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Blowing-out effect in epoxy composites flame retarded by DOPO-POSS and its correlation with amide curing agents

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ABSTRACT

A novel polyhedral oligomeric silsesquioxane containing 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO-POSS) has been used to flame retard DGEBA (diglycidyl ether of bisphenol A) epoxy resins cured by two amides, namely the aliphatic oligomeric polyamide 650 (PA650) and the aromatic 4,4′-diaminodiphenylsulphone (DDS). The epoxy composites with DOPO-POSS showed different flame retardant properties depending on the amide used. The results of UL-94 tests show that the DEGBA/DDS with DOPO-POSS exhibits a blowing-out effect through vigorous emission of pyrolytic gases, but the DEGBA/PA650 does not. Moreover, only 2.5 wt.% DOPO-POSS imparts to the epoxy resin DEGBA/DDS a LOI value of 27.1% and UL-94 V-1 rating. In contrast, 10 wt.% DOPO-POSS in the DEGBA/PA650 results in a LOI value of 25.9% and a UL-94 V-1 rating. The details of fire behaviour, such as the values of TTI, HRR, p-HRR, COPR, and CO_2PR have been tested using a cone calorimeter. DOPO-POSS in the DEGBA/DDS causes a lower value of p-HRR and longer TTI than in the DEGBA/PA650. The DEGBA/DDS with even as little as 2.5 wt.% DOPO-POSS easily forms a compact char. However, the DEGBA/PA650 with DOPO-POSS does not char until 10 wt.% DOPO-POSS has been added. The thermal stability and pyrolytic gases of the two kinds of epoxy resins were assessed by TGA-FTIR under a nitrogen atmosphere. DOPO-POSS performs better in accelerating charring in the DDS curing system compared with the PA650 curing system. It is postulated that for the DEGBA/DDS/DOPO-POSS, fast and dense charring and accumulating of pyrolytic gases in the char contribute to the blowing-out effect. By contrast, the aliphatic chain of the PA650 is easy to break down and produce combustible gases, so does not easily form a crosslinked structure in the condensed phase until enough DOPO-POSS has been added. These results may be very helpful for investigation of the conditions under which the blowing-out effect in epoxy resins can be caused by synergy of phosphorous (DOPO) and silicon (POSS).

1. Introduction

Epoxy resin (EP) has become a very important thermosetting material because of its excellent mechanical and chemical properties. It is used as a high-performance material in many fields, such as an adhesive, coating, laminating capsulation, electronic/electrical insulation, and for composite applications. However, the fire risk remains a major drawback of these materials [1–4]. Halogen-containing flame retardants are reported to be effective flame retardants for epoxy resins. However, some of these are restricted in their use because they generate dense toxic smoke and corrosive products during combustion [5]. Therefore, the preparation and application of halogen-free flame retardants has been the subject of extensive investigation.

Organic–inorganic hybrid composites are normally considered to be a new generation of high-performance materials, as they combine the advantages of inorganic materials with those of organic polymers [6,7]. Polyhedral oligomeric silsesquioxanes (POSS) have the chemical composition ($RSiO_{1.5}$), where R is hydrogen or any alkyl, alkylene, aryl, or arylene group, or a number of other organo-functional derivatives, and is similar in composition to both silica (SiO_2) and silicone (R_2SiO) [8,9]. POSS molecules, with a nanosized, cage-shaped, three-dimensional structure, can be incorporated into almost any type of thermoplastic or thermosetting polymer to improve their thermal properties and oxidation resistance and flame retardancy [10,11].

Phosphorous compounds can impart flame retardancy through flame inhibition in the gas phase and the condensed phase [12,13]. Several non-reactive and reactive phosphorus-containing flame

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retardants for epoxy resins have been investigated in recently published work [14–16]. 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) is a cyclic phosphate with a diphenyl structure which has high thermal stability, and good resistance to oxidation and water [17,18]. Using DOPO or its derivatives as flame retardants, significant improvements in the fire behaviour of epoxy resins have been reported [14–16].

In our previous work, the DOPO-containing polyhedral oligomeric silsesquioxane (DOPO-POSS) (Scheme 1) was synthesized successfully [19]. In addition, an interesting phenomenon, called the “blowing-out effect”, has been detected in flame retarded epoxy resins loaded with DOPO-POSS. The model of the blowing-out effect is shown in Scheme 2 [20,21]. In order to further understand the reasons behind and the factors that influence the blowing-out effect, we have examined the use of DOPO-POSS as a flame retardant for epoxy resins cured by both oligomeric polyamide 650 (PA650) and 4,4′-diaminodiphenylsulphone (DDS) (Scheme 3). This work presents a study of the responses of flame retarded EP composites following exposure to fire.

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. The oligomeric polyamide 650 (PA650) and 4,4′-diaminodiphenylsulphone (DDS) were purchased from TianJin GuangFu Fine Chemical Research Institute. DOPO-POSS was synthesized in our laboratory. DOPO-POSS was mixture of perfect T_8 cage and imperfect T_9 cage with one Si—OH group on it [19].

2.2. Preparation of the cured epoxy resins

The cured epoxy resins were obtained using a thermal curing process. 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. After that, the curing agent DDS was then added relative to the amount of DGEBA. The equivalent weight ratio of DGEBA to DDS was 20:9. The epoxy resins were cured at 180 °C for 4 h. For the PA650, the mixture cooling to 40 °C, the curing agent then added relative to the amount of DGEBA. The equivalent weight ratio of DGEBA to PA650 was 2:1. The epoxy resins were cured at 80 °C for 4 h. The LOI and UL-94 test samples were strips. The contents of the DOPO-POSS in the EP composites are listed in Tables 1 and 2.

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 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 unclassified, depending on its behaviour (dripping and burning time).

Thermal gravimetric analysis (TGA) was performed with a Netzsch 209 F1 thermal analyser, 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 samples were 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 averages of three measurements. To detect the gas species given off, the TGA was coupled with a Fourier transform infrared spectrometer (TGA-FTIR, Nicolet 6700). The connection between the TGA and FTIR was effected with a quartz capillary held at a temperature of 200 °C.

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 of three measurements.

To investigate the condensed phase of the EP composites, all the cone calorimeter tests were stopped at 500 s. The residue was cooled under room conditions. A sample of the exterior char of about 1 cm thickness was ground and analysed by FTIR (Nicolet 6700) in ATR mode.

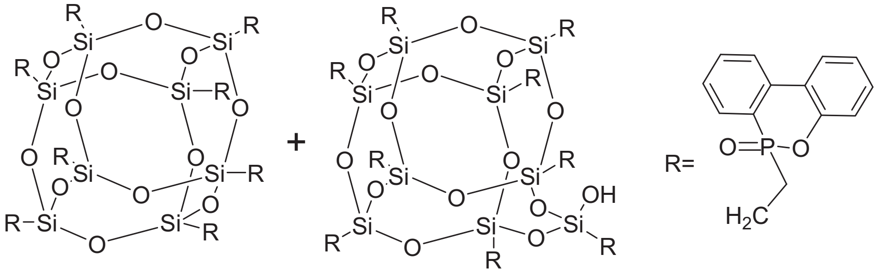
3. Results and discussion

3.1. Flame retardancy of the cured epoxy resins

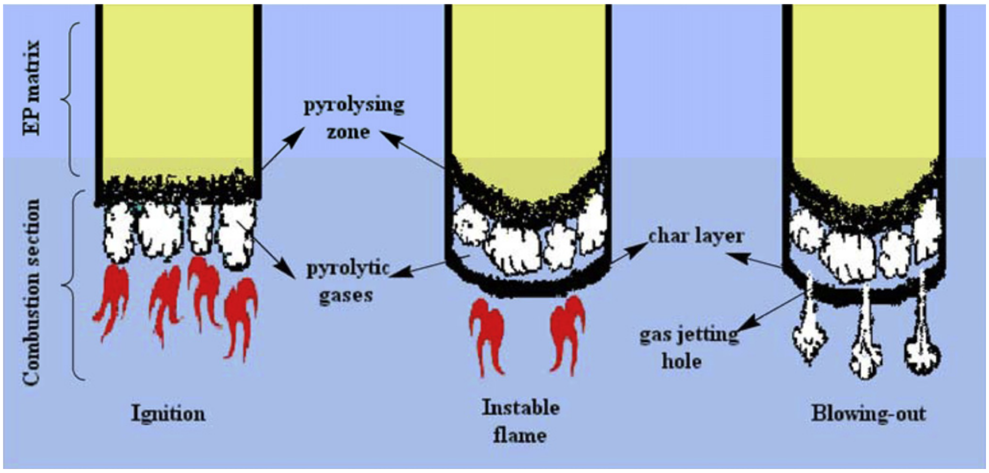
In order to understand the connection between the presence of DOPO-POSS and the blowing-out effect, the flame retardancy of epoxy resins (EP) cured using both oligomeric aliphatic PA650 and aromatic DDS curing agents has been investigated by way of the LOI and UL-94 tests.

The UL-94 test results of the DGEBA/DDS composites are shown in Table 1. It is clear that the flame retardancy of the epoxy resins is enhanced by loading with DOPO-POSS. No dripping is observed for any of the samples and self-extinguishing is observed with samples loaded with 2.5 and 5.0 wt.% DOPO-POSS. It is important to point out that the extinguishing is caused by the blowing-out effect [20] but this effect is weakened with increase of the DOPO-POSS content.

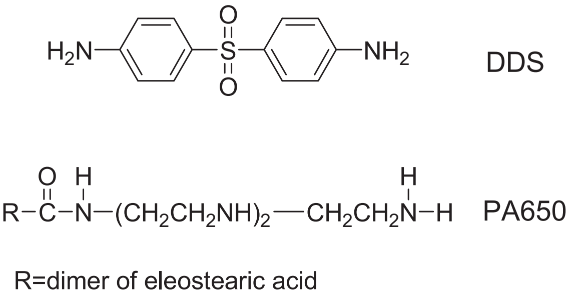
In the case of the DGEBA/PA650 composites, as shown in Table 2, enhanced flame retardancy appears with the increase of DOPO-POSS loading. The dripping phenomenon is no longer observed and self-extinguishing takes place with 10 wt.% DOPO-POSS



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



Scheme 2. The model of the blowing-out effect.



Scheme 3. The chemical structures of DDS and PA650.

loading. Unfortunately, however, none of the blowing-out characteristics were observed during the UL-94 test. The effect of DOPO-POSS in the DGEBA/PA650 system corresponds well with the traditional concept that introducing phosphorous and silicon into epoxy resins would enhance the flame retardancy by enhancing the formation of char.

Visual observation of the combustion experiments reveals different flame retardancy performances for epoxy resins loaded with DOPO-POSS and cured with DDS and PA650. In the case of pure DGEBA/DDS (Fig. 1A), a small amount of char forms at the end of the samples. The thermally decomposing surface of pure DGEBA/DDS exposes in the fire directly and the fire diffuses quickly from the location of the ignition. For the sample DGEBA/DDS/2.5 wt.% DOPO-POSS, a char layer survives and grows in first few seconds following ignition, yielding a rigid char-brick with the same dimensions as the original sample (Fig. 1B). At the same time, frequent high speed jetting of the pyrolytic gases can be detected and the fire is quickly blown out. This phenomenon is simply the blowing-out effect, and has been reported before [20]. However, a weak blowing-out effect was observed in the test on the sample DGEBA/DDS/5 wt.% DOPO-POSS. In the case of DGEBA/DDS/10 wt.% DOPO-POSS (Fig. 1C), the char layer formed quickly and the fire at the end of the sample diffused slowly upwards. However, spurting and self-extinguishing of the pyrolytic gases was not observed.

By contrast, the DGEBA/PA650 composites can be ignited easily and no char formation can be observed. The boiling decomposing surface (Fig. 2A) of pure DGEBA/PA650 exposes in the fire directly. A little char formation can be observed with 2.5 and 5 wt.% DOPO-POSS loading in DGEBA/PA650 composites, but the boiling decomposing surface can still be observed (Fig. 2B). In the case of DGEBA/PA650/10 wt.% DOPO-POSS, an obvious char layer was formed after ignition and the boiling decomposing surface totally disappeared. Afterwards the self-extinguishing could be detected (Fig. 2C), but there was no evidence for jetting of the pyrolytic gases in this sample.

These visible studies have shown that DOPO-POSS imparts different effects on the gas phase and condensed phase in epoxy composites cured by DDS or PA650. In DGEBA/DDS, the presence of only 2.5 wt.% DOPO-POSS produced a dense char layer on the surface of the test bar. However, the boiling condensed phase could be observed even when 5 wt.% DOPO-POSS was incorporated into the DGEBA/PA650 composite. This result indicates that the decomposing products from the DGEBA/PA650/DOPO-POSS composites in the condensed phase possess a low viscosity, because the aliphatic PA650 chains are easy to break down to produce combustible gases. They do not easily form a crosslinked structure in the condensed phase until enough DOPO-POSS has been added.

The effects of DOPO-POSS on the LOI values of DGEBA/DDS system are presented in Table 1. We observe that the LOI values increase with increase in the loading of DOPO-POSS. When 2.5 wt.% DOPO-POSS is incorporated, the LOI value of the epoxy resin is increased from 22.0% to 27.1%. However, further increases of the DOPO-POSS content lower the LOI value from 27.1% to 24.8%. A

Table 1
Flame retardancy of DGEBA/DDS/DOPO-POSS composites.

Samples	Cured epoxy resin (wt.%)	Content of DOPO-POSS (wt.%)	LOI (%)	UL-94 (3.2 mm)	t_1 (s)	t_2 (s)	Dripping
DGEBA/DDS	100.0	0.0	22.0	NR	>30	/	Yes
DGEBA/DDS/2.5 wt.% DOPO-POSS	97.5	2.5	27.1	V-1	8	5	No
DGEBA/DDS/5 wt.% DOPO-POSS	95.0	5.0	26.2	NR	44	35	No
DGEBA/DDS/10 wt.% DOPO-POSS	90.0	10.0	24.8	NR	>30	/	No

Table 2
Flame retardancy of DGEBA/PA650/DOPO-POSS composites.

Samples	Cured epoxy resin (wt.%)	Content of DOPO-POSS (wt.%)	LOI (%)	UL-94 (3.2 mm)	t_1 (s)	t_2 (s)	Dripping
DGEBA/PA650	100.0	0.0	20.0	NR	>30	/	Yes
DGEBA/PA650/2.5 wt.% DOPO-POSS	97.5	2.5	21.5	NR	>30	/	Yes
DGEBA/PA650/5 wt.% DOPO-POSS	95.0	5.0	23.5	NR	>30	/	Yes
DGEBA/PA650/10 wt.% DOPO-POSS	90.0	10.0	25.9	V-1	14	15	No

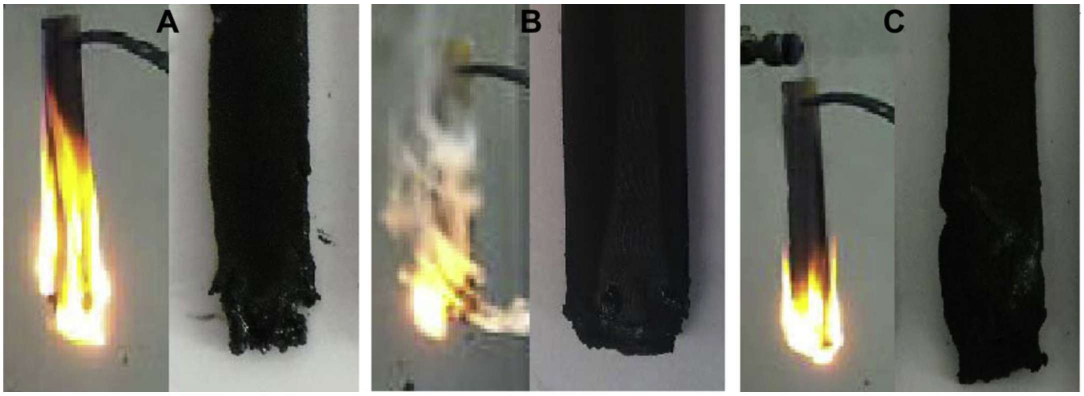


Fig. 1. Videos screenshots and photo of bars after UL-94 test of (A) DGEBA/DDS, (B) DGEBA/DDS/2.5 wt.% DOPO-POSS, and (C) DGEBA/DDS/10 wt.% DOPO-POSS.

similar effect for DOPO-POSS was obtained in a previous study of the flame retarded epoxy resin cured by another aromatic curing agent [20].

However, as shown in Table 2, the effects of DOPO-POSS on the LOI values of DGEBA/PA650 system are quite different. The LOI values of DGEBA/PA650/DOPO-POSS composites gradually increase with increase of the DOPO-POSS loading. When 10 wt.% DOPO-POSS incorporated, the LOI value increases from 20.0% to 25.9%. It was reported that the epoxy resins' LOI values showed a linear relationship with the amount of phosphorus and silicon in the epoxy resins [6,22]. From the results of the LOI test, we can detect that DOPO-POSS have different flame retardant performances in the EP composites cured by these two curing agents.

3.2. TGA-FTIR analysis of the cured epoxy resins

In order to understand the different behaviours of DOPO-POSS in the condensed phase, the TGA data have been used to analyse the thermal stability of the epoxy composites cured by DDS and PA650. 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 800 °C, are given in Tables 3 and 4.

The mass loss temperature of DOPO-POSS is much higher than that of the pure DGEBA/DDS. However, with 2.5, 5, and 10 wt.% DOPO-POSS incorporated, one-step rapid degradation is observed in the TGA analysis, as shown in Fig. 3, and the T_{max} values of the DGEBA/DDS/DOPO-POSS composites are similar to that of pure DGEBA/DDS. The most significant results are shown in Table 3, which shows that the char yield of the DGEBA/DDS/DOPO-POSS composites are much higher than that of DGEBA/DDS. In the case of DGEBA/DDS/2.5 wt.% DOPO-POSS, in particular, the presence of DOPO-POSS clearly increases the char of the sample from 9.9% to 16.3%. However, when 5 and 10 wt.% DOPO-POSS are incorporated in DGEBA/DDS composites, the char yields of the samples increased only a little, from 16.3% to 18.6% and 20.9%. These small increments of char yield may be attributed to the increase of DOPO-POSS content, which possesses a high char yield. We believe that the DOPO-POSS may participate and accelerate the crosslinking reaction of the decomposed products in the condensed phase, which

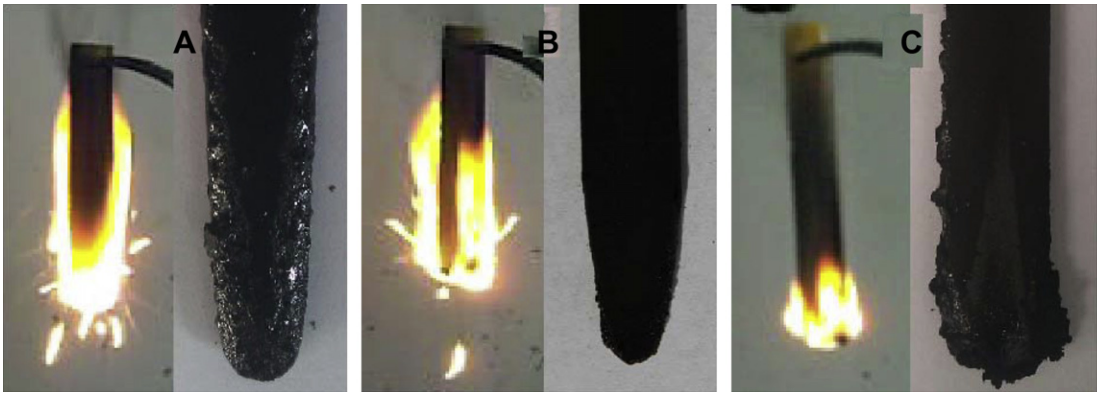


Fig. 2. Videos screenshots and photo of bars after UL-94 test of (A) DGEBA/PA650, (B) DGEBA/PA650/2.5 wt.% DOPO-POSS, and (C) DGEBA/PA650/10 wt.% DOPO-POSS.

Table 3
TGA data of DOPO-POSS and DGEBA/DDS/DOPO-POSS composites in nitrogen atmosphere.

Samples	T_{onset} (°C)	T_{max} (°C)	Residues at 800 °C (%)
DGEBA/DDS	383	430	9.9
DGEBA/DDS/2.5 wt.% DOPO-POSS	384	424	16.3
DGEBA/DDS/5 wt.% DOPO-POSS	385	424	18.6
DGEBA/DDS/10 wt.% DOPO-POSS	382	426	20.9
DOPO-POSS	334	479	40.6

Table 4
TGA data of DOPO-POSS and DGEBA/PA650/DOPO-POSS composites in nitrogen atmosphere.

Samples	T_{onset} (°C)	$T_{max}1$ (°C)	$T_{max}2$ (°C)	Residues at 800 °C (%)
DGEBA/PA650	319	372	426	2.6
DGEBA/PA650/2.5 wt.% DOPO-POSS	316	372	421	4.3
DGEBA/PA650/5 wt.% DOPO-POSS	316	364	425	6.6
DGEBA/PA650/10 wt.% DOPO-POSS	313	369	426	8.4
DOPO-POSS	334	479	/	40.6

helps to enhance the strength and thermal stability of the char layer. Moreover, this remarkable enhancement of char yield explains why DGEBA/DDS/DOPO-POSS composites could form a dense char layer, which may act as a barrier for accumulation of the pyrolytic gases and contribute to the blowing-out effect.

The thermal stability of DOPO-POSS is also much higher than that of pure DGEBA/PA650. However, as shown in Fig. 4 and Table 4, whether 2.5, 5 or 10 wt.% DOPO-POSS is loaded in DGEBA/PA650/DOPO-POSS composites, the important parameters for characterization of the thermal stability, such as T_{onset}, $T_{max}1$, and $T_{max}2$, are similar to those of pure DGEBA/PA650. Moreover, it is also noticeable that although the char yields of the DGEBA/PA650/DOPO-POSS composites increase gradually, the main increments are due to the residues of DOPO-POSS itself. As shown in the DTG curves in Fig. 4, the decomposition rate of the epoxy resins at $T_{max}2$ reduce gradually with increasing DOPO-POSS content. This indicates that DOPO-POSS can increase the thermal stability of the decomposition products in condensed phase.

The TGA analyses of these samples indicate that DOPO-POSS has a different performance on promotion of char yield in the epoxy composites cured by PA650 and DDS. For the DDS cured systems, which possess a high concentration of compounds with an aromatic structure, a significant increase of char yield is detected when loaded with DOPO-POSS. The DOPO-POSS may participate and accelerate the crosslinking reaction, which increases the char yield and the thermal stability of the char. For the PA650 systems, slight and gradual enhancements of the thermal stability of the decomposition products and char yield are detected with increase of loading with DOPO-POSS. We believe that when more than 30 wt.% of the aliphatic PA650 is present, this dilutes the aromatic compounds and prevents the crosslinking reaction happening because the DOPO-POSS content is not high enough. These influences of DOPO-POSS indicate that the formation of a crosslinked char layer is determined not only by the content of DOPO-POSS but also by the structures of the amide curing agent used to prepare the DGEBA epoxy resin.

In order to understand the blowing-out effect, it is important to know the identity of the pyrolytic gases produced by the epoxy resins composites. Accordingly, the pyrolytic gas species 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. 5.

The major pyrolytic gases detected from the decomposition of DGEBA/PA650 and DGEBA/DDS 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}) [23]. As shown in Fig. 5, although the gas species from the DGEBA/PA650 composites are similar to those from the DGEBA/DDS composites, the DGEBA/PA650 composites produce more aliphatic and less aromatic components. This is caused by the fact that the oligomeric PA650 possesses lots of aliphatic structures in its molecule, but DDS is an aromatic amine curing agent. In addition, no characteristic absorptions from the gas products of DOPO-POSS were found in the epoxy resin composites. It should be noted that no change of pyrolytic gases species is observed with DOPO-POSS loading in the two epoxy resin systems.

Releases of aromatic and aliphatic components as a function of temperature for the epoxy composites are shown in Figs. 6 and 7. As shown in Fig. 6, the releases of aliphatic and aromatic components of DGEBA/PA650/DOPO-POSS are gradually reduced with increase of the DOPO-POSS content. Similar reductions are shown in Fig. 7 for DGEBA/DDS/DOPO-POSS composites. However, comparing Fig. 6 with Fig. 7, we note that 2.5 wt.% DOPO-POSS makes the absorbance intensity of gases released from the DGEBA/DDS composites is reduced by 50%. However, the reduction shown by DGEBA/PA650 composites is only 25%. The gaseous products from DGEBA/DDS composites are significantly reduced compared with

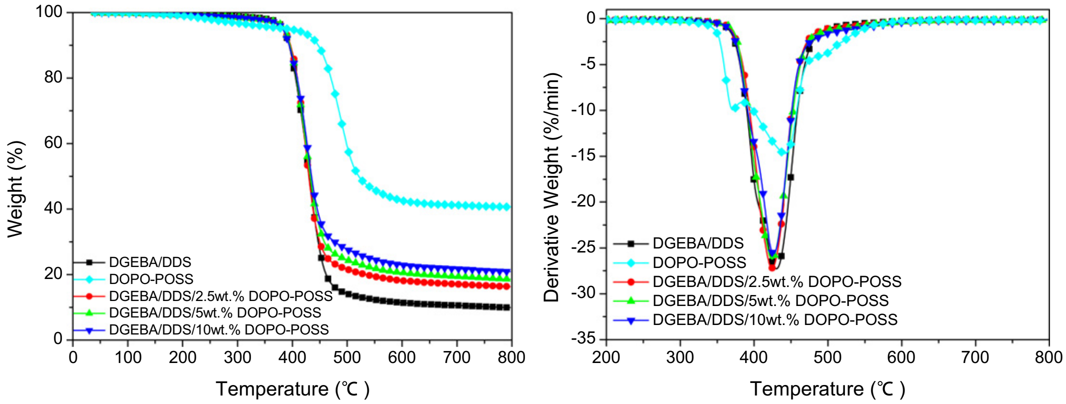


Fig. 3. TGA and DTG curves of DOPO-POSS and DGEBA/DDS/DOPO-POSS composites in nitrogen atmosphere.

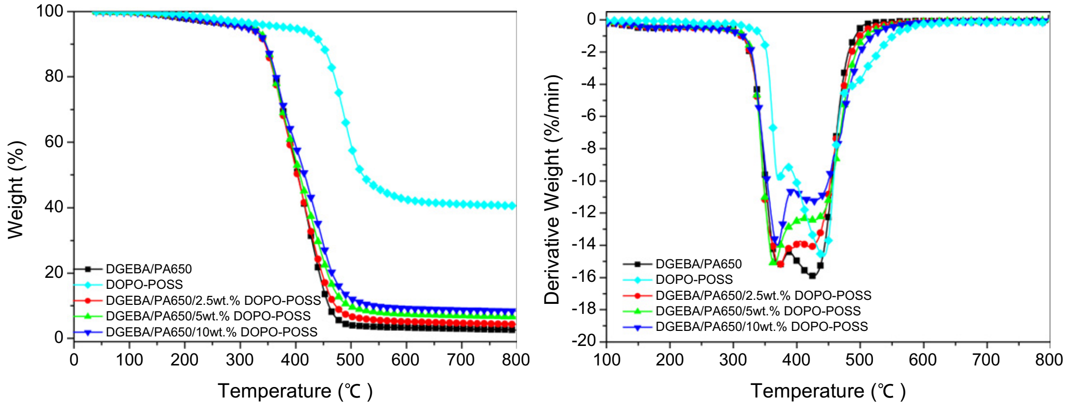


Fig. 4. TGA and DTG curves of DOPO-POSS and DGEBA/PA650/DOPO-POSS composites in nitrogen atmosphere.

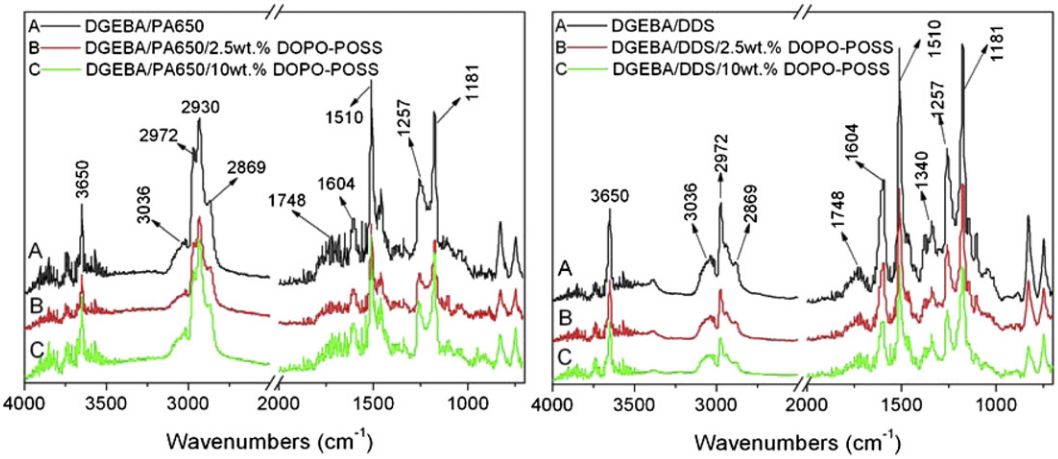


Fig. 5. FTIR spectra of pyrolytic products of DGEBA/PA650 composites (at $T_{max}2$) and DGEBA/DDS composites.

the DGEBA/PA650 composites. This result indicates that the rate release of pyrolytic gases bears a close relationship to the structure of the amide curing agents.

3.3. Cone calorimeter analysis of flame retarded epoxy resins

The cone calorimeter, which can provide a wealth of information for the simulation of real fire conditions, has been used to investigate the effects of DOPO-POSS on the behaviour in fire of two epoxy resin systems. The relevant 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 Tables 5 and 6 for different samples.

TTI is used to determine the influence of flame retardant on ignitability. As shown in Tables 5 and 6, the TTI of the flame retarded epoxy resins with DOPO-POSS loading do not show any effective enhancement.

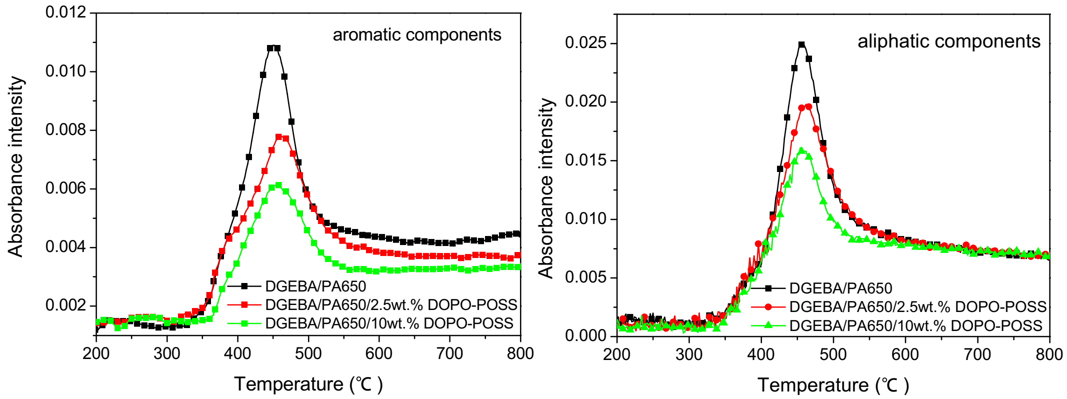


Fig. 6. The aromatic and aliphatic components release with temperature according to TG-FTIR spectra of DGEBA/PA650 composites.

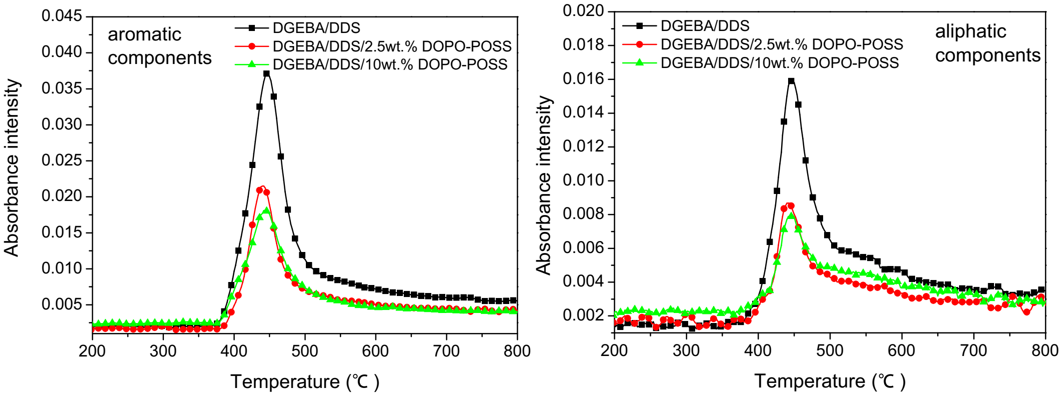


Fig. 7. The aromatic and aliphatic components release with temperature according to TG-FTIR spectra of DGEBA/DDS composites.

The HRR versus time curves for the DGEBA/PA650 composites are presented in Fig. 8. It can be seen that the DGEBA/PA650 composites burn rapidly after ignition and boiling of the decomposition products in the condensed phase is again observed. The p-HRR of DGEBA/PA650, DGEBA/PA650/2.5 wt.% DOPO-POSS, and DGEBA/PA650/5 wt.% DOPO-POSS are 892, 963, and 937 kW/m^2, respectively. In this situation, DOPO-POSS apparently accelerates the decomposition of the epoxy resin matrix as shown in their mass loss curves in Fig. 9. However, the p-HRR of DGEBA/PA650/10 wt.% DOPO-POSS is 690 kW/m^2, a small reduction of p-HRR is observed due to its decent char layer. This phenomenon means that the crosslinking structures could not be created in the condensed phase until sufficient DOPO-POSS had been added. Moreover, as shown in Table 5, the THR values of the DGEBA/PA650 composites decrease with increase of the DOPO-POSS content. The calculated data for the THR as a function of the mass fraction of DOPO-POSS in the epoxy resins are shown in Table 5. It is noted that the THR values for the DGEBA/PA650 composites decrease with increasing DOPO-POSS content. However, the experimental THR value for DGEBA/PA650 with only 10 wt.% DOPO-POSS is lower than the calculated, a result clearly due to the protection of its effective char layer.

In the case of DGEBA/DDS composites (Fig. 8), the DGEBA/DDS burn rapidly after ignition and HRR reaches a sharp peak with a p-HRR of 839 kW/m^2. Moreover, with DOPO-POSS incorporated, the p-HRR of the DGEBA/DDS composites is clearly reduced as the loading of DOPO-POSS increases. For instance, the p-HRR of DGEBA/DDS/10 wt.% DOPO-POSS is drastically reduced, from 839 kW/m^2 to 346 kW/m^2. These results correspond well with their mass loss curves (Fig. 9) which indicate that the DOPO-POSS could increase the thermal stability of the char layer. The stable char layer could reduce the p-HRR of samples significantly. Moreover, as shown in Table 6, the THR values of the DGEBA/DDS composites are reduced with increase of the DOPO-POSS content and their experimental THR values are much lower than those calculated. These results indicate that DOPO-POSS has a very beneficial effect on the flame retardancy of the DGEBA/DDS composites so it must have some synergy with DGEBA/DDS matrix.

Based on the blowing-out effect observed in the UL-94 test, we think the releases of CO and CO_2 during the combustion are worth investigating.

We observe that, as shown in Tables 5 and 6, the mean CO yield (COY) of all epoxy composites increases gradually with increased DOPO-POSS content and, at the same time, the mean CO_2 yield (CO_2Y) of the samples is reduced. Increases of incomplete combustion products, typically CO, indicate the flame retardancy effect of DOPO-POSS can take place in the gas phase. It is reported that some halogen- and phosphorus-based flame retardants 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 [24].

The curves of the CO production rate (COPR) and CO_2 production rate (CO_2PR) of DGEBA/PA650 composites are shown in Fig. 10. In the case of DGEBA/PA650/2.5 wt.% DOPO-POSS and DGEBA/PA650/5 wt.% DOPO-POSS, the COPR are higher than those for pure DGEBA/PA650. Moreover, the values of CO_2PR are equal to that for pure DGEBA/PA650. For DGEBA/PA650/10 wt.% DOPO-POSS, the COPR are higher than that of pure DGEBA/PA650. However, the CO_2PR are lower than that of pure DGEBA/PA650. It is a pity that no matter whether the production rates of gases from the DGEBA/PA650/DOPO-POSS composites are higher or lower than that of pure DGEBA/PA650, no blowing-out effect could be detected in the resins cured with PA650. This result indicates that the accomplishment of the blowing-out effect may be determined not only by the rate of production of gases, but also by the properties of the condensed phase.

As shown in Fig. 11, the values of COPR and CO_2PR for the DGEBA/DDS composites reduce gradually with increase of DOPO-POSS loading compared with that of pure DGEBA/DDS. This trend

Table 5
Cone calorimeter data for the DGEBA/PA650 composites.

Samples	DGEBA/PA650	DGEBA/PA650/2.5 wt.% DOPO-POSS	DGEBA/PA650/5 wt.% DOPO-POSS	DGEBA/PA650/10 wt.% DOPO-POSS
TTI (s)	46	46	47	46
p-HRR (kW/m^2)	892	963	937	690
THR (MJ/m^2)	137	129	128	113
Calculated THR (MJ/m^2)	137	134	130	123
Mean COY (kg/kg)	0.07	0.08	0.10	0.12
Mean CO_2Y (kg/kg)	2.1	1.99	1.98	1.76
TSR (m^2/m^2)	4224	4179	4266	4771
Mean SEA (m^2/kg)	932	947	978	1083

Table 6
Cone calorimeter data for the DGEBA/DDS composites.

Samples	DGEBA/DDS	DGEBA/DDS/2.5 wt.% DOPO-POSS	DGEBA/DDS/5 wt.% DOPO-POSS	DGEBA/DDS/10 wt.% DOPO-POSS
TTI (s)	58	58	62	61
p-HRR (kW/m^2)	839	631	404	346
THR (MJ/m^2)	129	104	87	79
Calculated THR (MJ/m^2)	129	126	123	116
Mean COY (kg/kg)	0.09	0.09	0.11	0.12
Mean CO$_2$Y (kg/kg)	2.03	1.83	1.67	1.63
TSR (m^2/m^2)	4271	3972	4520	4829
Mean SEA (m^2/kg)	996	941	1103	1167

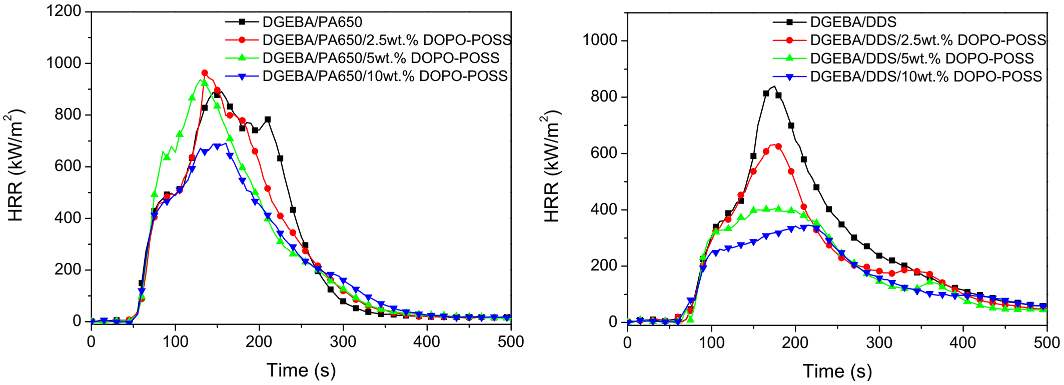


Fig. 8. Heat release rate curves of flame retarded DGEBA/PA650 composites and DGEBA/DDS composites.

corresponds well with the weakening blowing-out effect of DGEBA/DDS/DOPO-POSS composites with increase of DOPO-POSS content. However, we think the reduction of the rate of gas production can only partly explain the weakened blowing-out effect, since the condensed phase must also play an important role.

Photographs of chars after the cone calorimeter test are shown in Figs. 12 and 13. In Fig. 12, we observe that there is no char formation during the combustion process for DGEBA/PA650, DGEBA/PA650/2.5 wt.% DOPO-POSS, and DGEBA/PA650/5 wt.% DOPO-POSS, but a clear intumescent char layer, which is thin and weak, is created by the DGEBA/PA650/10 wt.% DOPO-POSS sample. This observation may explain the reason why the HRR of DGEBA/PA650/10 wt.% DOPO-POSS is only slightly reduced compared with pure DGEBA/PA650. The lack of effective char layer may be attributed to the presence of more than 30 wt.% of aliphatic PA650, whose chains are easy to break down to produce gaseous hydrocarbons, restricting the formation of the char layer in the condensed phase. Under the rigid char layer, the gaseous products may accumulate to a certain pressure until they can break through the char. In contrast, the absence of a rigid char layer does not result in the blowing-out effect, as shown by the UL-94 tests on the DGEBA/PA650/DOPO-POSS composites.

As shown in Fig. 13, some interesting information is provided by visual observation of the char layer of the DGEBA/DDS composites. There is no obvious char for pure DGEBA/DDS, whereas cellular intumescent char layers are created for all the DGEBA/DDS/DOPO-POSS composites. From the photographs of the char layer sections, we can observe that the dimensions of single cells in the char layer are reduced and the densification of the char layer is enhanced with increase of DOPO-POSS content. This result indicates that the crosslinking yield in the condensed phase is enhanced by greater DOPO-POSS content. At the same time, from

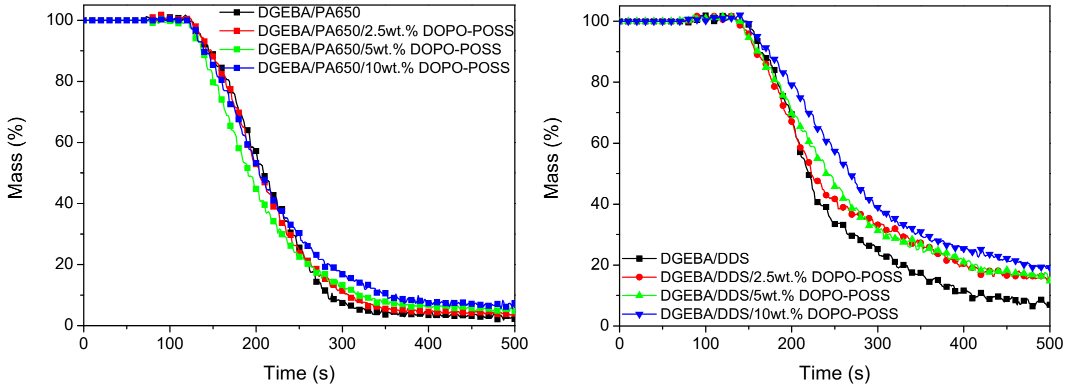


Fig. 9. Mass loss curves of flame retarded DGEBA/PA650 composites and DGEBA/DDS composites.

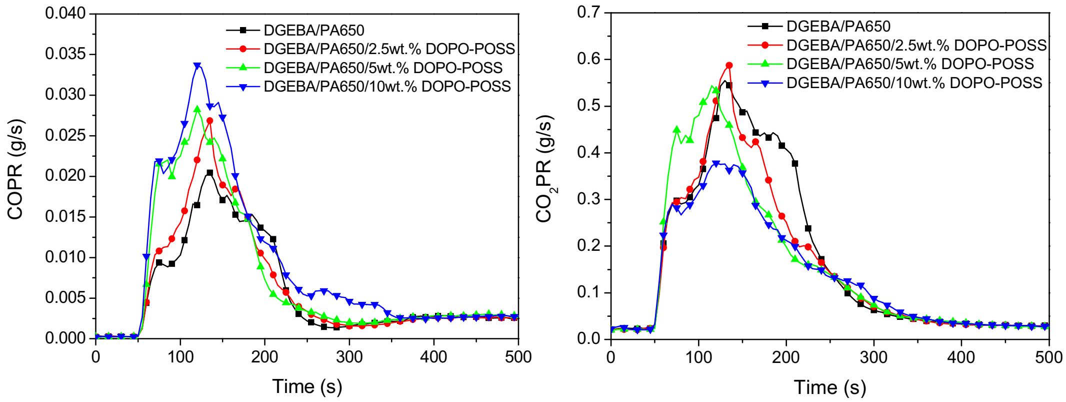


Fig. 10. CO production rate (COPR) and CO_2 production rate (CO_2PR) of DGEBA/PA650 composites.

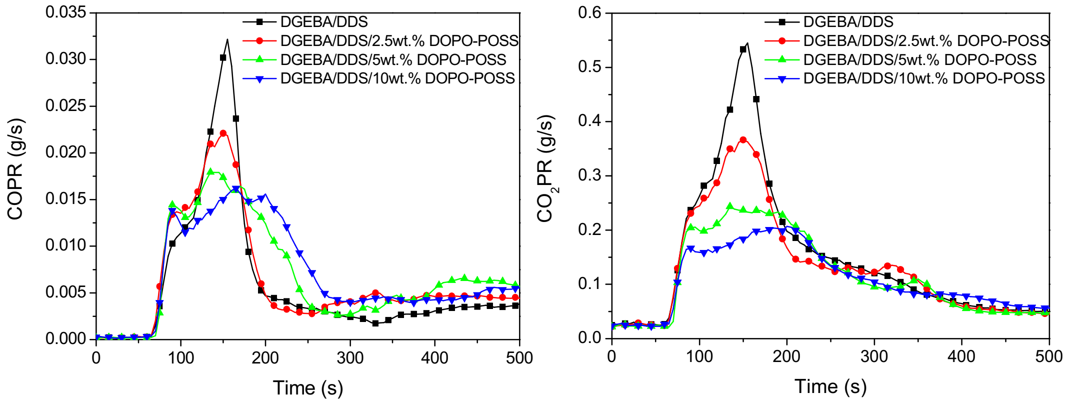


Fig. 11. CO production rate (COPR) and CO_2 production rate (CO_2PR) of DGEBA/DDS composites.

these photographs, we can conclude that the strength and integrity of the char layer are enhanced with increase of DOPO-POSS loading. The strengthened char layer could explain well the excellent HRR results for the DGEBA/DDS/DOPO-POSS composites. However, although a superabundant, solid and rigid char layer helps to protect the unburned EP matrix, this is then difficult to break by the pyrolytic products, which is the key step for the blowing-out effect. Moreover, greater char formation means less gaseous products, which is also disadvantageous for achieving the blowing-out effect. This could explain why the blowing-out effect of the DGEBA/DDS resins weakens with increasing DOPO-POSS loading.

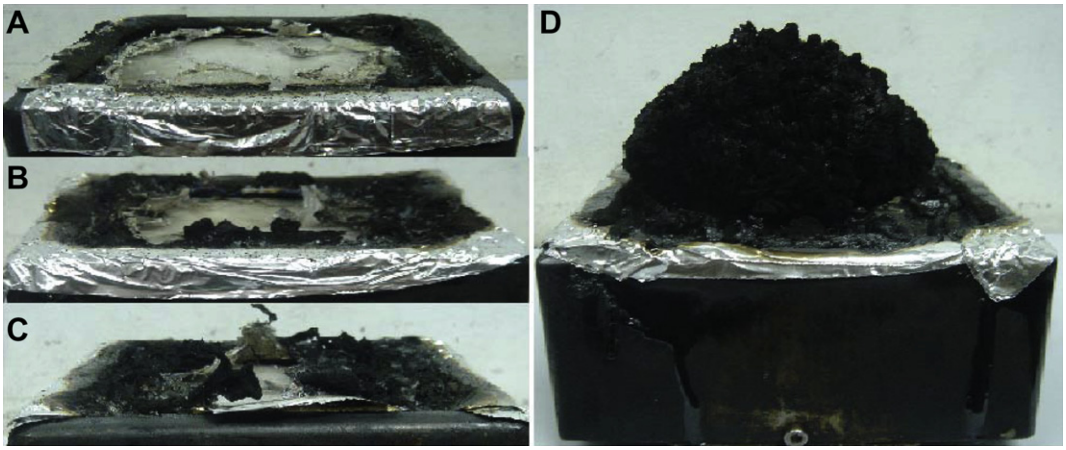


Fig. 12. The chars of (A) DGEBA/PA650, (B) DGEBA/PA650/2.5 wt.% DOPO-POSS, (C) DGEBA/PA650/5 wt.% DOPO-POSS, and (D) DGEBA/PA650/10 wt.% DOPO-POSS after cone calorimeter test.

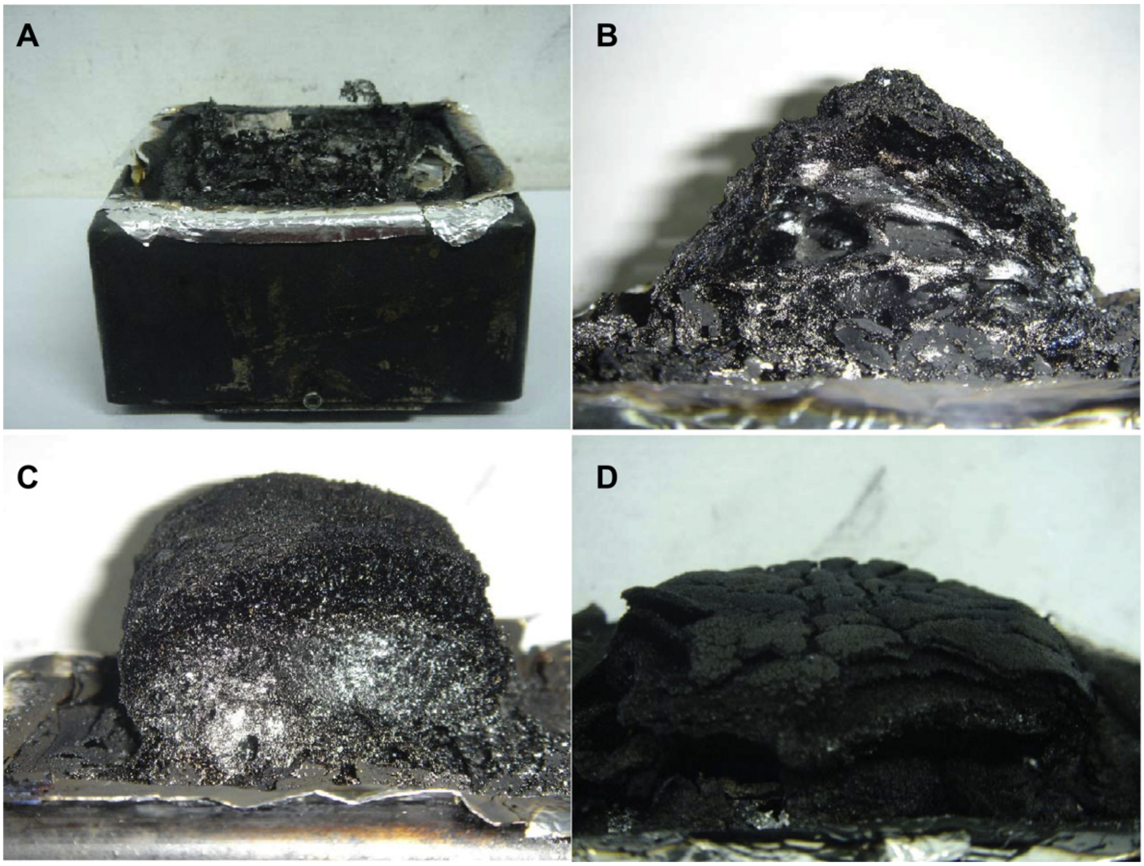


Fig. 13. The chars of (A) DGEBA/DDS, (B) DGEBA/DDS/2.5 wt.% DOPO-POSS, (C) DGEBA/DDS/5 wt.% DOPO-POSS, and (D) DGEBA/DDS/10 wt.% DOPO-POSS after cone calorimeter test.

3.4. Analysis of the char residue of the EP composites

The flame retardancy of the epoxy composites with DOPO-POSS is affected by the structures of the amide curing agents. In order to understand the reason for this result, the char layers of epoxy composites after the cone calorimeter test were investigated by FTIR.

In Fig. 14, the only absorbance from the pure EPs is the broad peak at 1601 cm^{-1}, which indicates the formation of polyaromatic carbons. The pure EPs cured with different curing agents do not show any different structures in the char, with just a small quantity of polyaromatic compounds remaining. When 2.5 wt.% DOPO-POSS incorporated, although the appearance of the char layer of DGEBA/DDS is quite different compared with that from DGEBA/PA650, the FTIR spectra of these two systems are almost the same. The C=C stretching vibration of polyaromatic carbons at 1601 cm^{-1} is clearly enhanced and some C_{Ar}—H deformation vibration could be detected at 781 cm^{-1}. In addition, the new broad absorbance at 1059 cm^{-1} becomes clearly apparent, which means more C—O and Si—O structures remain in the char layer. Another new absorbance peak at 954 cm^{-1}, which represents the Si—O—phenyl and P—O—phenyl stretching vibrations, is detected [23]. With 10 wt.% DOPO-POSS loading, the structure of char layer of DGEBA/DDS is still quite different to that of DGEBA/PA650. However, the FTIR spectra of these epoxy composites are similar. The more obvious absorbances, at 1059 cm^{-1} and 954 cm^{-1}, are detected, which means more C—O, Si—O—phenyl and P—O—phenyl structures remain in the char layer.

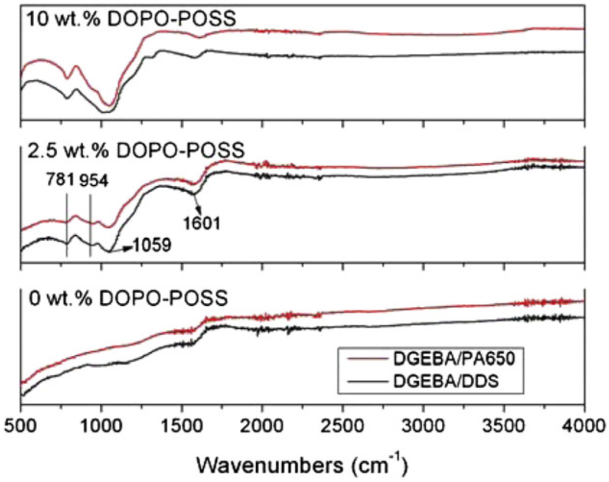


Fig. 14. The FTIR spectra of char residues of epoxy composites after cone calorimeter test.

Analysis of the FTIR spectra indicates that the chemical structures of the char layers of the epoxy composites are almost the same when they contain the same quantity of DOPO-POSS. Therefore, the different morphology of the char layers of the epoxy composites are caused by the different structures of the curing agents. As shown in Fig. 15, because the crosslinking net of the DGEBA/PA650 system includes some aliphatic segments that are easy to break down at high temperature, the crosslinking structures in the condensed phase are continually destroyed. The crosslinking structures cannot survive until almost all the aliphatic segments have disappeared and the content of DOPO-POSS (or aromatic

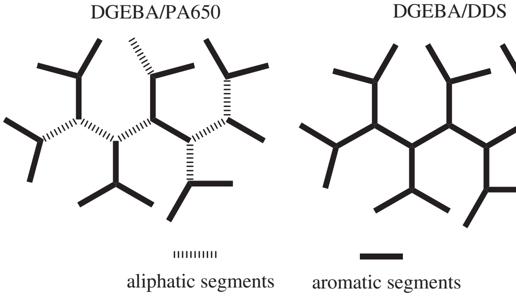


Fig. 15. Simulation of crosslinking structures of epoxy composites.

segments) reaches a critical level. In the case of the DGEBA/DDS system, the proportion of aromatic segments is high, so when as little as 2.5 wt.% DOPO-POSS is added to the epoxy resin, the crosslinking structures are created and easily survive. The rigid char layer is very helpful for the accumulation of the gaseous products during the combustion process.

4. Conclusions

Epoxy resins cured by PA650 and DDS can be flame retarded by DOPO-POSS. The DOPO-POSS shows different influences on the flame retardancy depending on the structures of the amide curing agents. In the PA650 curing system, the LOI value of the DGEBA/PA650/10 wt.% DOPO-POSS is 25.9% and the UL-94 rating is V-1. However, the addition of only 2.5 wt.% DOPO-POSS gives an epoxy resin cured by DDS that possesses a LOI value of 27.1% and a UL-94 rating of V-1. In the UL-94 tests, the DEGBA/DDS with DOPO-POSS exhibits a blowing-out effect through spurting of the pyrolytic gases, but the DEGBA/PA650 resin does not. The thermal stability analysis indicates that DOPO-POSS has a remarkable effect on the increase of char yield for the DGEBA/DDS composites. However, for the PA650 systems, only slight enhancements of thermal stability and char yield are detected. The analyses of TTI, HRR and THR values for the epoxy composites indicate that DOPO-POSS has better flame retardant effects on DGEBA/DDS composites than on DGEBA/PA650 composites. The COPR and CO_2PR of DGEBA/PA650 composites are higher than on the DGEBA/DDS composites. However, the blowing-out effect could not be detected in the PA650 cured system. This result reveals that the blowing-out effect may be determined not only by the production rate of gases, but also by the properties of the condensed char. The char analyses of DGEBA/PA650/DOPO-POSS composites show that little crosslinking char layer is formed until 10 wt.% DOPO-POSS loading, because the aliphatic chains of PA650 are easy to break down to produce gaseous hydrocarbons. For the DGEBA/DDS/DOPO-POSS composites, the crosslinking and dense char layer are created easily, which is very helpful for the accumulation of the gaseous products under it during the combustion process. This could explain the occurrence of the blowing-out effect during the UL-94 test. Therefore the structures of amide curing agents are as important as the presence of DOPO-POSS, and can influence the formation of the crosslinking char layer and the rate of release of pyrolytic gases, which subsequently influences whether the blowing-out effect happens or not.

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