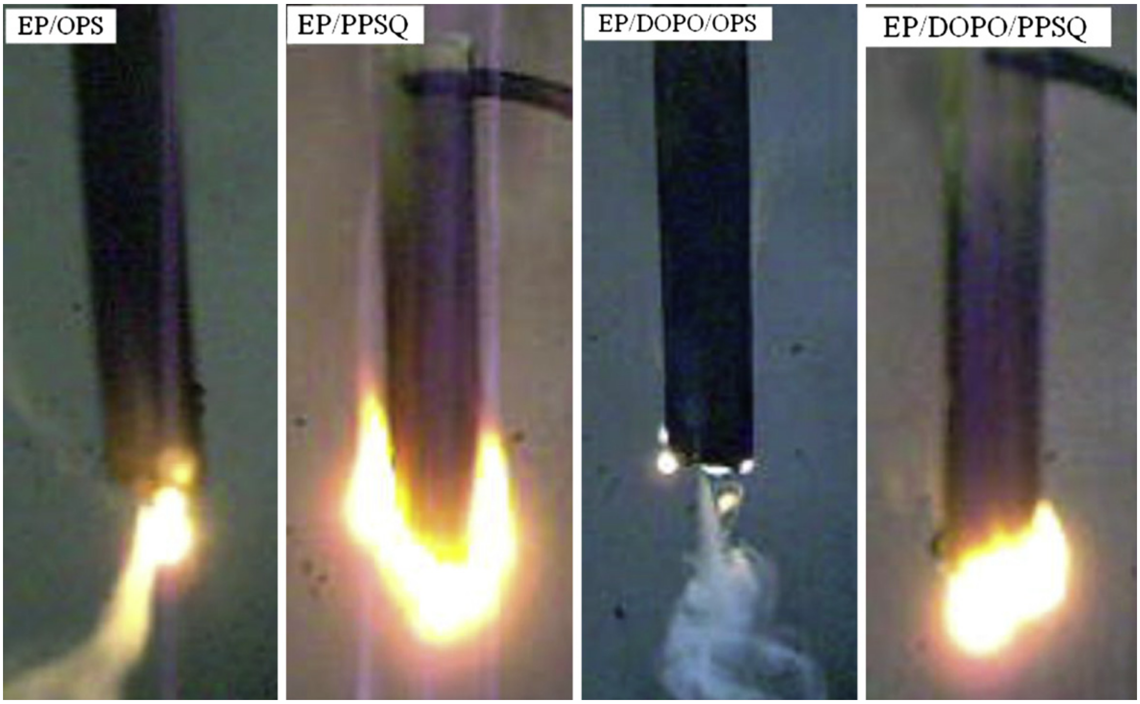


Fig. 3. Video screenshots of flame-retarded EP composites.

Table 3
TGA data of EP composites.

Samples	T_{onset} (°C)	$T_{max}1$ (°C)	$T_{max}2$ (°C)	Residues at 800 °C (%)
OPS	450	517	656	8.5
PPSQ	504	612	692	45.8
EP	345	370	559	0.0
EP/OPS	364	379	576	0.6
EP/PPSQ	360	381	577	0.4
EP/DOPO	336	354	588	0.0
EP/DOPO/OPS	348	363	581	3.9
EP/DOPO/PPSQ	346	361	567	2.5

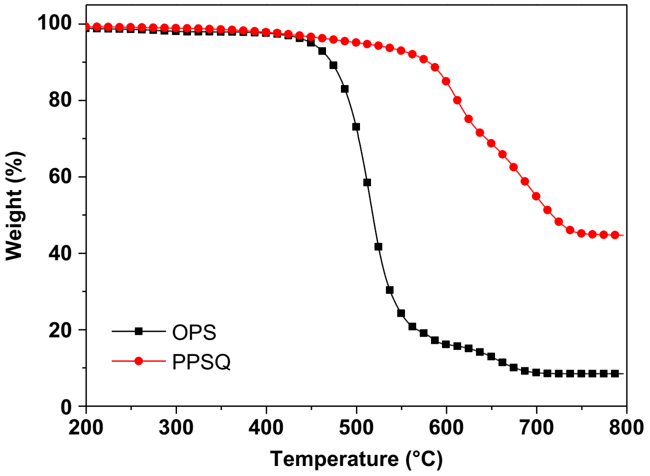


Fig. 4. TGA curves of OPS and PPSQ in air.

(p-HRR), and total heat release (THR). These parameters are reported in Table 4 for all of the samples.

TTI is used to determine the influence of a flame-retardant on ignitability. As shown in Table 4, the flame-retarded EP composites each had a longer TTI than that of the pure EP. The increase of TTI is very valuable for enhancement of the flame retardancy of epoxy resins. Besides, the EP composites with OPS showed a longer TTI than those with PPSQ.

The HRR curves and the p-HRR values of these samples are presented in Fig. 6 and Table 4. It was observed that the pure EP burned rapidly after ignition and HRR showed a sharp peak with a peak heat release rate (p-HRR) of 855 kW/m^2. When either OPS or PPSQ was added to pure EP, to our surprise, they exerted tremendously different effects on the flame retardation of EP. In Fig. 6, the p-HRR of EP/OPS is seen to be reduced remarkably from 855 kW/m^2 to 626 kW/m^2. However, most unexpectedly, the p-HRR of EP/PPSQ was measured as 925 kW/m^2, which is higher than that of pure EP. When OPS or PPSQ was added to the EP/DOPO composite, similar results were obtained, as is also apparent from Fig. 6. OPS can reduce the p-HRR of EP/DOPO, while PPSQ apparently increases the p-HRR of EP/DOPO. It has been reported that POSS can create a stable char layer of silicon dioxide on the surface of EP [28], which is effective in reducing the p-HRR. The behaviors of PPSQ in EP and EP/DOPO seem to be anomalous, considering that neat PPSQ can produce much larger residue than that of OPS in TGA. One possibility is in that once PPSQ ladder chain may break down as like a zip is zipped even though the ladder structure is very stable before zipping. The active broken segments of PPSQ accelerate the decomposition of the EP matrix and cause high heat release. Relatively, the OPS can produce limited broken segments when one OPS cage breaks.

In addition, curves of CO production rate (COPR) and CO_2 production rate (CO_2PR) of the EP composites are shown in Fig. 7. In Fig. 7A, the COPR and CO_2PR of EP/PPSQ are seen to be the highest among the three EP composites; in Fig. 7B, the COPR and CO_2PR of EP/DOPO/PPSQ remain the highest among the three EP/DOPO composites. Further, the COPR and CO_2PR of the EP composites with OPS are the lowest among the respective EP and EP/DOPO systems. These results indicate that the ladder-type PPSQ can give rise to fast release of CO and CO_2 than the cage-type OPS. Nevertheless, the mean COY andCO_2Y (CO and CO_2 yields) were almost same for both composites of OPS and PPSQ in Table 4.

The enhancement of COPR and CO_2PR is usually considered to be advantageous for the blowing-out effect. However, as shown in Fig. 3, the blowing-out effect in EP/PPSQ and EP/DOPO/PPSQ is negligible in comparison with that in EP/OPS or EP/DOPO/OPS. Nevertheless, according to our previous research [28,29], the blowing-out effect may be determined not only by the release of pyrolytic gases, but also by the properties of the condensed phase. Therefore, the different behavior observed for PPSQ and OPS in EP and EP/DOPO may be attributed to processes occurring in the condensed phase under the combustion conditions.

3.5. Analysis of the char residue of the EP composites

3.5.1. Visual observation

After the cone calorimeter tests, some valuable information was obtained by visual observation of the residues (Fig. 8). The char layers of EP/OPS and EP/PPSQ appeared distinctly intumescent, and were covered with white silicon dioxide (SiO_2) of continuous construction, which means accumulation of SiO_2 on the surface.

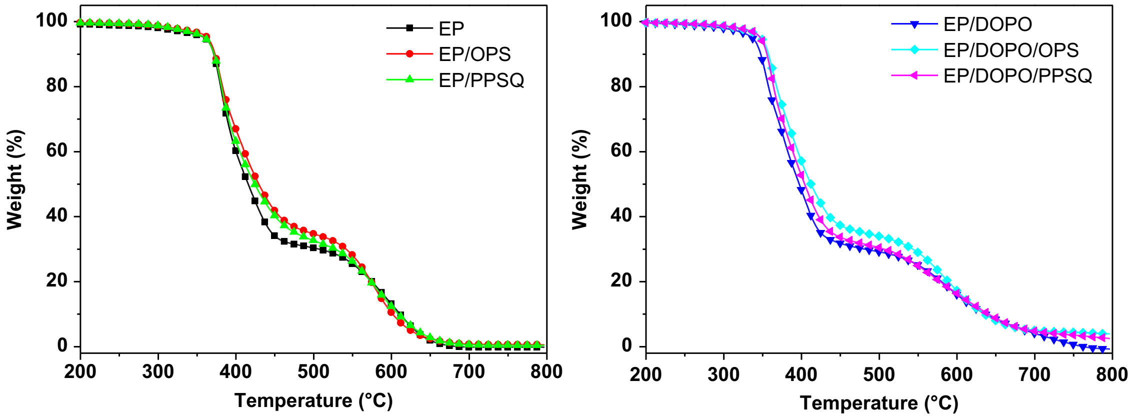


Fig. 5. TGA curves of EP composites in air.

Table 4
Cone calorimeter data for the EP composites.

Samples	EP	EP/OPS	EP/PPSQ	EP/DOPO	EP/DOPO/ OPS	EP/DOPO/ PPSQ
TTI (s)	45	55	50	54	51	49
p-HRR (kW/m^2)	855	626	925	686	557	895
THR (MJ/m^2)	112	112	116	96	95	100
Mean COY (kg/kg)	0.07	0.08	0.08	0.13	0.11	0.11
Mean CO_2Y (kg/kg)	1.82	2	2.05	1.7	1.82	1.84

When the DOPO was added into the composites, no accumulation of SiO_2 on the surface was observed as shown in Fig. 8. This can be attributed to formation of crosslinked –(O=)P–O–Si– structures in the condensed phase [32], which resulted in the more –Si–O– structure connecting to polyaromatic carbons like bridges, therefore no SiO_2 could migrate to the surface.

In addition, the chars of EP/PPSQ and EP/DOPO/PPSQ were much cracked when compared the chars with OPS to that with PPSQ.

3.5.2. SEM analysis

SEM images of the exterior chars from flame-retarded EPs are shown in Fig. 9. It can be seen that the chars of EP/OPS and EP/DOPO/OPS exhibited a continuous membrane-like microscopic structure, whereas those of EP/PPSQ and EP/DOPO/PPSQ showed cracked pieces or an island-like microscopic structure.

Clearly, in EP and EP/DOPO, the cage-type OPS induces the formation of a dense and protective char layer, but the ladder-type PPSQ does not. Since a dense and homogeneous char layer is advantageous for reducing heat and mass transfer between the condensed phase and gas phase, the observed char morphology can help to explain why the EP composites with OPS gave the minimum p-HRR, while those with PPSQ gave the maximum p-HRR.

3.5.3. XPS analysis

In order to further understand why the ladder-type PPSQ and cage-type OPS gave rise to different char structures, these chars were investigated by XPS. The concentrations of C, O, Si, P, and N in the exterior and interior of the chars are listed in Table 5.

For the EP/OPS and EP/PPSQ, there is little C, and abundant Si and O elements in the exterior of char; in the interior of the char, the principal constituent is C element. These were caused by migration of much SiO_2 to the char surface from the condensed phase.

For the EP/DOPO/OPS and EP/DOPO/PPSQ, a significant enhancement of C element and decrease of the Si and O elements in the exterior of char were detected compared with for the EP/OPS and EP/PPSQ. It seems that synergistic effect of P and Si could inhibit formation of SiO_2 and its migration to the surface.

In the interior of chars, concentrations of the Si and O elements showed little change with and without addition of DOPO.

3.6. Mechanism discussion

The main differences between OPS and PPSQ in retarding flames of EP and EP/DOPO are summarized in Table 6 on the basis of the above experimental results.

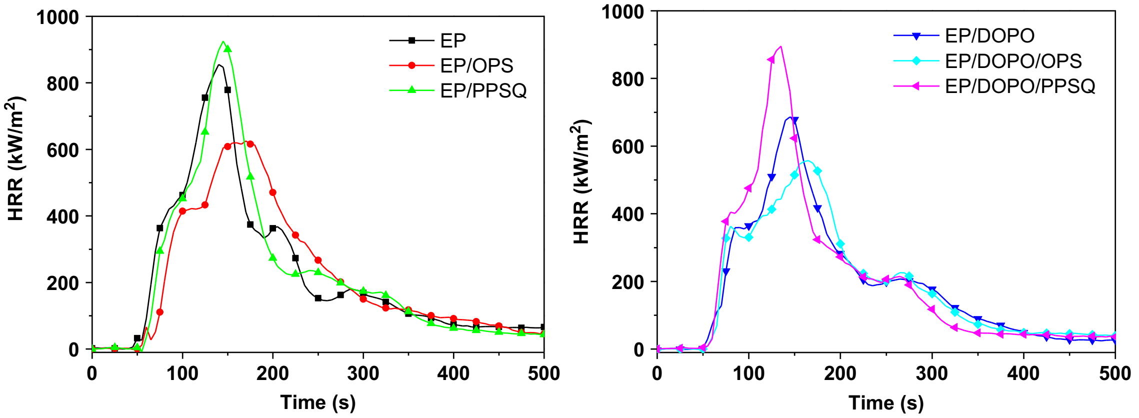


Fig. 6. Heat release rate curves of EP composites.

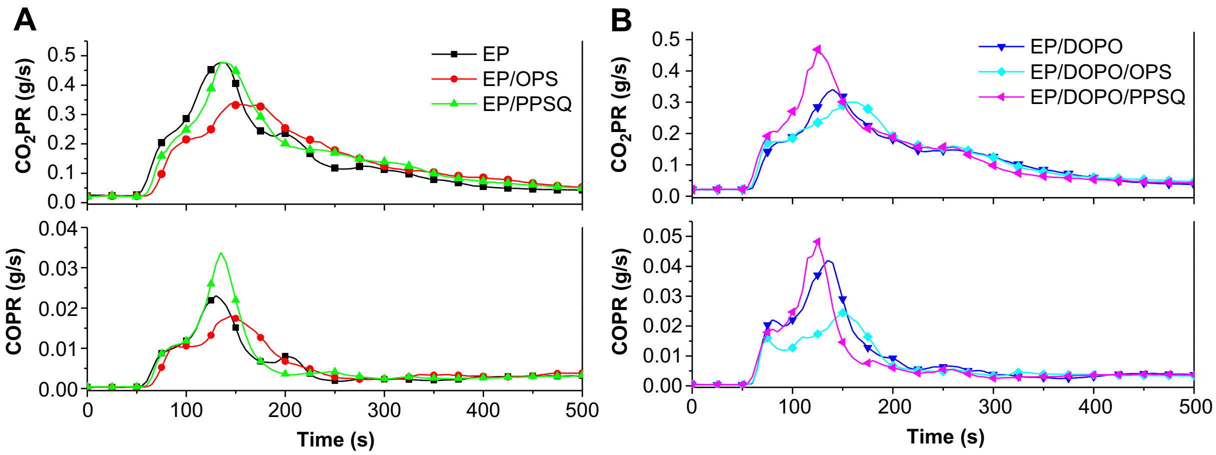


Fig. 7. CO and CO_2 production rate curves of EP composites.

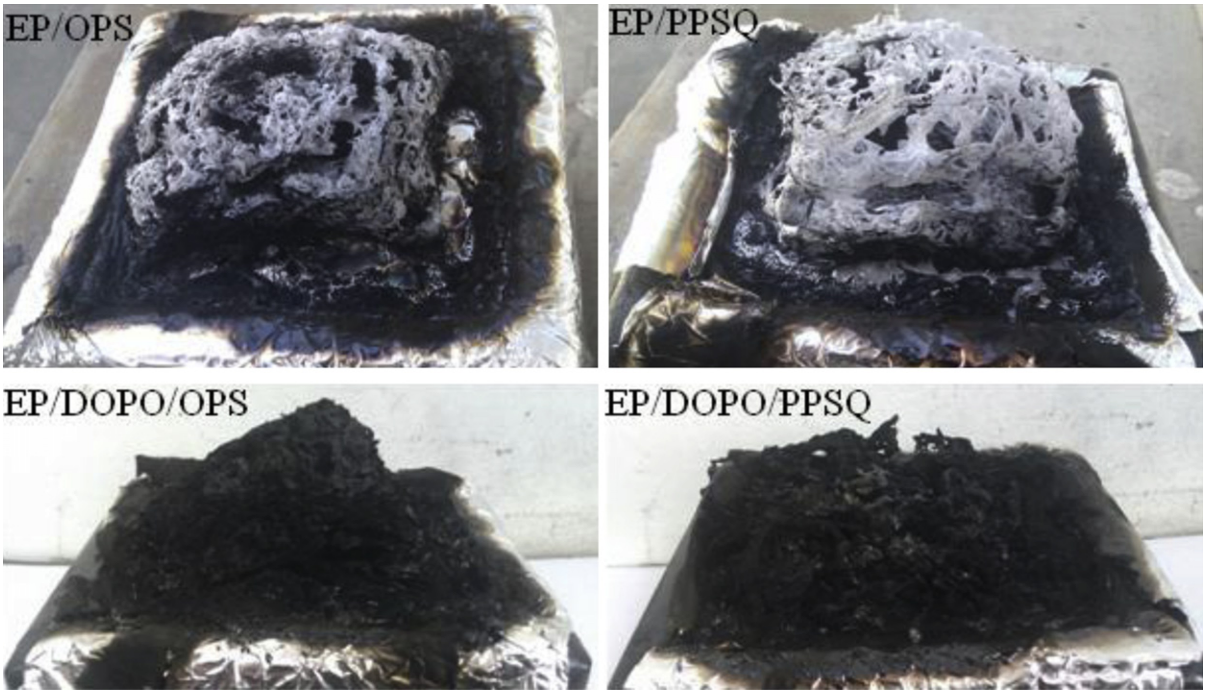


Fig. 8. Photographs of chars from flame-retarded EP composites after cone calorimeter tests.

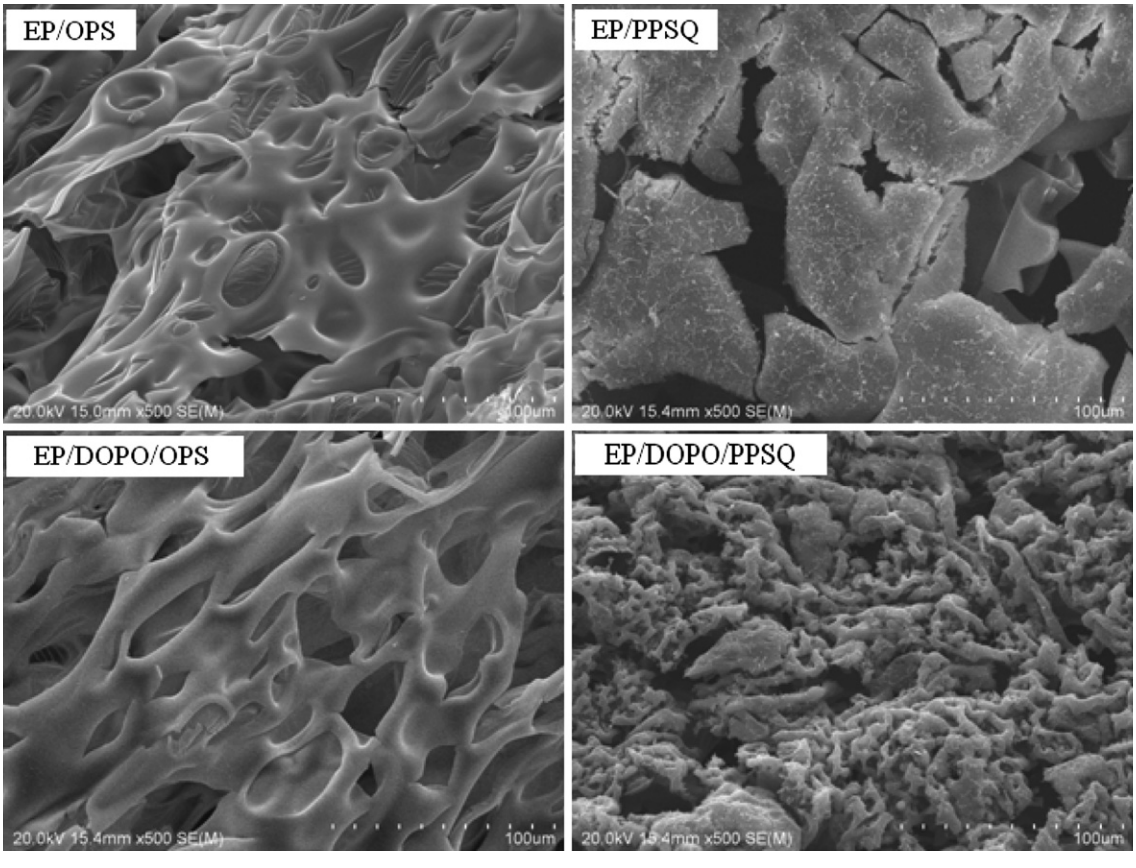


Fig. 9. SEM images of exterior chars from flame-retarded EP composites.

Table 5
Elemental compositions (%) of the chars of EP composites determined by XPS.

Samples	Exterior					Interior				
	C	O	Si	P	N	C	O	Si	P	N
EP	78.58	19.27	0.00	0.00	2.15	80.50	17.01	0.00	0.00	2.49
EP/OPS	6.74	65.92	27.34	0.00	0.00	82.54	11.17	2.33	0.00	3.97
EP/PPSQ	3.29	68.24	28.46	0.00	0.01	54.69	31.36	11.40	0.00	2.55
EP/DOPO	77.06	14.20	0.00	1.92	6.82	81.18	15.88	0.00	0.58	2.35
EP/DOPO/OPS	24.45	53.88	19.11	2.55	0.00	80.70	11.47	2.39	0.29	5.16
EP/DOPO/PPSQ	37.39	43.74	12.35	2.67	3.85	64.13	23.35	6.10	1.35	5.07

Table 6
Comparison of flame retardancies of OPS and PPSQ in EP and EP/DOPO.

Testing items	UL-94		Blowing-out effect	p-HRR	COPR and CO_2PR	Char layer	Si in interior char
	EP/	EP/DOPO/					
OPS	NR	V-0	Yes	Minimum	Low	Dense and continuous	Less
PPSQ	NR	NR	No	Maximum	High	Cracked	More

The previous investigation [32] revealed that in EP/DOPO/OPS the interactions between DOPO and OPS in the condensed phase can form −P(=O)−O−Si− structures, which can further connect Si(−O)$_4$ and polyaromatic carbons like bridges, thereby contributing to the dense and continuous char of EP/DOPO/OPS under combustion conditions. In addition, it is evident from Fig. 4 that neat PPSQ is more thermally stable and yields much more residue than OPS at 800 °C.

Accordingly, it may be supposed that, compared to OPS, PPSQ in EP or EP/DOPO can very slowly produce −Si−O−C− or −Si−O−P(=O)−C− cross-linked structures in the condensed phase under the action of heat, leading to the prophase formation of solid carbonaceous char containing little Si (as well as little P for EP/DOPO). Therefore, such a solid char may be very brittle, and may crack very easily. Cracking of the solid char uncovers fresh bulk EP, causing further combustion with ensuing high heat release and productions of CO and CO_2. In other words, the ladder structure of PPSQ reacts too slowly to cause cross-linking and charring in the condensed phase to match the intumescent and charring process of the EPs during combustion, the solid chars cannot develop a layer structure, and are damaged before they can protect the bulk EP. On the contrary, cross-linking in the condensed phase caused by OPS seems to have the desired retarding effect.

4. Conclusions

Improvements in the flame retardancy of EPs with OPS have been detected by UL-94 tests. The cage-type OPS makes EP composite self-extinguishing and elevates the rating of EP/DOPO to V-0 in the UL-94 test. Furthermore, a blowing-out effect was observed during UL-94 tests on EP/OPS and EP/DOPO/OPS. However, the ladder-type PPSQ has a negligible effect on LOI and UL-94 tests of EP composites. The analysis of TTI, HRR, p-HRR, and THR values for the epoxy composites has indicated that cage-type OPS has better flame-retardant effects on EP composites than ladder-type PPSQ.

Cone calorimeter measurements imply that the EP composites with OPS gave the minimum p-HRR and low CO and CO_2 productions, while those with PPSQ gave the maximum p-HRR and high CO and CO_2 productions. Based on visual observation, SEM, and XPS analysis, the char residues from EP/PPSQ and EP/DOPO/PPSQ were cracked, whereas those from EP/OPS and EOP/DOPO/OPS were dense and continuous. In addition, there was more Si in the interior of the chars from EP/PPSQ and EP/DOPO/PPSQ than in those from EP/OPS and EOP/DOPO/OPS.

It is suggested that the cross-linking and charring induced by PPSQ in the condensed phase of the EP composites cannot match the intumescent and charring process of the EPs during combustion, whereas with OPS the two processes seem to be able to match each other.

Acknowledgment

This work was funded by National Natural Science Foundation of China (No. 51273023).

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