

## Thermal Degradation Behaviors and Flame Retardancy of Epoxy Resins with Novel Silicon-Containing Flame Retardant

Ming Gao,<sup>1,2</sup> Weihong Wu,<sup>3</sup> Zhi-qiang Xu<sup>4</sup>

<sup>1</sup>Department of Materials Science and Engineering, College of Environmental Engineering, North China University of Science and Technology, Box 206, Yanjiao Beijing 101601, China

<sup>2</sup>Mineral Processing Engineering, School of Chemical and Environmental Engineering, China University of Mining and Technology, Beijing 100083, China

<sup>3</sup>Chemical Department, College of Science, Agriculture University of Hebei, Baoding 071000, China

<sup>4</sup>School of Chemical and Environmental Engineering, China University of Mining and Technology, Beijing 100083, China

Correspondence to: M. Gao (E-mail: gmscy@hotmail.com)

**ABSTRACT:** A novel macromolecular silicon-containing intumescent flame retardants (Si-IFR) was synthesized, and its structure was a caged bicyclic macromolecule containing phosphorus-silicon characterized by IR. Epoxy resins (EP) were modified with Si-IFR to get the flame retardant EP, whose flammability and burning behavior were characterized by UL 94 and limiting oxygen index (LOI). Twenty percentage of weight of Si-IFR was doped into EP to get 27.5% of LOI and UL 94 V-0. The degradation behavior of the flame retardant EP was studied by thermogravimetry, differential thermogravimetry, scanning electron microscopy, and X-ray photoelectron spectroscopy analysis. The experimental results exhibited that when EP/Si-IFR was heated, the phosphorus-containing groups firstly decompose to hydrate the char source-containing groups to form a continuous and protective carbonaceous char, which changed into heat-resistant swollen char by gaseous products from the nitrogen-containing groups. Meanwhile, SiO<sub>2</sub> reacts with phosphate to yield silicophosphate, which stabilizes the swollen char. The barrier properties and thermal stability of the swollen char are most effective in resisting the transport of heat and mass to improve the flame retardancy and thermal stability of EP. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** epoxy resins; degradation; flame retardant; synthesis; thermogravimetry

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### INTRODUCTION

Epoxy resins (EP) are one of the most versatile classes of polymers. Their long service life and good physical and chemical properties often provide a favorable cost benefit ratio when compared to other thermosets.<sup>1,2</sup> When listing their advantages, the high flammability of EP certainly has to be considered as a major disadvantage.

The main fields where fire retardancy of EP is required in are electronic and electrical applications and transportation.<sup>3–5</sup> Therefore, cured EP containing bromine are particularly useful when flame retardancy is desired. However, major problems encountered with this system include the generation of toxic and corrosive fumes during combustion and waste disposal. This led to the search for alternate flame retardants.

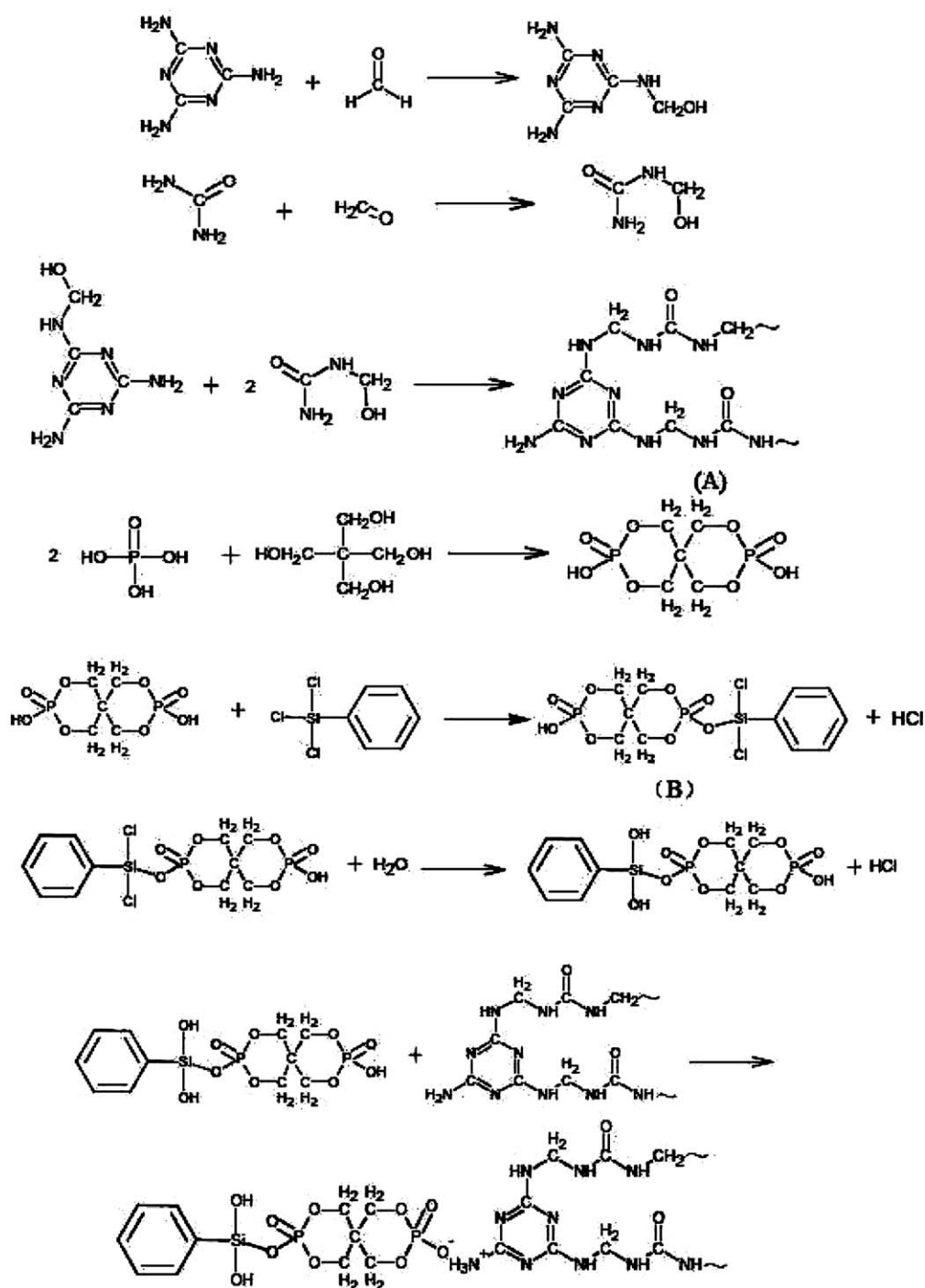
Recently, halogen-free intumescent flame retardant (IFR) are attracting more and more attention from both academic and industrial communities for their multifold advantages including

low toxic, low smoke, low corrosion, no corrosive gas production, and so on.<sup>6,7</sup> To form an IFR, three ingredients are necessary: acid source, carbon source, and gas source.<sup>6</sup> Phosphorus-containing compounds are often used as an acid source, whereas nitrogen-containing compounds are used as a blowing agent.

In the former work of our group, a novel macromolecular IFR which contains an acid source, a gas source and a char source simultaneously had been synthesized. Thermal degradation and flame retardancy of EP were improved after blending with the IFR.<sup>8,9</sup>

It is already known that IFR and silicon-containing FRs exhibit a synergistic effect on the flame retardancy of polymers when they are used together.<sup>10,11</sup> So, in this work, silicon element was incorporated into the IFR to improve its flame retardancy, and the degradation behavior of EP modified with the silicon-containing intumescent flame retardants (Si-IFR) was investigated by

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Scheme 1. Synthesis of Si-IFR.

thermogravimetry (TG), differential thermogravimetry (DTG), and scanning electron microscopy (SEM).

## EXPERIMENTAL

### Materials

Pentaerythritol, 85% of phosphoric acid, melamine, 37% of formalin as formaldehyde, urea, and phenyl trichlorosilane were received from Beijing Chemical Reagents Co., Beijing in China. EP (E-51) and 4,4'-

diamino-diphenyl methane (DDM) was supplied by Beijing Jin Tai Chemical Co., Beijing in China.

### Instrumentation

The IR spectra were measured on a NEXUS-470 FTIR (Nicolet) spectrophotometer using KBr. The limiting oxygen index (LOI) values were measured on a JF-3 oxygen index meter (Jiangning, China) with sheet dimensions of  $130 \times 6.5 \times 3 \text{ mm}^3$  according to ASTM D 2863-97. Vertical burning tests were conducted on a vertical burning test instrument (CZF-2-type) (Jiangning,

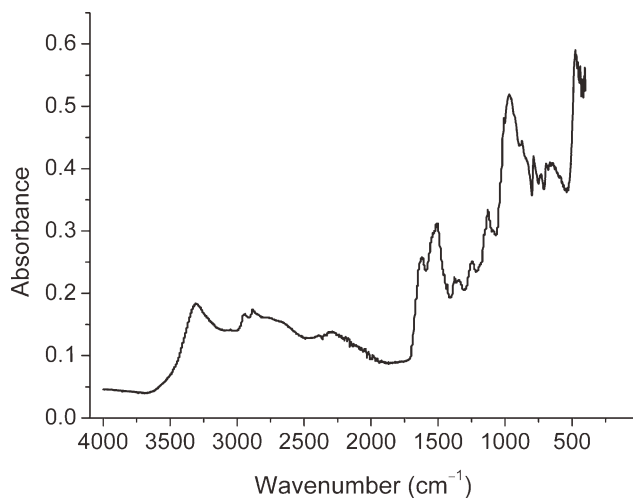


Figure 1. The fourier transform IR spectra of Si-IFR.

China) with sheet dimensions of  $127 \times 12.7 \times 3 \text{ mm}^3$  according to ASTM D3801. TG and DTG were carried out on a DTA-2950 thermal analyzer (Dupont Co.) under air at a heating rate of  $10^\circ\text{C min}^{-1}$ . The X-ray photoelectron spectroscopy (XPS) data were obtained using a Perkin-Elmer PHI 5300 ESCA system at 250W (12.5 kV at 20 mA) under a vacuum. The char residues after LOI test were simultaneously observed with a JSM-5600LV SEM using 15 kV and 60 mA of electric current.

#### Synthesis of Si-IFR

Si-IFR is synthesized according to Scheme 1. Thirty-seven percent formalin as formaldehyde [F] 1 mol was brought to pH 8–8.5 with NaOH and heated. Then, melamine [M] 0.2 mol and urea [U] 0.5 mol were added to the above solution, stirred until dissolved and heated under reflux for 50 min. Heating was stopped, and the solution was allowed to cool to get MUF prepolymer A.

Eighty-five percent phosphoric acid 1 mol and pentaerythritol 0.5 mol were mixed, heated to  $120^\circ\text{C}$ , stirred for 4 h until without water distilled to get caged bicyclic pentaerythritol diphosphonate. Then, phenyl trichlorosilane was doped into under stirring, heated to  $80^\circ\text{C}$ , stirred for 1 h to get B. B was added slowly into A under stirring to obtain Si-IFR.

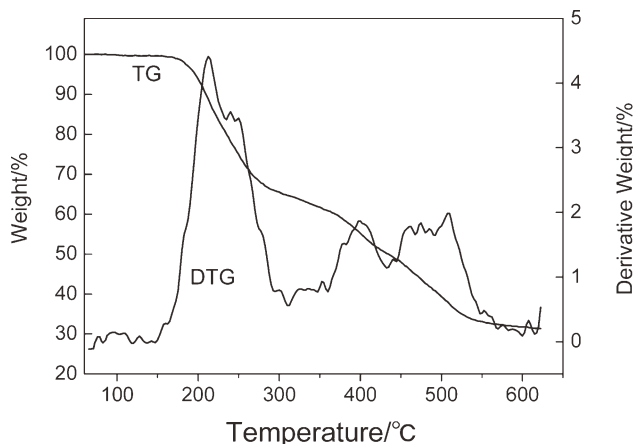


Figure 2. TG and DTG curves of IFR.

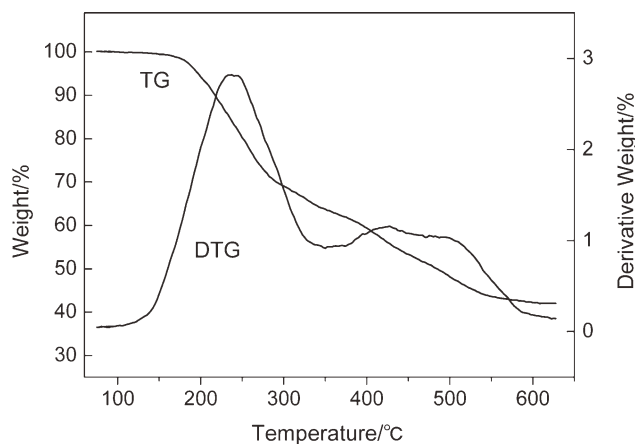
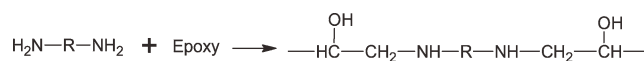


Figure 3. TG and DTG curves of Si-IFR.

Apparently, intermediate A is an amino resin, which can be cured in acidic intermediate B. The yield of Si-IFR obtained by the reaction of A and B is 100%, which is favorable. As a copolymerization amino resin, its structure in Scheme 1 is only the main one of the products. Meanwhile, intermediate B maybe contains some pentaerythritol phosphonate containing Si. However, as an IFR, all those by-products (mono- or tri-substituted melamine, urea resin, pentaerythritol phosphonate containing Si, and others) can be used as its good components (gas source, acid source, and carbon source), which are not necessary to purify the Si-IFR.

#### Sample Preparation

The flame retardant EP with Si-IFR content of 15 and 20 wt % were cured with DDM. The EP and DDM were mixed homogeneously in an epoxy/amino equivalent ratio of 1/1. The reaction mixtures were cured at  $100^\circ\text{C}$  for 2 h and post cured at  $150^\circ\text{C}$  for 2 h. After curing, all samples were cooled to room temperature. The cured mechanism was shown as follows:



#### Characterization of Si-IFR

IR (KBr) to see Figure 1, ( $\text{cm}^{-1}$ ): 3328 ( $-\text{OH}$ ,  $\text{NH}$ ), 2938, 2890 ( $\text{w}$ ,  $\text{CH}_2$ ), 1240 ~ 1280 ( $\text{P}=\text{O}$ ), 1521, 814 ( $\text{C}=\text{N}$ ), 1020, 880, 787, 655 (dicyclic  $\text{P}-\text{O}-\text{C}$ ), 736 ( $\text{P}-\text{O}-\text{Si}$ ).

TG/DTG to see Figures 2 and 3 and Table I: The initial decomposition temperature (IDT), char yield and  $T_m$  of Si-IFR are higher than those of IFR while the maximum weight loss rate ( $R_{\text{max}}$ ) is lower, which show the higher thermal stability.

Table I. TG Parameters of IFR and Si-IFR

FR	IDT ( $^\circ\text{C}$ )	$T_m$ ( $^\circ\text{C}$ )	$R_{\text{max}}$ ( $\%/\text{C}$ )	Char yield (%)
IFR	195	212	4.41	31.7
Si-IFR	197	256	3.24	42.5

**Table II.** Flame Retardancy of EP Containing Different Contents of Si in Si-IFR

Si-IFR/wt %		Si content in Si-IFR/%					
		0	2.0	3.0	4.0	5.0	6.0
15	LOI/%	25.0	26.0	26.4	26.6	26.7	26.7
	UL 94	not rated	V-2	V-1	V-1	V-1	V-1
20	LOI/%	26.5	27.1	27.5	27.9	28.2	28.3
	UL 94	V-1	V-1	V-0	V-0	V-0	V-0

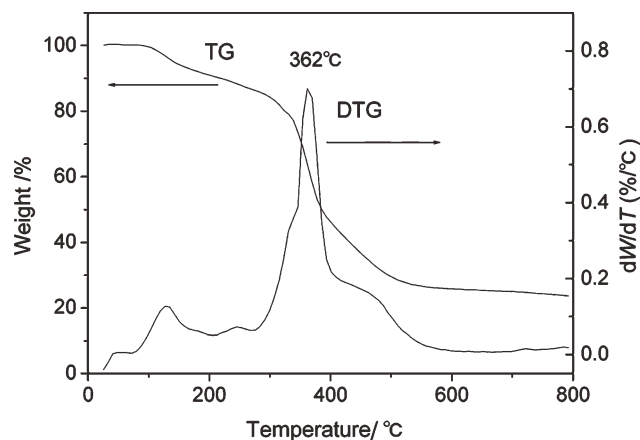
## RESULTS AND DISCUSSION

### Flame Retardancy of EP

The LOI values describe a procedure for measuring the minimum concentration of oxygen that will just support flaming combustion in a flowing mixture of oxygen and nitrogen. The UL-94 test is commonly used to determine the ignition resistance of materials. The test results are classified by flammability ratings V-0, V-1, or V-2. The V-0 rating indicates a material with the best flame retardancy. Table II presents the LOI values and UL-94 testing results of EP with and without IFR. As we know, when IFRs are exposed to a fire, they will form a nonflammable, multicellular char layer on the surface of polymers. This layer provides an efficient shield and insulation for the underlying material against direct contact with fire, oxygen, and heat.<sup>12</sup> As a result, the structure and formation of the char layer are a critical factor for the flame retardancy of Si-IFRs. From Table II, we can see that the LOI values of EP are increased to 26.7% when Si-IFR is added by a 15 wt % total loading level of additives. In general, an LOI value of at least 26% is needed for a realistic degree of flame retardancy.<sup>13</sup> However, the UL-94 rating of the flame retardant systems did not exceed V-1, indicating an inadequate level of char layer in the experiments. When 20% dosage is added, the LOI values reached a maximum of 28.3%, and UL-94 rating changed from V-1 to V-0. The EP obtained for the UL 94 V-0 rating at low Si contents of 3.0 % get a LOI of 27.5%.

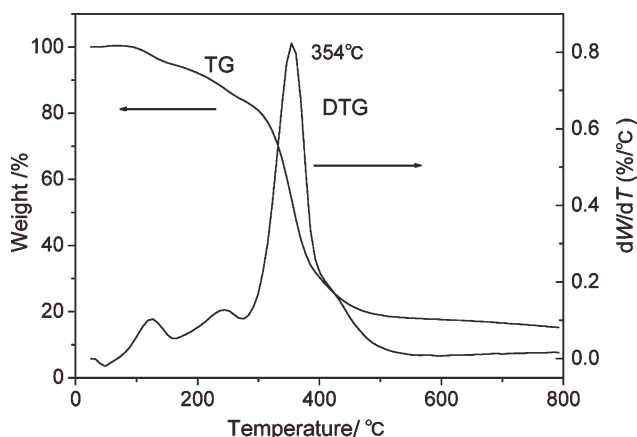
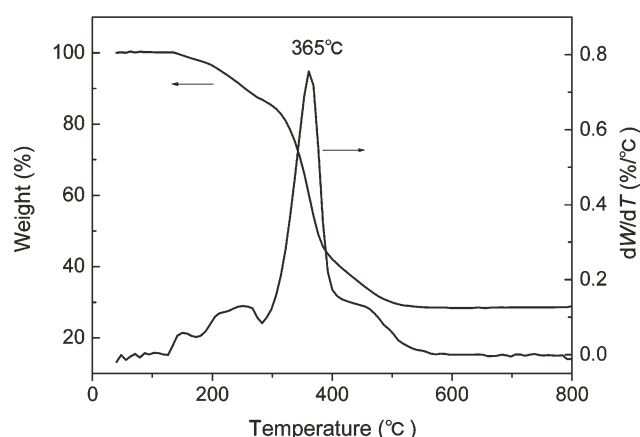
### Degradation of EP

TGA can, in suitable circumstances, serve as useful indicators of polymer flammability.<sup>14,15</sup> The simultaneous DTG and TG

**Figure 5.** TG and DTG curves of EP containing IFR.

curves of EP, EP/IFR, and EP/Si-IFR of 3.0% Si contents were carried out in air from ambient temperature to 800°C and are shown in Figures 4–6. The IDT is defined as the temperature when the weight loss is 5%, integral procedure decomposition temperature (IPDT), char yields at 600°C, temperatures at the maximum weight loss rate ( $T_m$ ), and the value of the maximum weight loss rate ( $R_{max}$ ) were measured and listed in Table III.

The results indicate that neat EP is thermally stable below 150°C, and IDT is 160°C. It has a small amount of volatile until the temperature rises to 300°C, and it has a weight loss of less than 20% at 300°C. When the temperature further increases, weight loss increases rapidly and a quantity of volatile is produced until almost exhaust at 500°C, and char yields at 600°C are 15.2%. TG and DTG curves of EP/IFR are different. It is noted that IDT (145°C) and  $R_{max}$  (0.70%/°C) are decreased while char yields (23.9%) is increased. This is because the IFRs in EP/IFR begin to decompose at relative low temperatures, generating some small molecules such as water, ammonia, etc.<sup>16</sup> With the increase of temperature, it is observed that IFR can increase the amount of residues remarkably, which means that IFR promotes charring to form carbonaceous materials. This is one of the reasons for the improvement in flame retardancy of EP. EP/Si-IFR has similar TG behaviors to those of EP/IFR,  $R_{max}$  (0.75%/°C) is decreased while char yields (28.6%) is remarkably increased. However, its IDT

**Figure 4.** TG and DTG curves of EP.**Figure 6.** TG and DTG curves of EP containing Si-IFR.

**Table III.** Thermal Data of the Epoxy Resins From Thermogravimetric Analysis

No.	IFR (%)	Weight (%)	IDT (°C)	IPDT (°C)	Char yield (%)	$T_m$ (°C)	$R_{max}$ (%/°C)	$E_a$ /(kJ/mol)
EP-1	-	-	160	422	15.2	354	0.82	230.4
EP-2	IFR	20	145	490	23.9	362	0.70	186.8
EP-3	Si-IFR	20	212	490	28.6	365	0.75	246.2

(212°C) are increased, which shows that the thermal stabilities of EP are improved by incorporation of Si-IFR. It is possible that Si-IFR can form effective charring layer in lower decomposition (<5%), preventing the char layer from oxidation, getting good flame retardancy due to the synergistic effect between IFR and Si. The higher LOI values in Table II support it.

### Thermal Stability of EP

The thermal stability of the EP is assessed with two parameters: IDT and IPDT. IDT indicates the apparent thermal stability of the EP, i.e., the failure temperatures of the resins in processing and moulding. On the other hand, IPDT exhibits the resins' inherent thermal stability, i.e., the decomposition characteristics of the resins' volatile composition. From Table III, phosphorus-containing EP EP/IFR show relatively lower IDT than do the phosphorus-free resin (EP), since phosphorus-groups decompose at low temperatures. On the other hand, the existence of flame retardants (EP/IFR, EP/Si-IFR) exhibits higher IPDT than EP, retarding the weight loss rate of the polymers at high temperatures. The high IPDT implies the EP' potential application in highly anti-thermal coatings and thermal insulating materials. The temperatures at the maximum weight loss rate ( $T_m$ ) are also increased.

### The Decomposition Activity Energies

The decomposition activity energies of EP-1, EP-2 and EP-3 were studied by the equation of Kissinger.<sup>17</sup> The equation is as follows:

$$\frac{d\ln(\Phi/T_m^2)}{d(1/T_m)} = \frac{-E_a}{R}$$

where  $\Phi$  is the rate of temperature increase in K/min ( $\Phi = 2, 5, 10, 20$ ),  $T_m$  the maximum temperature at the peak position in K,  $E_a$  the decomposition activity energy, and  $R$  the gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>). From the slope of the plot of  $\ln(\Phi/T_m^2)$  versus  $1/T_m$ , the activation energy can be calculated, i.e.,  $E = R \times \text{slope}$ . Table III presents the activation energies ( $E_a$ ) for EP-1, EP-2, and EP-3.

The activation energy for the decomposition of EP is 230.4 kJ/mol while it becomes 186.8 kJ/mol when IFR is doped into, decreased by 43.6 kJ/mol, which shows that IFR can catalyze decomposition of EP. It is supported by the lower IDT (145°C). When Si-IFR is doped into EP, its activation energy becomes

**Table IV.** XPS Results of the Residual Char of EP Samples

Element		C/%	N/%	O/%	P/%	Si/%
EP-2	Surface	57.95	1.85	36.82	3.38	0
	Interior	67.84	0.68	30.69	0.79	0
EP-3	Surface	51.89	1.14	35.47	3.76	7.74
	Interior	65.63	0.67	31.75	0.64	1.31

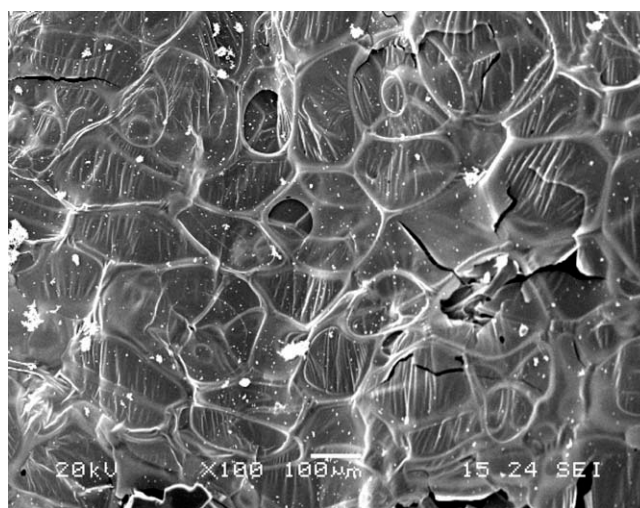
246.2kJ/mol, which is higher than those of EP/IFR and EP. It is suggested that thermal stability of EP/Si-IFR is higher than those of EP/IFR and EP, which is favorable for EP.

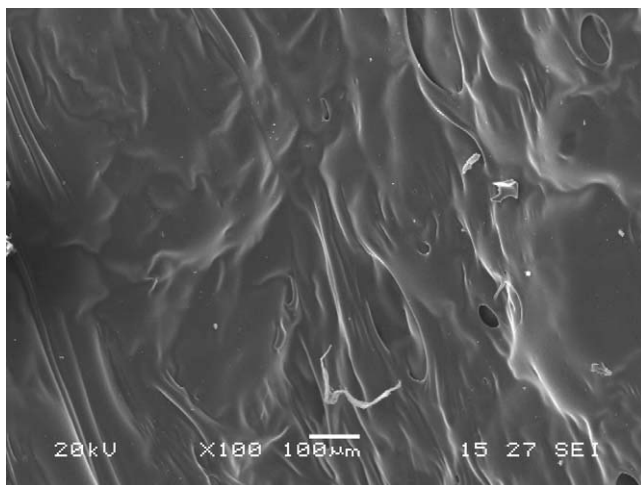
### XPS Spectra Analysis of EP Char

Elemental compositions at the surface and in interior of the residues of EP/IFR and EP/Si-IFR obtained after LOI test are investigated by XPS analysis. The concentrations of C, O, N, Si, and P are listed in Table IV. For EP/IFR and EP/Si-IFR, the percentage of carbon atom at the surface of residue is lower than that in the interior. The percentage of oxygen atom at the surface of the residue is higher than that in the interior. The reason is that the surface of char is highly oxidized under the rich oxygen condition.<sup>18</sup> In addition, it is noted that in Table IV, for the EP/Si-IFR, the amounts of Si and P at the surface of residue are higher than that in the interior. These results imply that Si and P can accumulate at the surface of char. Therefore, the presence of Si-IFR can improve the thermal-oxidative stability of the char layers<sup>19</sup> and reduce the release of volatile products from the matrix.

### Morphology of EP/Si-IFR Chars

Figures 7 and 8 present the SEM photographs of the surface of char of EP/IFR and EP/Si-IFR. From Figure 7, it can be observed that the char of EP/IFR is very fragile and fragmentary, which could not effectively protect the underlying material from fire. Figure 8 shows that the surface of the char of EP/Si-IFR is continuous and compact. Consequently, it is possible that IFR and Si have synergistic effect and could promote the formation of effective charring layer. It is already known that SiO<sub>2</sub> reacts easily with phosphate to yield silicophosphate which is known to stabilize the swollen char.<sup>19</sup> The barrier properties and thermal stability of the expanded char are most effective in

**Figure 7.** SEM micrograph of the char of EP/IFR.



**Figure 8.** SEM micrograph of the char of EP/Si-IFR.

resisting the transport of heat and mass.<sup>20,21</sup> The char retards the overflow of the flammable volatiles at high temperature. All these do help to improve the flame retardancy and thermal stability of EP.

## CONCLUSIONS

We succeed in synthesizing a novel macromolecular Si-IFR with a structure of a caged bicyclic macromolecule containing phosphorus-silicon. Twenty percent weight of the Si-IFR is doped into EP to get 27.5% of LOI and UL 94 V-0. For EP containing Si-IFR, compared with EP, incorporating Si-IFR into EP alters degradation characteristics, which decreases weight loss,  $R_{max}$  and activation energy, increases IDT and char yield. In the thermal degradation of EP containing Si-IFR, the phosphorus-containing groups firstly decompose to hydrate the char source-containing groups to form a continuous and protective carbonaceous char, which changed into heat-resistant swollen char by gaseous products from the nitrogen-containing groups. Meanwhile,  $\text{SiO}_2$  reacts with phosphate to yield silicophosphate, which stabilizes the swollen char. The barrier properties and thermal stability of the swollen char are most effective in resisting the transport of heat and mass to improve the flame retardancy and thermal stability of EP.

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