

# Synergistic Effect of Organic Silicon on the Flame Retardancy and Thermal Properties of Polycarbonate/Potassium-4-(Phenylsulfonyl) Benzenesulfonate Systems

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**ABSTRACT:** Melt blending was used to prepare a series of flame-retardant hybrids based on bisphenol A, polycarbonate (PC), potassium-4-(phenylsulfonyl)benzenesulfonate (KSS), and the organic silicon compounds *N*-( $\beta$ -aminoethyl)- $\gamma$ -aminopropylmethyldimethoxysilane (KH-602) and diphenylsilanediol. The flame retardancy and thermal stability of the hybrids were investigated by the limiting oxygen index (LOI) test, the UL-94 vertical burning test, and thermogravimetric analysis. The results show that the flame retardancy of the PC/KSS system and the weight of the residues improved with the addition of the organic silicon. When the content of diphenylsilanediol was 4 wt % and KH-602 was 1 wt %, the LOI value of the PC/KSS system was found to be 47, and Class V-0 of the UL-94 test was achieved. The microstructures observed by scanning electron microscopy indicated that the surface of the char for PC/KSS systems with KH-602 and diphenylsilanediol hold a more cohesive and denser char structure when compared with the pure PC/KSS system. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** synergistic effect; polycarbonate; organic silicon; flame retardancy

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## INTRODUCTION

Polycarbonate (PC), one of the fastest growing engineering polymers, is widely used in construction, medical equipment, transport, and other fields as to its excellent mechanical properties, outstanding electrical properties, high glass transition temperature, and so on.<sup>1</sup> PC is a naturally high charring polymer, showing a V-2 rating in the UL-94 test. However, strict flame-retardant performance is often required for electronic and electric applications, so the flame retardancy of PC still needs to be improved.<sup>2–4</sup>

Because of the environmental problems, some halogen-containing flame-retardants that have high flame-resistant efficiency have been forbidden gradually.<sup>5,6</sup> Consequently, it is essential that new flame-retardant systems should be developed to meet the constantly changing demand of new regulations, standards, and test methods.

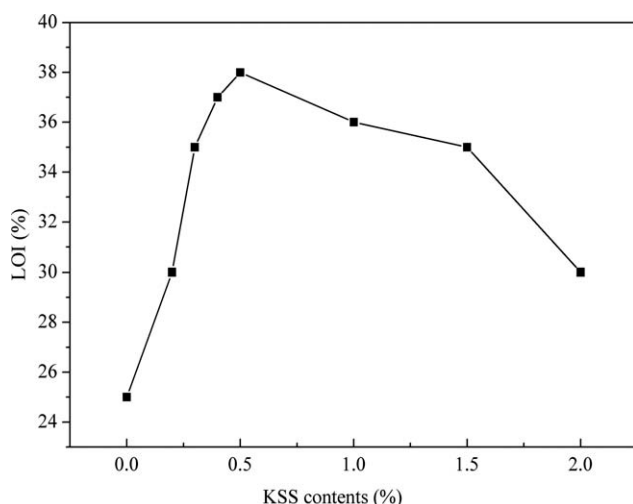
In 1970s, it has been reported that sulfosalt was absolutely beneficial for the flame retardancy of PC. Innes<sup>7</sup> studied the effect of flame retardancy of potassium butylperfluorosulfonate for PC. When 0.1 wt % potassium-4-(phenylsulfonyl)benzenesulfonate (KSS) was incorporated into PC, the limiting oxygen index

(LOI) value of PC could achieve at 25–35%.<sup>8,9</sup> However, the content of KSS in PC is generally less than 1% because the addition of KSS could lead PC be susceptible to hydrolysis.

Recently, silicon-containing compounds used as flame-retardant have received more and more attention owing to the environmentally friendly consideration.<sup>10–13</sup> For example, polysilsesquioxanes with  $(\text{RSiO}_{3/2})_n$  formula, where R is an organic substituent, have been used as flame retardants due to their excellent flame retardancy, high impact resistance, superior moldability, recyclability, and the potential to replace halogen-containing flame retardants.<sup>13–15</sup> He and coworkers<sup>16,17</sup> investigated the synergistic effects of polyhedraoligomeric silsesquioxane and oligomeric bisphenyl A bis(diphenyl phosphate) on thermal and flame retardancy of PC. Periadurai et al.<sup>18</sup> reported thermal decomposition and flame-retardant behaviors of SiO<sub>2</sub>-phenolic nanocomposite.

Owing to the presence of phenyl, diphenylsilanediol is inferred to be compatible with PC. *N*-( $\beta$ -aminoethyl)- $\gamma$ -aminopropylmethyldimethoxysilane (KH-602) is a kind of organic silicon with nitrogen element, which may have excellent flame retardancy. As is known, the flame-retardant efficiency is in connection with compatibility and reactivity, so, we investigated the

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**Figure 1.** Effect of KSS content on flame retardant of PC.

synergistic effect of the organic silicon, including diphenylsilanediol and KH-602, on the flame-retardant and thermal properties of PC/KSS systems. The effect of the organic silicon on the burning behaviors, thermal stabilization, and char formation of KSS flame-retardant PC was studied by LOI, UL-94, thermogravimetric analysis (TGA), and scanning electron microscopy (SEM) tests.

## EXPERIMENTAL

### Materials

PC (S23001R) was purchased from Mitsubishi Engineering Plastics Corporation (Japan). KSS was supplied by Sloss Industries Corporation (United States). Antioxidizer (1010) was provided by Tientsin Chemical Factory (Tianjing, China). KH-602 and diphenylsilanediol were acquired from Nanjing Union Silicon Chemical Co. (Nanjing, China) and Bluestar Chemical Research Institute (Chengdu, China), respectively.

### Preparation of the Samples

PC, dried at 120°C for 6 h, antioxidant (1010), KSS, and the organic silicon retardants were premixed based on a calculated

amount of ratio. Then, all samples were extruded by a parallel twin-screw extruder (length-to-diameter ratio was 33; TSSJ-25, Bluestar Machine Research Institute, Chengdu, China) with a screw rotating rate of 50 rpm, and the barrel setting temperatures were 230, 240, 245, 250, 245, and 240°C. After the extrudate was pelletized and the blend was dried at 120°C for 7 h, all test specimens were prepared by an injection-molding machine (PS40E5ASE, Nissei Plastic Industrial Co., Japan). The injection temperature profile was Zone 1, 250°C; Zone 2, 250°C; Zone 3, 240°C, and the mold pressure was between 50 and 80 kgf/cm<sup>2</sup>.

### Flame Retardancy Tests

The flammability of the flame-retarded PC/KSS blends was evaluated by LOI and UL-94 tests. LOI data of all samples were obtained at room temperature on an oxygen index instrument (XYC-75) produced by Chende Jinjian Analysis Instrument Factory, according to ASTM D2863-77 standard. The dimensions of all samples were 130 × 6.5 × 3 mm<sup>3</sup>. Vertical burning rates of all samples were measured on a CZF-2 instrument produced by Jiangning Analysis Instrument Factory, with sample dimensions of 125 × 12.5 × 3.2 mm<sup>3</sup>, according to UL-94 test ASTM D635-77.

### TGA Tests

All TGA tests were performed on a Mettler Toledo TG/DSC1 instrument thermal analyzer with a heating rate of 10°C/min in the temperature range of 50–800°C and a pure nitrogen flow of 60 mL/min. The weight of the samples was kept within 8–10 mg.

### SEM

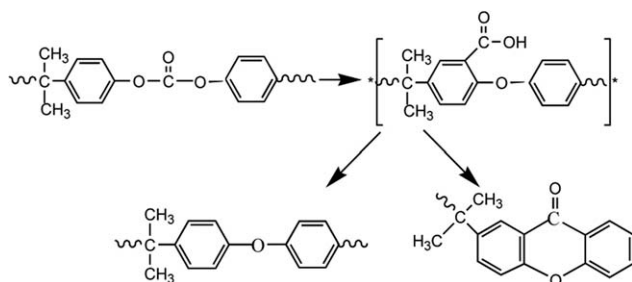
The surface morphology of the char obtained after LOI test was observed by a HITACHI X-650 SEM. The specimens were previously coated with gold to make the surface conductible.

### Fourier Transform Infrared Spectrophotometry

The char residues on the surface of the flame-retarded PC/KSS systems after LOI tests were characterized with a Nicolet IS10 Fourier transform infrared (FTIR) spectrophotometer using KBr pellets.

**Table I.** Compositions and the Flame Retardancy of the PC/KSS/Organic Silicon Systems

Sample	Components (wt %)				LOI (%)	UL-94
	PC	KSS	Diphenylsilanediol	KH-602		
1	100	—	—	—	25	V-2
2	99.5	0.5	—	—	38	V-1
3	97.5	0.5	2	—	41	V-1
4	95.5	0.5	4	—	42	V-0
5	93.5	0.5	6	—	39	V-0
6	98.5	0.5	—	1	43	V-0
7	97.5	0.5	—	2	43	V-0
8	95.5	0.5	—	4	44	V-0
9	95.1	0.5	4	0.4	41	V-0
10	94.8	0.5	4	0.7	45	V-0
11	94.5	0.5	4	1.0	47	V-0



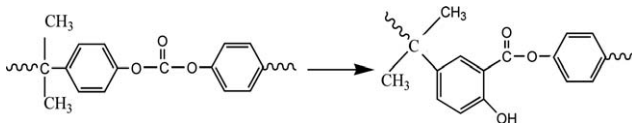
Scheme 1. Isomerization reaction of PC.

## RESULTS AND DISCUSSION

### Flammability

To investigate the effect of KSS content on the flame retardancy of PC, we tested the LOI values of the flame-retardant PC systems. As could be seen from Figure 1, the LOI values increased with the increase of KSS contents and reached 38 when the KSS content was 0.5%. It is reported that the mechanism of KSS flame retardant is probably because of the generation of  $\text{SO}_3$  after combustion, which was beneficial to the formation of char layer for PC.<sup>19</sup> However, there were some decreases of LOI values when more KSS was added. So, the optimum content of KSS in PC was 0.5 wt %.

The synergistic effects of the organic silicon on the flame retardancy of PC/KSS systems were investigated. Table I shows the LOI values and vertical burning rates for PC matrix with a constant loading of KSS additives of 0.5 wt %. Pure PC had a LOI value of 25 and Class V-2 of UL-94. All the LOI values increased when the organic silicon was incorporated into PC/KSS systems. This possibly ascribed to the fact that the organic silicon prompted PC deacidification and dewater, which resulted from isomerization reaction, as shown in Scheme 1.<sup>20</sup> The isomerization reaction was favor for crosslinking and the formation of char layer. And, the organic silicon rearranged units of PC to enhance the formation of residue formation, which was beneficial to the formation of char layer.<sup>21</sup> The pattern of rearrangement occurred was shown in Scheme 2. In addition, the organic silicon with excellent flowability could spread to outside from inside during combustion and accumulate on the surface to act as a thermal insulation layer, creating a less flammable material.<sup>22</sup> So, the flame retardancy of PC was improved greatly. From Table I, the maximum LOI values of the PC/KSS/diphenylsilanediol system without KH-602 and PC/KSS/KH-602 system without diphenylsilanediol were 42 and 44, respectively. This demonstrated that diphenylsilanediol and KH-602 alone showed low efficiency in flame retardancy of PC/KSS system. However, when the mixture of diphenylsilanediol and KH-602 was incorporated into PC/KSS, the LOI value reached the maximum of 47 and Class V-0 of UL-94 was passed. These results



Scheme 2. Fries rearrangement of PC.

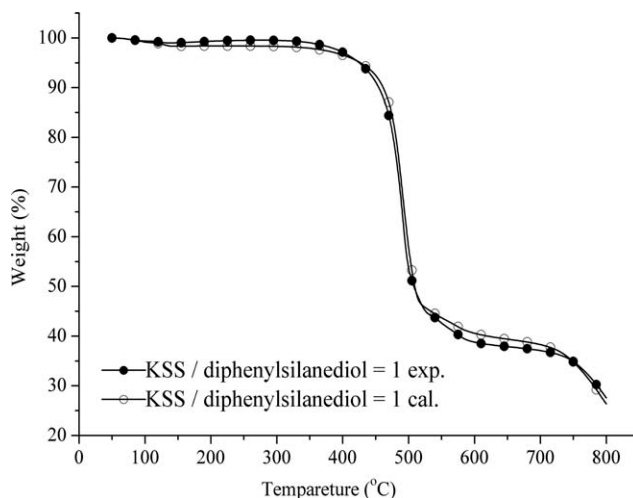


Figure 2. Experimental and theoretical TG curves of KSS/diphenylsilanediol system.

proved that there was a distinct synergistic effect among KSS, diphenylsilanediol, and KH-602.

It was postulated that the improvement of flame retardancy resulted from the interaction of KSS with organic silicon. To examine the validity of the interaction between KSS and organic silicon, a mixture of KSS and organic silicon at a 1 : 1 ratio was analyzed by TGA. The theoretical TG curves were calculated by the following equation:

$$M_{\text{theo}}(T)_{\text{KSS-X}} = \text{wt}\% \times M_{\text{exp}}(T)_X + (1 - \text{wt}\%) \times M_{\text{exp}}(T)_{\text{KSS}},$$

where X is diphenylsilanediol or KH-602, KSS-X is a blend of KSS and organic silicon,  $M_{\text{theo}}(T)_{\text{KSS-X}}$  is the theoretical residual mass of KSS-X, wt % is the weight percentage of X (X mass/system mass),  $M_{\text{exp}}(T)_X$  is the experimental residual mass of X, and  $M_{\text{exp}}(T)_{\text{KSS}}$  is the experimental residual mass of KSS. The onset degradation temperature ( $T_{\text{onset}}$ ) is defined as the temperature at which the weight loss of the sample reached 5 wt %.<sup>23</sup> There was little difference between the curves of KSS/

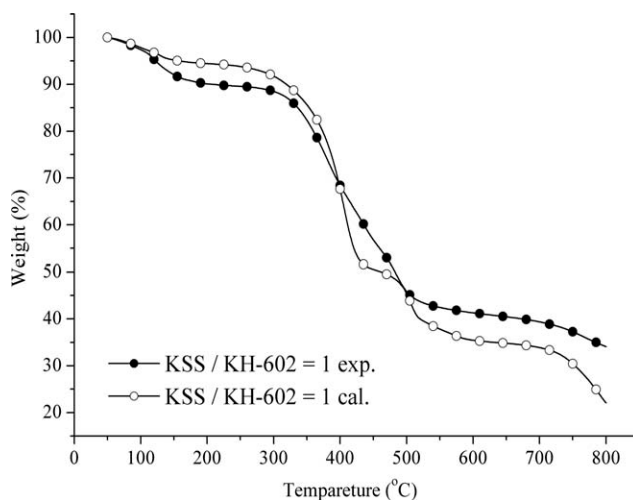
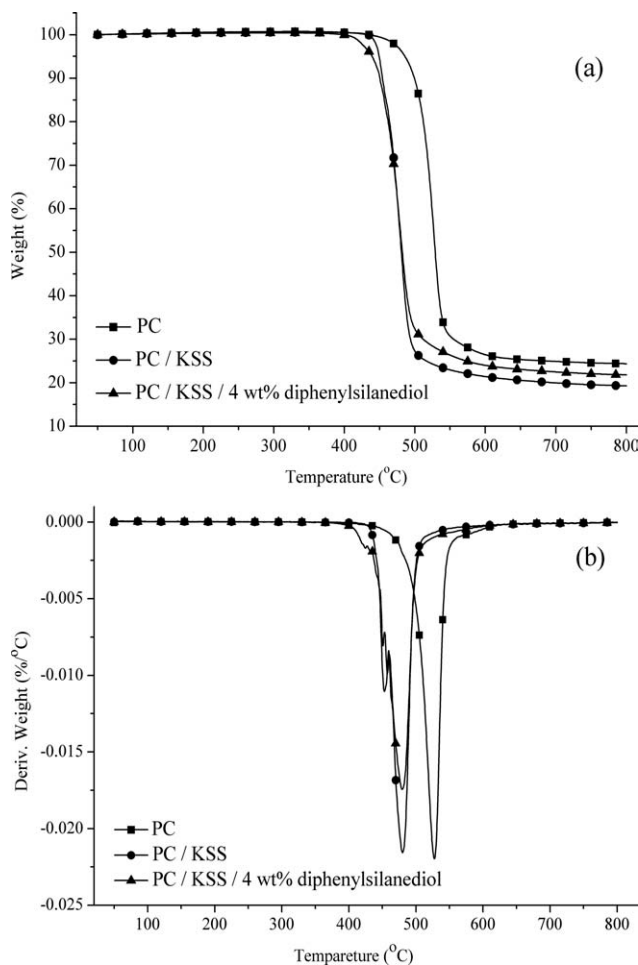


Figure 3. Experimental and theoretical TG curves of KSS/KH-602 system.



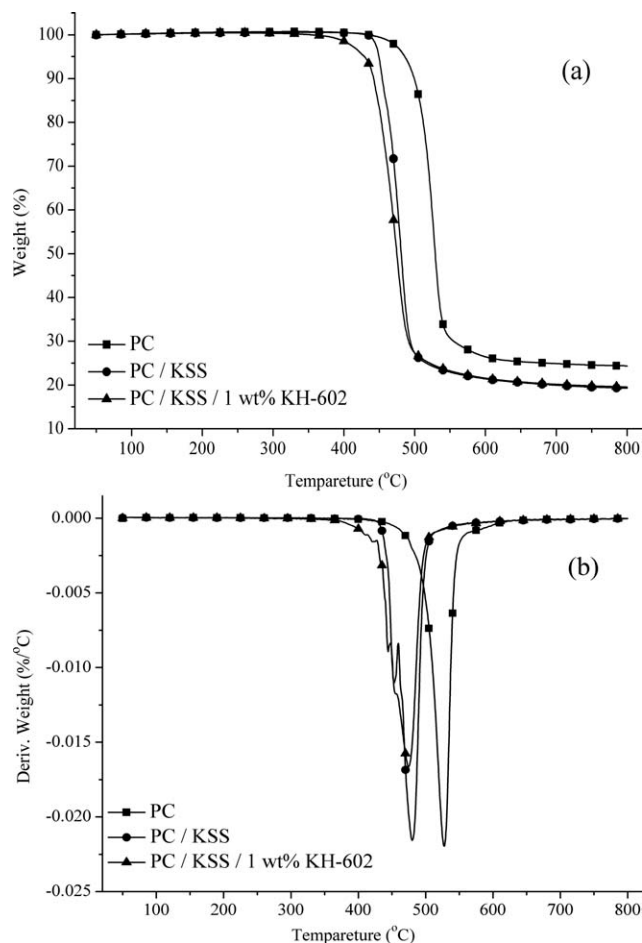
**Figure 4.** TG (a) and DTG (b) curves of the PC, PC/KSS, and PC/KSS/4 wt % diphenylsilanediol system.

diphenylsilanediol exp. and KSS/diphenylsilanediol cal., as shown in Figure 2. The calculated curve was a linear combination of the thermograms of the single components of the mixture; therefore, it was representative of a noninteracting behavior between KSS and diphenylsilanediol. It was inferred that the most important factor in producing protective charred layer for PC was not the interaction between KSS and diphenylsilanediol. However, one could observe the remarkable difference between the experimental and theoretical TG curves of KSS/KH-602 (Figure 3). The curve of KSS/KH-602 exp. exhibited a small weight decrease at 90–190°C followed by the main stage of weight loss starting at 290°C. Through the comparison of the experimental and calculated curves, the  $T_{\text{onset}}$  of the experimental curve for KSS/KH-602 system was clearly lower than that of the theoretical curve and there was a decrease in the weight-loss onset. In addition, the char residues at 500, 600, and 700°C for KSS/KH-602 experimental data were 45.9, 41.3, and 39.4 wt %, respectively, while the calculated data were 45.1, 34.9, and 33.1 wt %. It speculated that a chemical interaction between KSS and KH-602 may exist at lower temperature and promote the formation of crosslinking structure. Thus, the decomposition at higher temperature was inhibited.

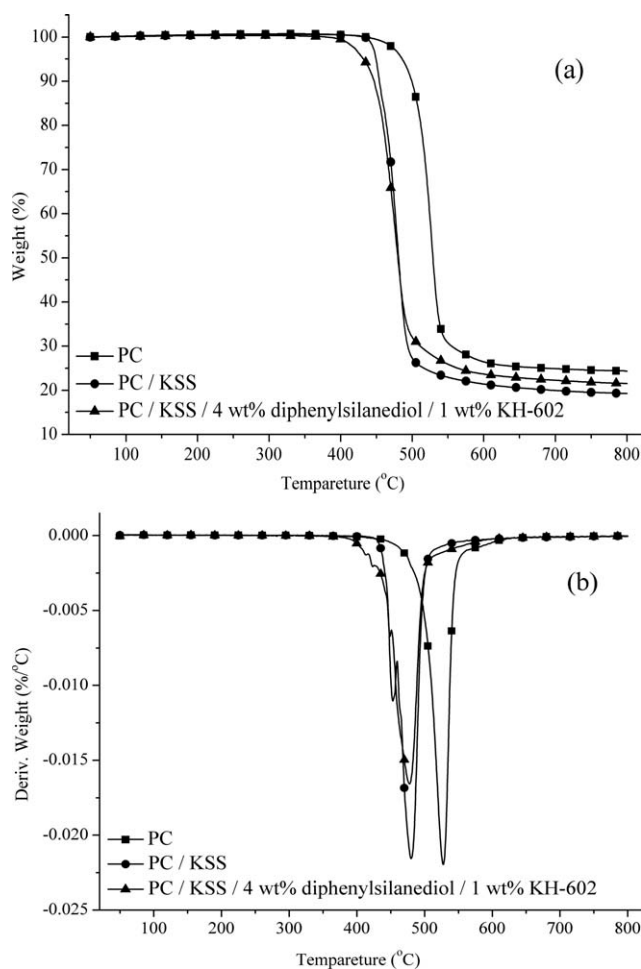
### Thermal Stability

The influence of the organic silicon on the thermal properties of the PC/KSS systems was investigated by TGA, as shown in Figures 4–6. The main data collected from TG and DTG curves were listed in Table II. The thermal degradation process of pure PC exhibited one step in the inert atmosphere. The major degradation of pure PC occurred between 480 and 550°C,  $T_{\text{onset}}$  was 469.5°C, and the  $T_{\text{max}}$  was 527.5°C. The char residue of pure PC at 800°C was 24.37 wt %. The degradation process of PC/KSS system turned to two-step because of the presence of KSS.  $T_{\text{onset}}$  of the PC/KSS system was lower than that of PC, and the char residues at 800°C decreased to 19.29 wt %. Thus, the incorporation of KSS decreased the thermal stability of the PC matrix.

The thermal degradation process of PC/KSS/organic silicon systems also had two steps similar to that of PC/KSS system.  $T_{\text{onset}}$ ,  $T_{\text{max}1}$ ,  $T_{\text{max}2}$ ,  $R_{\text{max}1}$ , and  $R_{\text{max}2}$  of PC/KSS/organic silicon systems were all lower than those of PC/KSS system; only char residues were higher than that of PC/KSS system. Thermogravimetry provided evidence that organic silicon improved the thermal stability of the flame-retarded systems because of the increase in solid residue and the decrease in the  $T_{\text{onset}}$  of the formulation containing organic silicon. Compared with PC/KSS system, the



**Figure 5.** TG (a) and DTG (b) curves of the PC, PC/KSS, and PC/KSS/1 wt % KH-602 system.



**Figure 6.** TG (a) and DTG (b) curves of the PC, PC/KSS, and PC/KSS/4 wt % diphenylsilanediol/1 wt % KH-602 system.

decrease of  $T_{\text{onset}}$  for PC/KSS/organic silicon systems probably resulted from the acceleration of the degradation for KSS. In addition, the  $T_{\text{onset}}$  was on the order of PC/KSS > PC/KSS/diphenylsilanediol > PC/KSS/diphenylsilanediol/KH-602 > PC/KSS/KH-602. From this order, it could be inferred that KH-602 accelerated the degradation of PC/KSS easily than that of diphenylsilanediol. The temperatures at the maximum weight-loss

rate ( $T_{\text{max1}}$ ) decreased from 453°C for PC/KSS system to 431.5, 444, and 423.5°C for PC/KSS/diphenylsilanediol, PC/KSS/KH-602, and PC/KSS/diphenylsilanediol/KH-602 systems, respectively. It probably ascribed to the presence of decomposable Si—O group at lower temperature in the systems.<sup>24</sup> The final char yield at 800°C was enhanced with the addition of organic silicon, as listed in Table II. It was proposed that the decomposition of Si—O group at lower temperature resulted in the formation of silicone-containing group, which participated in the crosslinked carbonization and effectively retarded the decomposition at higher temperature.<sup>25–27</sup> The char residues at 800°C of PC/KSS/diphenylsilanediol system were higher than those of PC/KSS/KH-602 and PC/KSS/KH-602/diphenylsilanediol systems. Diphenylsilanediol was more beneficial for the forming of char layer than that of KH-602. Furthermore, when the organic silicon was incorporated into PC/KSS, the  $R_{\text{max2}}$ , the major degradation stage, decreased. This could be favor for improving the flame retardancy of PC.

### SEM Analysis

The morphology of char residue after LOI tests was further investigated by SEM (Figure 7). It could be observed from Figure 7(a, b), the structure of char layer for PC and PC/KSS system was loose or porous. This poor char layer could not be efficiently acted as a barrier to shield the underlying polymer from heat and air. Therefore, in vertical burning tests, the rating of V-0 for PC and PC/KSS system could not be achieved. But, the surface of the char for PC/KSS/organic silicon illustrated on Figure 7(c–e) was improved with a more cohesive, smoother, and denser structure, which could prevent the underlying polymer from the heat, combustible gases, and free radicals during fire and was also less susceptible to crack, in agreement with the improvement of flame retardancy. The char layer for the PC/KSS/KH-602 [Figure 7(d)] was looser compared with that of the PC/KSS/diphenylsilanediol [Figure 7(c)]. This was probably due to the generation of  $\text{NH}_3$ , leading to the formation of little bubble in the char layer. Observation of the morphological structures of the residual char of the previous systems could be present if the flame retardancy of the flame-retarded PC/KSS systems was good. However, the significant differences in char layer among PC, PC/KSS, and PC/KSS/organic silicon systems could not be seen by SEM, which resulted in the difference in the fire properties.

**Table II.** Main Data Collected from TG and DTG Curves

Samples	$T_{\text{onset}}$ (°C) ± 2	$T_{\text{max1}}$ (°C) ± 2	$R_{\text{max1}}$ (%/°C)	$T_{\text{max2}}$ (°C) ± 2	$R_{\text{max2}}$ (%/°C)	Weight (%)
PC	469.5	527.5	−2.196	—	—	24.37
PC/KSS(99.5/0.5)	444.5	453	−1.100	480	−2.158	19.29
PC/KSS/diphenylsilanediol (95.5/0.5/4)	424	431.5	−0.186	479	−1.742	21.80
PC/KSS/KH-602(98.5/0.5/1)	406.5	444	−0.895	474.5	−1.665	19.54
PC/KSS/diphenylsilanediol/KH-602(94.5/0.5/4/1)	415.5	423.5	−0.206	477.5	−1.657	21.51

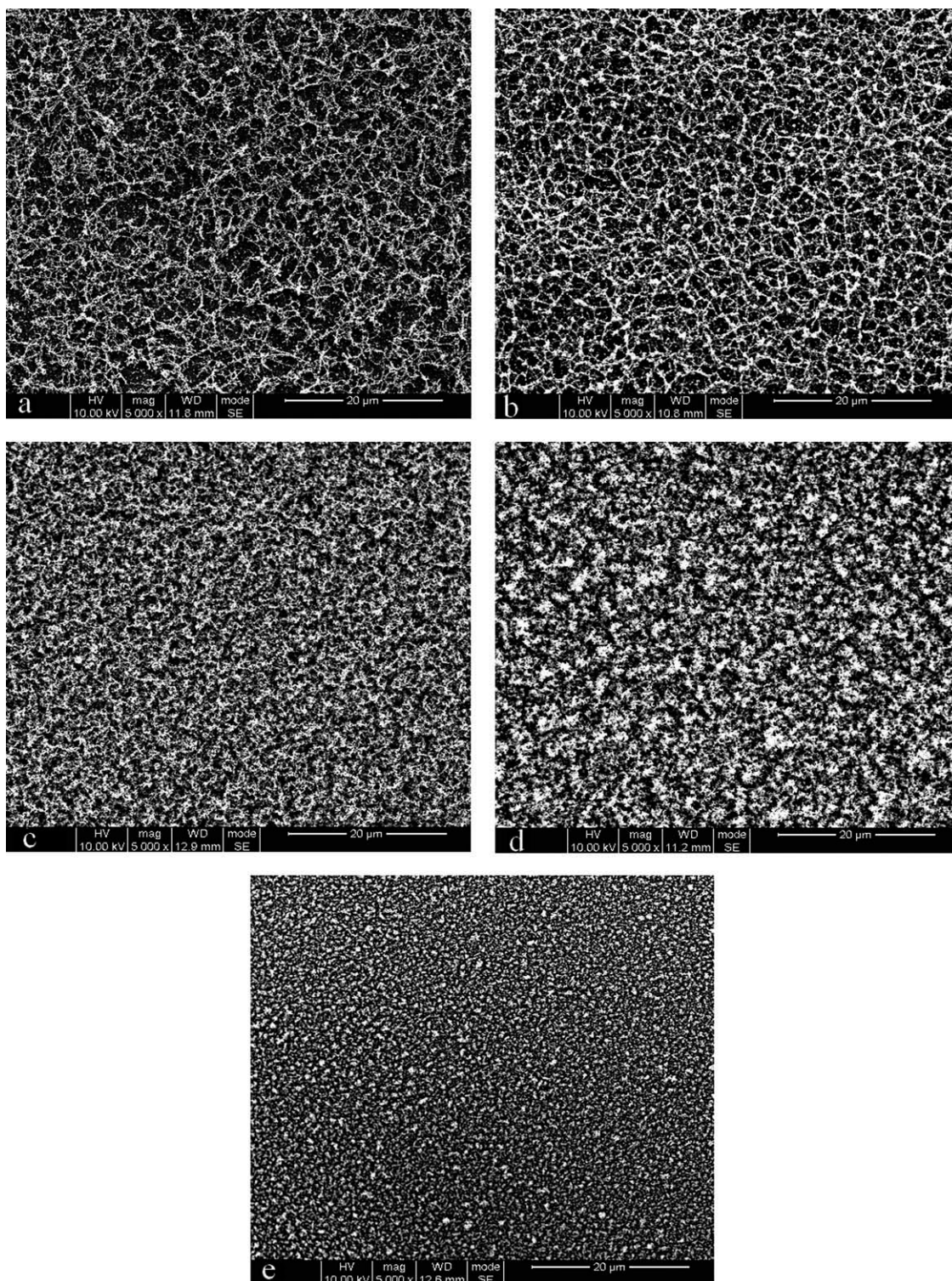
$T_{\text{onset}}$ : the initial decomposition temperature (based on 5 wt% weight loss).

$T_{\text{max1}}$ : the temperature of the first decomposition peak.

$R_{\text{max2}}$ : the decomposition speed at the first decomposition peak.

$T_{\text{max2}}$ : the temperature of the second decomposition peak.

$R_{\text{max2}}$ : the decomposition speed at the second decomposition peak.

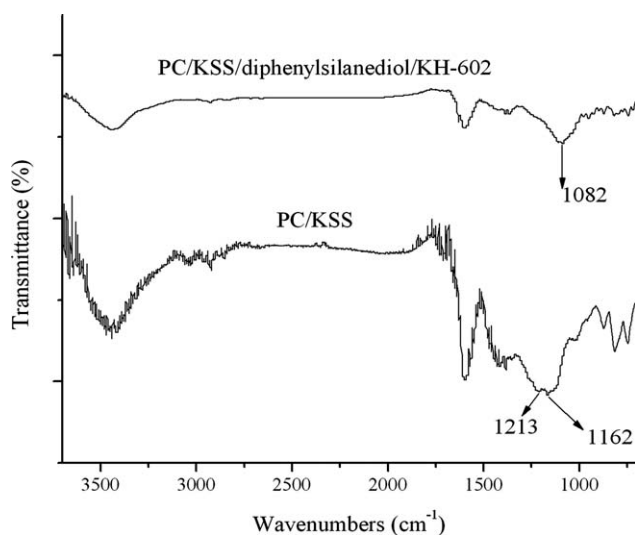


**Figure 7.** SEM morphology of the char residues of PC (a); PC/0.5 wt % KSS (b); PC/0.5 wt % KSS/4 wt % diphenylsilanediol (c); PC/0.5 wt % KSS/1 wt % KH-602 (d); PC/0.5 wt % KSS/4 wt % diphenylsilanediol/1 wt % KH-602 (e).

#### Char Analysis by FTIR

To clarify the structure of the flame-resistant barrier on the surface, the PC/KSS, PC/KSS/diphenylsilanediol/KH-602 systems after LOI tests were analyzed by FTIR measurement. The IR spectra of the systems are shown in Figure 8. The alcoholic

peak in a region of the  $3100\text{--}3500\text{ cm}^{-1}$  appeared in the two spectra, this indicated the presence of a considerable amount of alcohol groups in the char. The peaks at  $1213$  and  $1162\text{ cm}^{-1}$  observed in PC/KSS system were ascribed to  $\text{R-O-R}^1$  group, where R and  $\text{R}^1$  were aliphatic and aromatic structure,



**Figure 8.** FTIR spectra of char residues of the PC/KSS and PC/KSS/4 wt % diphenylsilanediol/1 wt % KH-602 systems.

respectively. From PC/KSS/diphenylsilanediol/KH-602 system, the peak at  $1082\text{ cm}^{-1}$  appeared, which was assigned to the Si—O group. The peaks at  $1213$  and  $1162\text{ cm}^{-1}$  were decreased in PC/KSS/diphenylsilanediol/KH-602 system. Based on the observed results for the systems, it was proposed that the organic silicon promoted to form a char on the surface of the systems during combustion, which was consisted of condensed aromatic compounds and Si—O units. Therefore, this char formulation was helpful for the enhancement of flame retardancy.

## CONCLUSION

In this article, the synergistic effect of the organic silicon on the thermal stability and the flame-retardant properties of PC/KSS systems was investigated. The combination of *N*-( $\beta$ -aminoethyl)- $\gamma$ -aminopropylmethyldimethoxysilane (KH-602) and diphenylsilanediol in the optimal ratio improved the flame retardancy greatly and changed the thermal degradation behavior of the PC/KSS systems. When 4 wt % diphenylsilanediol and 1 wt % KH-602 were incorporated into PC/KSS system, the LOI value achieved the maximum of 47 and Class V-0 of UL-94 test was passed. TGA curves demonstrated that there was a synergistic effect between KH-602 and KSS, which enhanced the char formation ability of KSS/KH-602 system. The char residues of this system reached 39.4 wt % at  $700^{\circ}\text{C}$ , whereas only 33.4 wt % according to calculation. The addition of the organic silicon improved the stability at high temperature and the yield of char residues of the hybrids. SEM showed that the surface of the char layer for PC/KSS/organic silicon systems was smoother and tighter than that of PC/KSS system.

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