

# Synergistic effects between silicon-containing flame retardant and DOPO on flame retardancy of epoxy resins

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**Abstract** A novel flame retardant, containing silicon and nitrogen (PSiN), was synthesized, and it was used together with 9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) to prepare a flame-retardant system for epoxy resins (EP). Flammability and thermal behaviors of EP systems were estimated by limited oxygen index (LOI), vertical burning test (UL-94), microscale combustion calorimetry test and thermogravimetric analysis. The results showed that synergistic effects on the flame retardancy of EP composites existed between the DOPO and PSiN. When 3 % PSiN and 7 % DOPO were incorporated, the LOI value of EP was found to be 34 %, and the UL-94 test found to be class V-0. The microstructures observed by scanning electron microscopy and FTIR indicated that the surface of the char for EP/DOPO/PSiN system holds a more cohesive and denser char structure when compared to the pure EP and EP/DOPO systems.

**Keywords** Organic silicon · Epoxy resins · Flame retardant · Thermal stability · Phosphorus

## Introduction

Epoxy resins (EPs) are widely used in the area of adhesives, coatings and advanced composites of the aerospace and electronic industries, because of their mechanical stiffness, toughness, superior adhesion, modulus, good chemical and corrosion resistance and excellent dimensional stability [1, 2].

EPs have a dominant position in the development of high-performance materials. However, the epoxy resins are difficult to satisfy the requirements of special engineering technology with the index (LOI) of 21 %, which limits the application of epoxy resin in many important areas, so the flame retardancy of EP needs to be improved [3–5].

Although halogen flame retardants have good flame retardancy on epoxy resins, the flame retardants would produce a large amount of toxic and corrosive smoke in combustion process [6]. So, low-smoke and halogen-free flame retardants of epoxy resin have attracted increasing attention [7–9].

Researches have shown that the addition of relatively small amounts of silicon compounds to various polymeric materials can improve their flame retardancy [10, 11]. And introducing silicon element and its groups into epoxy can also improve some other properties of the epoxy resins, such as thermal stability, high resistance to thermal oxidation, low surface energy and low toxicity [12, 13].

Phosphorus-containing compounds or resins have been demonstrated as effective flame retardants for epoxy resins, attributed to their advantages including high flame retardant efficiency and low production of corrosive and toxic gases in flames [14]. Among them, 9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) has attracted intensive attention due to its high flame retardant efficiency and thermal properties. Hence, various DOPO-based epoxy resins, curing agents and additives have been reported [15–22].

Moreover, effective synergistic effect of silicon and phosphorus on enhancing char formation and improving flame retardancy of the polymers was also observed [23]. A novel approach to obtain epoxy resins with excellent thermal properties as well as high flame retardancy was reached when simultaneously incorporating silicon and phosphorus into the epoxy resins.

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In this work, a novel organic silicon flame retardant containing silicon and nitrogen (PSiN) was synthesized and incorporated into the epoxy resins simultaneously with DOPO. The PSiN can use as a curing agent for epoxy resin. The synergistic effect of these components on the flame retardancy and thermal properties of epoxy resins was studied. The compatibilization, thermal degradation behavior and the flame retardant effect were investigated by scanning electron microscopy (SEM), microscale combustion calorimetry (MCC), differential scanning calorimetry (DSC), thermogravimetric analysis (TG) and limiting oxygen index (LOI).

## Experimental

### Materials

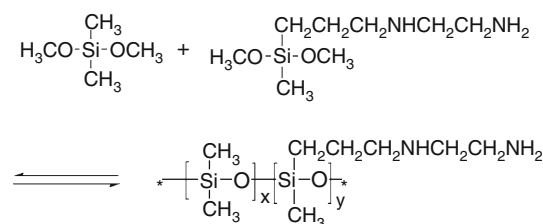
Diglycidyl ether of bisphenol A (DGEBA, EP, epoxy value = 0.44 mol/100 g) was supplied by Wuxi Bluestar Chemical Co., Ltd., China. 9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was supplied by Huizhou Shengshida Chemical Co., Ltd (China). N-( $\beta$ -aminoethyl)- $\gamma$ -aminopropylmethyl dimethoxysilane (KH-602) and dimethoxydimethylsilane were acquired from Nanjing Union Silicon Chemical Co., Ltd (Nanjing, China) and Bluestar Chemical Research Institute (Chengdu, China), respectively.

### Synthesis of PSiN

A 250-mL three-necked round-bottom flask equipped with a stirrer, a thermometer and a condenser was charged with 12 g (0.1 mol) dimethoxydimethylsilane, 20.6 g KH-602 (0.1 mol) and 5 g H<sub>2</sub>O. Then, a suitable amount of ammonia was added into the flask as catalyst. After being maintained at room temperature for 20 min, the solution was heated to 60 °C and kept refluxed until there is no increase in viscosity for the reaction system. After being cooled to room temperature, the raw product was washed by ethanol and *n*-hexane to remove the residual KH-602. The product was dried in a vacuum at 110 °C. The synthesis route is illustrated in Fig. 1.

### Blending of epoxy resin

EP/PSiN/DOPO was prepared as the following steps. First, appropriate amounts of epoxy were with DOPO stirring at 120 °C until the DOPO was in molten state. Second, stoichiometric DDM was casted into the blend above to dissolve at 90 °C. Third, the appropriate amount of PSiN and DDM was put into the epoxy at 60 °C. Compositions of the EP are shown in Table 1. Subsequently, the blend was put



**Fig. 1** Synthesis of PSiN

into a mold for curing and postcuring at oven as the following procedure: 80 °C/2 h + 120 °C/2 h + 150 °C/2 h. The blend molded into standard testing bars for further test.

### Instrumental analyses

FTIR spectroscopy was applied to a Nicolet IS10 Fourier transform infrared (FTIR) spectrometer using KBr pellets. <sup>1</sup>H NMR (400 MHz) spectrum were recorded on a FT-80A NMR using CDCl<sub>3</sub> as the solvent. The Q-200 (TA Instrument) was used for differential scanning calorimetry (DSC) under nitrogen atmosphere using a scanning rate of 10 °C min<sup>-1</sup>. The morphologies of the fractured surfaces of samples and the surface morphology of the char obtained after the LOI test were observed by using SEM. Thermogravimetric analysis (TG) was performed on a Mettler Toledo instrument TG/DSC1 at a heating rate of 10 °C min<sup>-1</sup>. About 10 mg of the sample was examined under pure nitrogen or air condition at a flowing rate of 60 mL min<sup>-1</sup> at temperatures ranging from 30 to 800 °C. LOI values of all samples were obtained at room temperature on an oxygen index instrument (XYC-75) produced by Chende Jinjian Analysis Instrument Factory, according to GB/T 2406-93 standard. The dimensions of all samples were 130 × 6.5 × 3 mm<sup>3</sup>. LOI value was an important parameter for evaluating the ease of extinguishment of polymeric materials in the same condition. It denotes the lowest volume concentration of oxygen sustaining candle

**Table 1** Flame retardancy of the EP systems

Sample	Components/mass%			LOI/%	UL-94	<i>t</i> <sub>1</sub> / <i>t</i> <sub>2</sub> /S
	EP	DOPO	PSiN			
1	100	–	–	21	NO	–
2	100	–	3	29	NO	–
3	100	4	–	31	V-1	15/21
4	100	7	–	32	V-1	5/30
5	100	10	–	30	V-0	5/12
6	100	4	3	32	V-0	3/14
7	100	7	3	34	V-0	1.95/2
8	100	10	3	29	V-0	2/3

burning of materials in the mixing gases of nitrogen and oxygen. A Govmark MCC-2 microscale combustion calorimetry (MCC) was used to determine the flammability characteristics of EP systems according to ASTM D7309-07. Samples of 4–6 mg were heated to 700 °C at a heating rate of 1 °C s<sup>-1</sup> in a stream of nitrogen flowing at 80 cm<sup>3</sup> min<sup>-1</sup>. The volatile and anaerobic thermal degradation products in the nitrogen gas stream were mixed with a 20-cm<sup>3</sup> min<sup>-1</sup> stream of pure oxygen before entering a 900 °C combustion furnace.

## Results and discussion

### Characterization of PSiN

Figure 2 presents the FTIR spectrum of the synthesized PSiN. The absorption bands at 2960 cm<sup>-1</sup> correspond to vibrations of C–H. The peaks at 1022 and 1087 cm<sup>-1</sup> are associated with the vibrations of Si–O–Si. The absorptions at 1260 and 800 cm<sup>-1</sup> are assigned to Si–CH<sub>3</sub>. The absorptions at 1476 cm<sup>-1</sup> are assigned to –CH<sub>3</sub> and –CH<sub>2</sub>. The peaks at 3356 cm<sup>-1</sup> are associated with the vibrations of –NH<sub>2</sub>. The information above confirms that the target product was synthesized successfully.

So as to further determine the structure of PSiN. Figure 3 shows the <sup>1</sup>H NMR spectrum of PSiN (ppm): 0.04 ppm (CH<sub>3</sub>–Si–CH<sub>3</sub>), 0.5 ppm (Si–CH<sub>2</sub>–), 1.3–1.6 ppm (–Si–CH<sub>2</sub>–CH<sub>2</sub>– N–), 1.8–2.1 ppm (–NH), 2.5–3.0 ppm (N–CH<sub>2</sub>) and 7.2 ppm (CDCl<sub>3</sub>). All these characteristic <sup>1</sup>H NMR bands indeed match the PSiN structure. These suggest that PSiN is successfully processed. On the other hand, the molar ratio (X:Y) of dimethyldimethoxysilane to KH602 was determined by the ratio of the area of peak a (–CH<sub>3</sub> in dimethyldimethoxysilane) to that of peak f (–NH in KH602), and the result indicates the value of X:Y is 1.

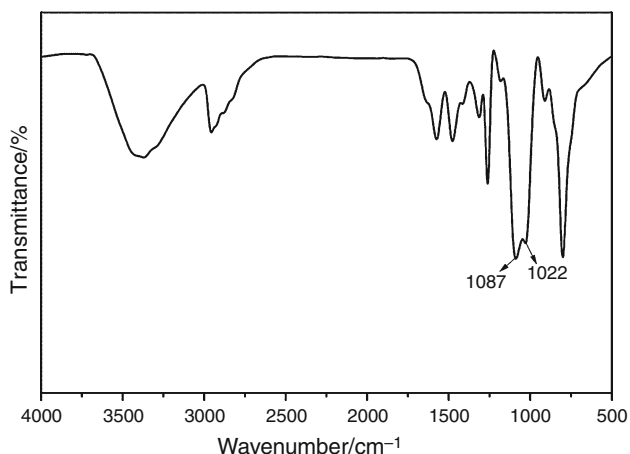


Fig. 2 FTIR spectrum of PSiN

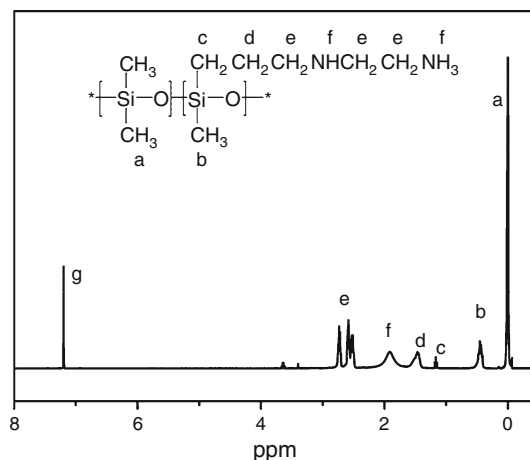


Fig. 3 <sup>1</sup>H-NMR spectrum of PSiN

### Differential scanning calorimetry (DSC)

Figure 4 gives DSC curves of cured EP systems. All of the epoxy systems exhibit single glass transition temperature ( $T_g$ ). It is well known that an absolutely miscible blend presents only one  $T_g$  peak. This single  $T_g$  phenomenon indicates a homogeneous morphology of these hybrid epoxy systems. This homogeneous morphology provides possibility to synergistic effect of DOPO and PSiN on the flame retardancy of epoxy resins.

### Flammability

The flame retardancy of cured EP, EP/DOPO and EP/PSiN/DOPO was evaluated by measuring their LOI values. Data are listed in Table 1. It is clear that a significant increase in LOI value (from 21.5 to 32 %) was observed when DOPO was utilized in the epoxy curing compositions. This indicates that incorporating phosphorus has an efficient effect

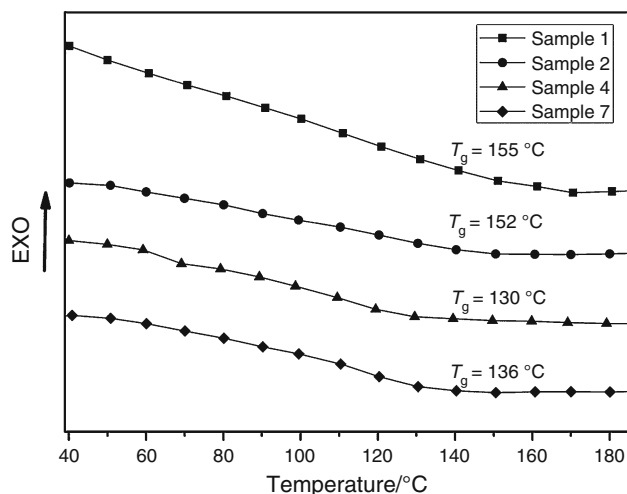
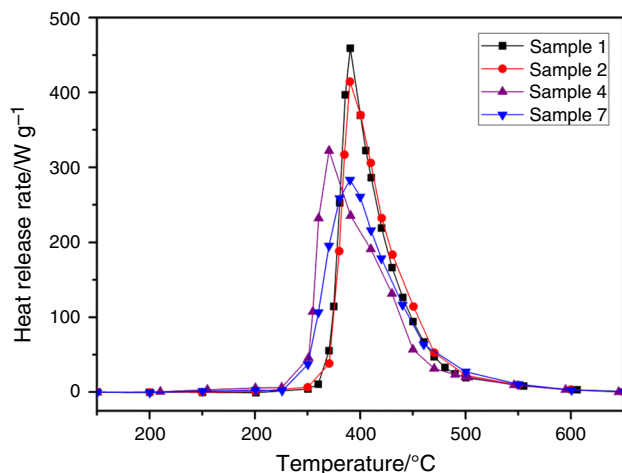


Fig. 4 DSC curves of finally cured products



**Fig. 5** Heat release rate curves versus temperature

on leveling up the flame retardancy of the epoxy resins. From the UL-94 results, it can be observed that when the total amount of DOPO was 7 %, the UL-94 of the system was only V-1 rating. While the total amount of DOPO was 10 %, the UL-94 of the system was V-0 rating, but the LOI value decreased. From Table 1, when the PSiN contents of the EP remain constant and DOPO contents of the EP are added from 4 to 7 %, the LOI values of the EP system reached a maximum of 34 %, and class V-0 of UL 94 was passed. PSiN will produce less smoke in the combusting process. Meanwhile, the mixtures with PSiN can keep the original shape and form hollow shell after burning.

### Microscale combustion calorimetry test

The heat release rate (HRR), the peak heat release rate (PHRR), heat release capacity (HRC) and the total heat

release (THR) are important parameters in quantitative material flammability analysis. The dynamic flammability data detected by microscale combustion calorimeter of EP and flame retardant EP samples are shown in Fig. 5 and Table 2. Figure 5 contains curves of the heat release rate (HRR) of EP systems. A sharp peak appeared in the HRR of EP with a peak heat release rate (PHRR) of  $467.5 \text{ W g}^{-1}$ , while EP/PSiN and EP/DOPO systems showed a slower burning rate with the peak reduced to 415,  $326 \text{ W g}^{-1}$ , respectively. EP/PSiN/DOPO showed the slowest burning rate with the PHRR of  $283 \text{ W g}^{-1}$ . The results suggest that the addition of PSiN and DOPO has a considerable effect on the stability of EP. The heat release capacity of EP, EP/PSiN and EP/DOPO systems are presented in Table 2. The heat release capacity (HRC) of EP/PSiN and EP/DOPO was lower than pure EP. The heat release capacity of EP/PSiN/DOPO was lowest among the EP systems. This lower HRC value indicates that a part of the EP system was not completely combusted, probably undergoing a carbonization process. It is believed that some char residues formed in the thermal decomposition process of EP, which could lead the heat release rates, decrease. This effectively improves the flame retardancy of the matrix.

### Thermal analysis

The thermal behaviors of the composites are investigated by TG under both air and nitrogen atmospheres. The typical data are obtained from TG and DTG curves as shown in Table 3.  $T_{5\%}$  represents the temperature at which mass loss is 5 % for the system (the initial decomposition temperature),  $T_{\max 1}$  represents the temperature of the first maximum mass loss rate for the

**Table 2** Combustion parameters obtained from MCC

Samples	PHRR/ $\text{W g}^{-1}$	THR/ $\text{kJ g}^{-1}$	$T_{\text{PHRR}}/^{\circ}\text{C}$	HRC/ $\text{J g}^{-1}$
EP	467.5	22.9	392.1	472
EP/PSiN	415	22.6	405	427
EP/DOPO	326	22.1	368.5	327
EP/DOPO/PSiN	283	21.9	389	287

**Table 3** Thermal property of finally cured products

Sample	$T_{5\%}/^{\circ}\text{C}$		$T_{\max 1}/^{\circ}\text{C}$		$T_{\max 2}/^{\circ}\text{C}$	$R_{\max}/\% \text{ min}^{-1}$		$Y_f/\%$	
	$\text{N}_2$	Air	$\text{N}_2$	Air		Air	$\text{N}_2$	Air	$\text{N}_2$
1	371	372	383	380	599	16	16	18	0
2	365	351	391	382	606	13	11	20	2.3
4	347	332	380	361	588	11	11	20	3.35
7	350	340	370	369	575	11	9	23	8.7

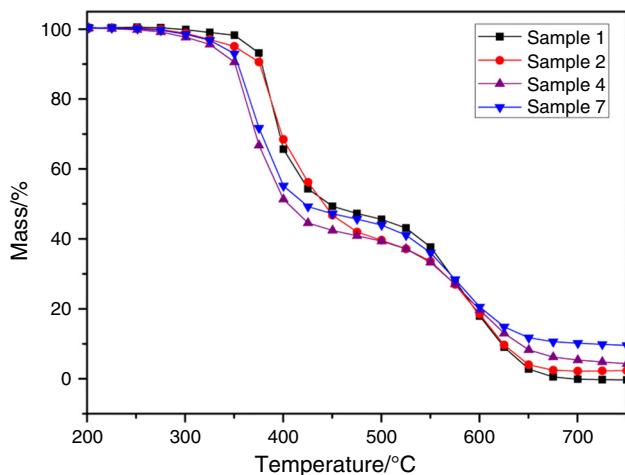


Fig. 6 TG curves of finally cured products in air

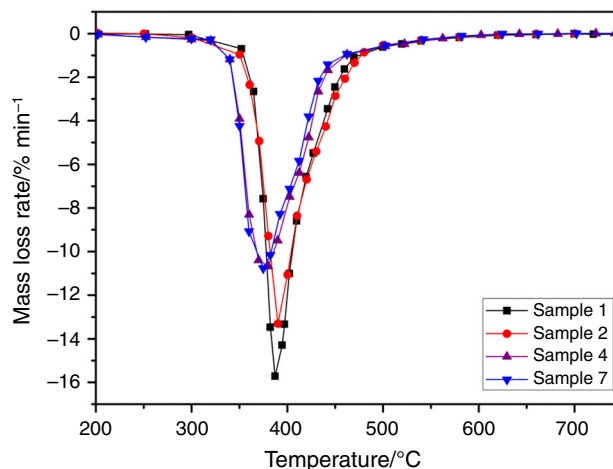


Fig. 9 DTG curves of finally cured products in N<sub>2</sub>

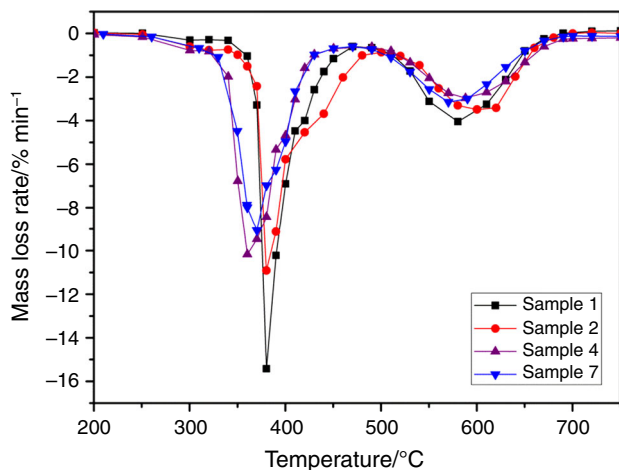


Fig. 7 DTG curves of finally cured products in air

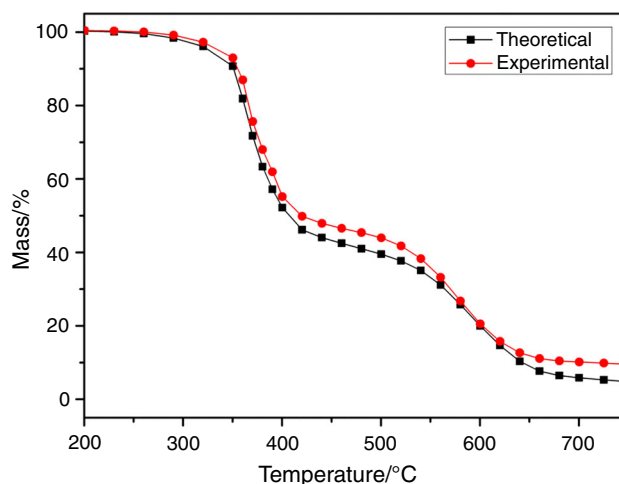


Fig. 10 Experimental and theoretical TG curve of Sample 7 system in air

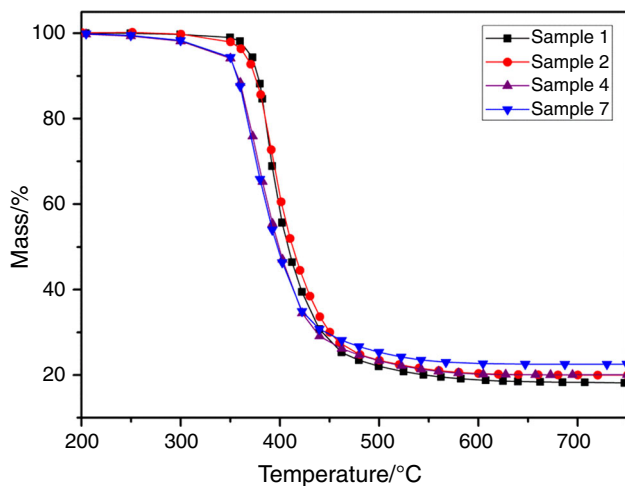


Fig. 8 TG curves of finally cured products in N<sub>2</sub>

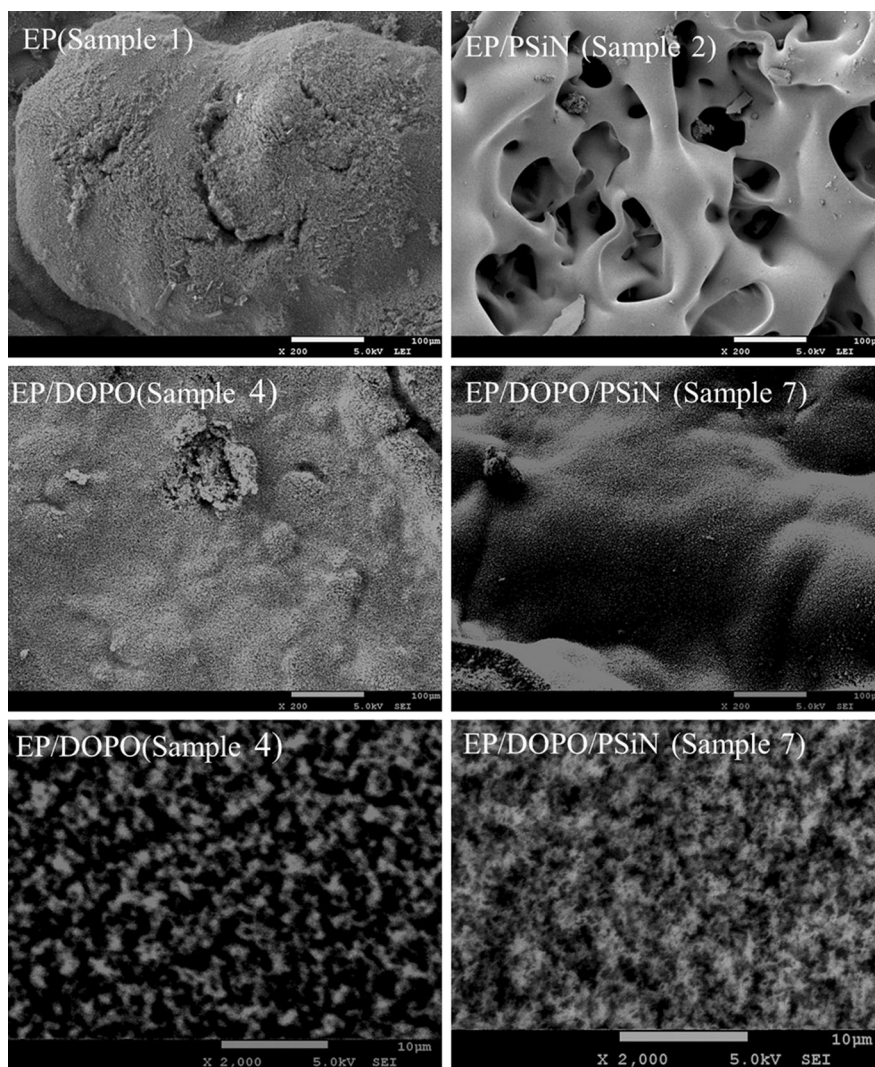
system,  $T_{max2}$  represents the temperature of the second maximum mass loss rate for the system,  $R_{max}$  represents the maximum mass loss rate for the system and  $Y_c$  represents the char yields at 800 °C [24].

Figures 6 and 7 show the TG and DTG curves of cured EP (Sample 1), EP/PSiN (Sample 2), EP/DOPO (Sample 4) and EP/PSiN/DOPO (Sample 7) resins in air atmosphere, and the data from the curves are shown in Table 3. TG curves showed two decomposition stages (Fig. 6), in which the first stage was assumed as the thermal degradation of the polymer network and the second one as the oxidation process of the char moiety. Epoxy resins have a very small amount of volatiles when the temperature was increased to 370 °C. As the temperature increases, mass loss increases remarkably and a

large quantity of volatiles is produced until almost no residue is left at 800 °C. The  $T_{5\%}$  of the EP/PSiN/DOPO and EP/DOPO is lower than epoxy resins. This can be explained as follows: The initial decomposition of DOPO occurs at inferior temperature. The low bond energy of P–O and P–C leads to the low initial decomposition temperature. However, with the addition of PSiN, the  $T_{5\%}$  increased which might be due to the fact that decomposition of DOPO at inferior temperature leads to the formation of the silicone-containing group, which will participate in the cross-linked carbonization. And PSiN can convert the usual organic decomposition to partially inorganic decomposition by forming the carbon–silicon residue to act as thermal insulation and to prevent gas evolution and achieve ultimate improvement on flame retardation of this phosphorous–silicone-containing

epoxy system [25–27]. In the temperature range of 600–800 °C, the EP/PSiN/DOPO (Sample 7) shows the highest char residues than the sum of EP/PSiN and EP/DOPO, indicating the synergistic effect between phosphorus and silicone. From Fig. 6, the DTG curves show that maximum mass loss rate was lower with adding of PSiN. This fact demonstrated that PSiN and DOPO could decrease the decomposition rate of EP obviously. Those phenomena may contribute great to high flame retardancy such as LOI and UL-94 results.

Figures 8 and 9 show the TG and DTG curves of cured EP (Sample 1), EP/PSiN (Sample 2), EP/DOPO (Sample 4) and EP/PSiN/DOPO (Sample 7) resins in nitrogen, respectively. It can be seen that the degradation processes of all the samples are very different from those under air atmosphere. From the DTG curves, it can be found that the



**Fig. 11** SEM of the residual char

mass loss rate of the flame retardant systems is lower than that of pure epoxy resins. Moreover, the char yield increases from 18 to 23 % at 800 °C. Those indicate that the incorporation of PSiN and DOPO can enhance the char yield, which can protect the underlying materials from further decomposition.

Generally, the PSiN and DOPO could improve the char residues of epoxy resins in both air and nitrogen atmospheres and the char layers are the critical factors which could slow down heat and mass transfer between the gases and condensed phases. It is reported that the silicon usually immigrates to the surface of the char and plays the role of char enhancer [28]. Due to the synergistic effect between phosphorus and silicon, this exhibits high flame retardancy and this can be suggested by the LOI and UL-94 results.

Figure 10 shows the experimental and theoretical TG curves of Sample 7 system in air. The theoretical curve was calculated based upon the mass percentage of the ingredients in the EP system. As could be seen, when the temperature was below 450 °C, the experimental and theoretical curves were almost same. However, the experimental residual char became more than the theoretical one after 450 °C. It could be deduced some high-temperature stable material was produced in the char. This fact was the proof of the synergistic effect of DOPO and PSiN and this synergistic effect could improve the char formation ability of EP.

It is well known that the effective protection of the char layer could improve the flame retardancy; thus, it is necessary to evaluate the char layers so as to further investigate the mechanism [29]. To further investigate the effect of DOPO and PSiN on the char formation of EP system during combustion, the morphologies of the char residues were examined by SEM. The SEM micrographs of the char residue of EP, EP/PSiN and EP/PSiN/DOPO are shown in Fig. 11. As for the char of pure EP, it displayed uneven and incompact surface char residues. This poor char cannot efficiently act as a barrier to shield the underlying polymer from heat and air. However, the char of EP with both DOPO and PSiN, illustrated in Fig. 11, was compact, smooth and dense. This structure of the char for EP composites could prevent heat transfer between the flame and the substrate and thus protect the underlying materials from further burning and pyrolysis, so they had much higher LOI values. In addition, EP/PSiN showed a smoother char than EP, and EP/DOPO showed a more connective char than EP. This indicates that phosphorus provides a tendency for better char formation; silicon provides an enhancement of the thermal stability of the char. It can be concluded that a significant synergistic effect existed between DOPO and PSiN when they were applied. The synergistic effects of DOPO and PSiN result in the condensed and intumescent char layers, which are in accordance with the TG results in air atmosphere.

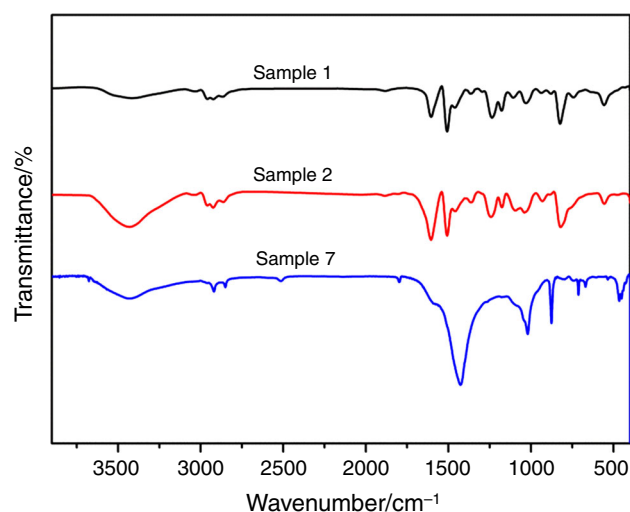


Fig. 12 FTIR spectra of the residue from burning

### Structural analysis of the combustion residue by FTIR

To further clarify the structure of the flame-resistant barrier on the surface, the EP (Sample 1), EP/PSiN (Sample 2) and EP/DOPO/PSiN (Sample 7) systems were analyzed after combustion using infrared (IR) spectroscopy. The IR spectra of this system are shown in Fig. 12. The broad peak at around  $1026\text{ cm}^{-1}$  appeared which are due to the stretching vibration of P–O, the Si–O–Si or benzene ring bonds [13]. Meanwhile, sharp absorption peaks appearing at  $1408\text{ cm}^{-1}$  is assigned to the stretching vibrations of C=C in the aromatic compounds. Moreover, the broad vibration bands at  $889\text{ cm}^{-1}$  are due to the superposition of stretching vibrations of P–O–P or P–O–Ph bonds. And  $3450\text{ cm}^{-1}$  becomes broader, which was assigned to the stretching mode of –OH from the P–OH group, indicating the presence of alcohol groups in the char. The P–O–P groups can be regarded as the cross-links which link to different aromatic species and reinforce carbon layers [30, 31]. Based on the observed results, it is proposed that DOPO and PSiN would form some silica–phosphate char residues with the matrix, which largely consists of condensed aromatic compounds and Si–O units [2]. The char acts as a good insulating barrier, which could well protect the EP matrix.

### Conclusions

This paper presents the preparation of novel polysiloxane (PSiN) flame retardants containing nitrogen and silicon. The PSiN was used together with DOPO to prepare a flame-retardant system for epoxy resins, and the flame retardancy of EP composites was characterized. The results

showed that synergistic effects on the flame retardancy of EP composites existed between the DOPO and PSiN. The char residues of EP/PSiN/DOPO composites were increased, and the highest char residues were obtained in air atmosphere when the DOPO was 7 mass% and PSiN was 3 mass%, which was in accordance with the highest LOI and UL-94 results. The SEM and FTIR results of pyrolysis products indicated that resulting in significant improvements in the flame retardancy of epoxy resins.

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