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Flame retarding mechanism of polycarbonate containing methylphenyl-silicone

Wenjun Zhou[a,b], Hui Yang[a,*]

[a] *Department of Materials Science and Engineering, College of Materials and Chemical Engineering, Zhejiang University, Hangzhou 310027, PR China*
[b] *Department of Chemistry, Hangzhou Teachers College, Hangzhou 310036, PR China*

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Abstract

The thermal degradation of polycarbonate (PC) containing methylphenyl-silicone with a branched structure (SFR-PC) was investigated by the thermogravimetric analysis (TGA). The decomposition activation energies were determined using the Ozawa method. It was found that the decomposition activation energy and the degradation residue of the SFR-PC at 800 °C in air atmosphere were much higher than those of the PC. The addition of methylphenyl-silicone enhanced the thermal stability of PC and promoted the formation of char. The silicone was found effective in retarding the combustion of the PC. The limited oxygen index of the PC containing 5 wt.% of methylphenyl-silicone was 34%. Surfaces of the SFR-PC before and after combustion were analyzed by energy dispersive X-ray analysis (EDX) and infrared (IR) spectroscopy. Based on these results obtained, the flame retarding mechanism of the SFR-PC was discussed.

Keywords: Polycarbonate; Methylphenyl-silicone; Flame retardant; Thermal degradation; Activation energy

1. Introduction

Due to excellent mechanical and thermal properties, bisphenol A polycarbonate (PC) has been commonly used as engineering plastics in a wide variety of applications. In some applications including business machineries, electric and electronic appliances, automobile and building fields, it is strongly desired to render the materials flame retardancy. To meet such needs, numerous flame retarding techniques have been proposed for PC [1–3]. Organic halogen compounds have been commonly used for polymeric materials flame retarding because of their extremely high flame retardancy [4]. However, these compounds might generate highly toxic and potentially carcinogenic substance during combustion [5,6]. For this reason, efforts were made on the technique of achieving flame retardance with no or less amount of toxic substances forming during combustion. Various halogen-free flame retardants have been tried to use for polymers in recent years [7,8].

Silicone has a characteristic of high heat resistance and non-toxicity. It releases less amounts of toxic gases in case of fire. Several types of silicone have been proposed as the flame retardant for the PC, and some of them are of effective flame retardancy. The addition of relatively small amount of silicone to polymeric materials can significantly improve their flame retardancy. They are considered to be ‘environmentally friendly’ additives [6,9]. Research efforts on the silicone flame retardants are increasing [10–12]. Iji and Serizawa investigated some silicone derivatives as flame retardants for the PC and its derivatives [13]. They found a special silicone with a branched structure, a phenyl-rich mixture of phenyl and methyl groups in the chain and methyl groups at the chain terminals to be effective in retarding the combustion of PC. They proposed that the superior flame retardant effect of the branched silicone with methyl and phenyl owing to its excellent dispersion in PC and its rapid movement to the surface of PC to form the highly flame resistant char barrier during combustion. Hayashida et al. studied the flame retarding mechanism of the PC with a trifunctional phenyl-rich silicone additive by pyrolysis-gas chromatography (PY-GC) [14]. They suggested that the formation of the cross-linking structures between the PC substrates and the phenyl silicone additives might play

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[*] Corresponding author. Tel.: +86 571 87951408; fax: +86 571 87953054.
E-mail addresses: cjhzwj@163.com (W. Zhou), yanghui@zju.edu.cn (H. Yang).

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an important role for the flame retardancy of the PC-silicone system.

The flame retardancy of a polymer is closely related to its thermal degradation behavior [15]. So, in order to clarify the mechanism of the flame retardant, understanding the degradation behavior of a polymer is necessary. In the present study, the thermal decomposition behavior of the PC containing methylphenyl-silicone with branched structure at different heating rates in air atmosphere was studied using the thermogravimetric analysis (TGA), and the thermal decomposition activation energies for the PC and the PC-silicone blend were investigated using Ozawa method. There are many methods of kinetic analysis of the thermal degradation of polymers [16–19]. Among these, the Ozawa method is the most useful one to obtain decomposition activation energy. Using this method, there is no need to consider any reaction models [20,21]. In addition, energy dispersive X-ray analysis (EDX) was used to detect the change of silicon content on the surface of the flame-retarded PC after combustion. Its flame retarding mechanism was discussed.

2. Experimental

2.1. Materials

The PC used in this study was produced by Idemitsu Petrochemical Co. Ltd. (Japan). The silicone sample was synthesized by hydrolysis and condensation of methoxysilane containing phenyl and methyl. It consists of 75 mol% phenylsiloxane and 25 mol% methylsiloxane units. Its end groups were mainly methyls with a few hydroxyls. The ratio of organic groups to silicon atoms (R/Si) which was used to indicate the branched extent of a polysiloxane structure was 1.2.

The PC was dried in the oven at 102 °C for 24 h prior to blending. The flame-retarded PC (SFR-PC) sample was blended with 90 wt.% of the PC substrate and 10 wt.% of silicone flame retardant by melt blending at 260 °C.

2.2. Thermal analysis

Thermogravimetry (TG) was carried out on a NETZSCH STA 409 PG/PC thermoanalyzer. About 10 mg of a tested sample was heated from 25 °C up to 800 °C under an air flow using heating rates of 5, 10, 15 and 20 °C/min, respectively. The temperature reproducibility of the TGA is ±3 °C and error range of the mass is ±3%.

The thermal degradation activation energy was determined directly from mass loss versus temperature data obtained at several heating rates by the Ozawa method [19]. According to this method, the equation of thermal decomposition can be expressed as follows:

$$\frac{\mathrm{d}(\log r)}{\mathrm{d}(1/T)} = -0.4567\frac{E}{R}$$

where r is the heating rate, T the absolute temperature at the different heating rate under the same mass loss, E the activation energy of the decomposition reaction and R is the gas constant.

The above equation shows that $\log r$ is linearly proportional to $1/T$. The activation energy can then be determined by a calculation of the slope from the $\log r - 1/T$ plots.

2.3. Energy dispersive X-ray analysis (EDX)

Scanning electron microscopy (SEM) was equipped with an X-ray detector for energy dispersive X-ray analysis (EDX) (EDAX GENENIS4000). Si atoms on the surface of the SFR-PC sample before and after combustion were analyzed by EDX.

2.4. Infrared (IR) measurement

The solid combustion residues were collected and analyzed using the standard KBr-pellet technique by an infrared analyzer (AVATAR 360FT Nicolet).

2.5. Limiting oxygen index (LOI) test

The LOI value was measured on an oxygen index instrument JF-3 produced by Jiangning Analysis Instrument Factory, according to ISO4589-1984 standard. The dimensions of all samples are 130 mm × 6.5 mm × 3 mm.

3. Results and discussions

3.1. Thermal analysis results

The thermogravimetric curves for the PC and the SFR-PC samples observed in an air flow at different heating rate are given in Figs. 1 and 2, respectively. Tables 1 and 2 show the corresponding characteristic mass loss data. The curves of the PC and the SFR-PC show a two-step degradation process. The first stage of mass loss of the pure PC occurs at 450–540 °C, which is almost similar to that in N_2 atmosphere [22]. A slower second degradation stage is the char oxidation. The temperature of degradation onset of the SFR-PC is lower than that of pure PC. The lower degradation onset temperature of the SFR-PC results from the thermal depolymerization of the silicone from

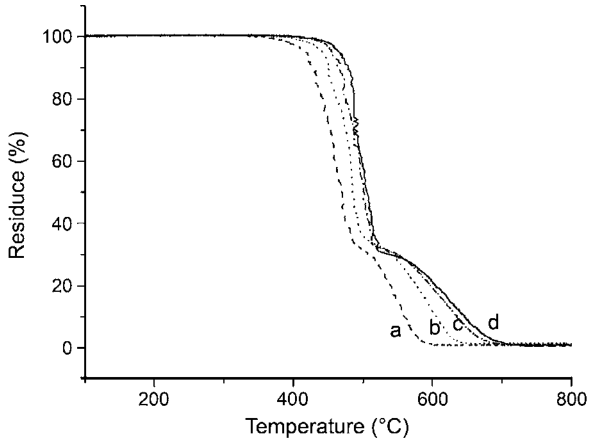

Fig. 1. TG curves of PC in air at heating rate: (a) 5 °C/min, (b) 10 °C/min, (c) 15 °C/min and (d) 20 °C/min.

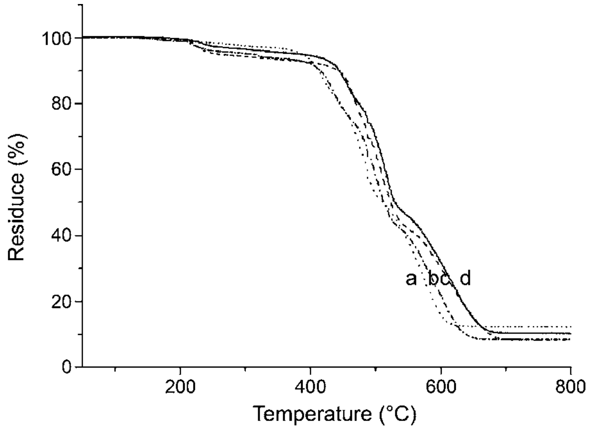

Fig. 2. TG curves of the SFR-PC in air at heating rate: (a) 5 °C/min, (b) 10 °C/min, (c) 15 °C/min and (d) 20 °C/min.

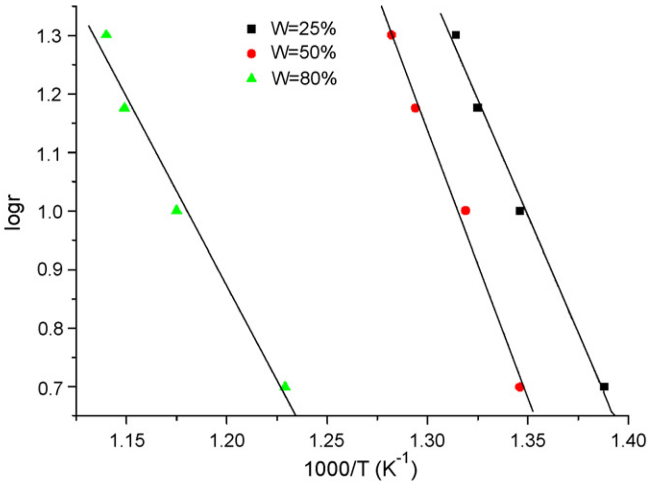

Fig. 3. The logarithmic heating rate vs. the reciprocal absolute temperature for PC with various mass loss (W: mass loss).

Table 3
The decomposition activation energies of PC and the SFR-PC

Mass loss	Activation energy (kJ/mol)	
	PC	SFR-PC
0.25	171.2	250.5
0.50	187.7	303.5
0.80	127.0	167.8
Mean	162.0	240.6

its chain ends. The end groups of the silicone to be used contain a few hydroxyls, which induce decomposition of the polymer from chain ends in lower temperature [23]. It is speculated that the decomposition of the silicone in lower temperature might be beneficial to cross-linking reactions and formation of the char in the silicone-PC system. However, the temperature at 50% of mass loss and the temperature at maximum mass loss rate for the SFR-PC are all higher than those of the PC, respectively. At the heating rate of 5 °C/min, the temperature at 50% of mass loss shifts from 470 °C for the PC to 511 °C for the SFR-PC. It can be observed from the TG curves and the data that the char residue at 800 °C in air atmosphere increased obviously when the 10 wt.% of methylphenyl-silicone was added to the PC. The char residue of the SFR-PC was 12.3% of the initial mass, but only 1.0% for PC at the heating rate of 5 °C/min. These results indicate that the addition of methylphenyl-silicone enhances the thermal stability of PC and promotes the formation of char.

With increasing the heating rate from 5 to 20 °C/min, the decomposition curves of both the PC and the SFR-PC shift to higher temperatures. The activation energies of the thermal degradation of the PC and the SFR-PC were determined using the Ozawa method. The linear plots of log r versus $1/T$ at mass loss values 25, 50 and 80% are shown in Fig. 3 for the PC and Fig. 4 for the SFR-PC, respectively. The calculation results are shown in Table 3.

Table 1
TG data of PC obtained in air atmosphere at different heating rate

Heating rate (°C/min)	Temperature (°C)			Char residue at 800 °C (wt.%)
	Onset of degradation[a]	50% mass loss	Maximum mass loss rate	
5	384	470	471	1.0
10	409	485	486	1.4
15	430	499	503	1.1
20	437	507	510	0.7

[a] Temperature for 1% mass loss.

Table 2
TG data of the SFR-PC obtained in air atmosphere at different heating rate

Heating rate (°C/min)	Temperature (°C)			Char residue at 800 °C (wt.%)
	Onset of degradation[a]	50% mass loss	Maximum mass loss rate	
5	211	511	488	12.3
10	209	515	509	8.4
15	216	523	513	8.3
20	223	530	516	10.3

[a] Temperature for 1% mass loss.

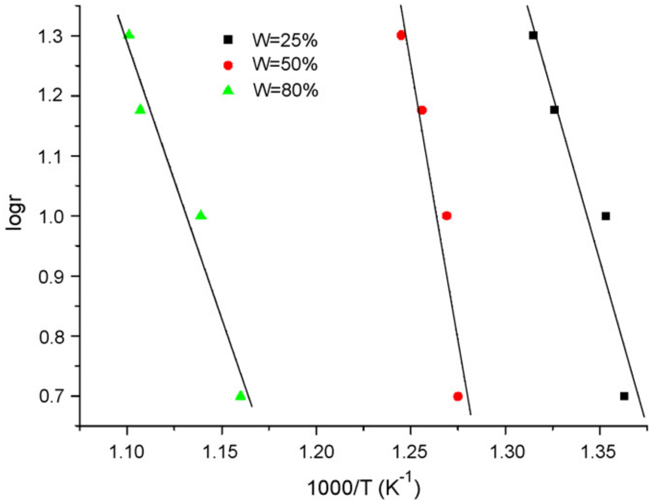

Fig. 4. The logarithmic heating rate vs. the reciprocal absolute temperature for the SFR-PC with various mass loss (W: mass loss).

It is found that the activation energy of the SFR-PC is greatly higher than that of pure PC. The branched silicone with methyl and phenyl increases the thermal degradation activation energy and reduces the decomposition rate of the PC. This result is consistent with the thermogravimetric analysis that the SFR-PC has an increasing char residue and higher thermal stability. The silicone flame retardant promotes the formation of char during the thermal degradation. The char layer might play an important role for the flame retardancy of the silicone based flame retardant-PC system.

3.2. Flame retarding mechanism of polycarbonate containing methylphenyl-silicone additive

Flame retardancy of the molded plastics was determined by the limited oxygen index (LOI) method, which detects the minimum oxygen concentration needed to support combustion after ignition. The LOI of the PC containing 5 wt.% of methylphenyl-silicone with branched structure was 34%, while the LOI of pure PC was 26%. This result indicated that the methylphenyl-silicone with branched structure to be used had a sufficient flame retardant effect for the PC.

The PC and the SFR-PC sample were thermally treated by heating each of them at 400 °C for 40 min in an electric oven under air atmosphere. The PC sample therefore charred and became black substance-like after combustion. However, the SFR-PC sample merely formed a thin brown char layer on the surface. Underneath the thin brown char layer, the sample remained white melting resin. This char layer was then put into chloroform for 2 days. The char was found insoluble in chloroform. This indicated that the char layer formed by cross-linking reactions in the silicone-PC system during the thermal degradation, and the char layer could serve as a good insulating barrier to reduce the radiant heat and the decomposition rate of the PC.

EDX analysis was carried out for surfaces of the SFR-PC before and after combustion, and the results were shown in Fig. 5 and Table 4. When the SFR-PC burnt for 5 s, the silicon content of its surface was 2.13 wt.%, which was less than that of the SFR-PC before combustion. However, after that silicon content

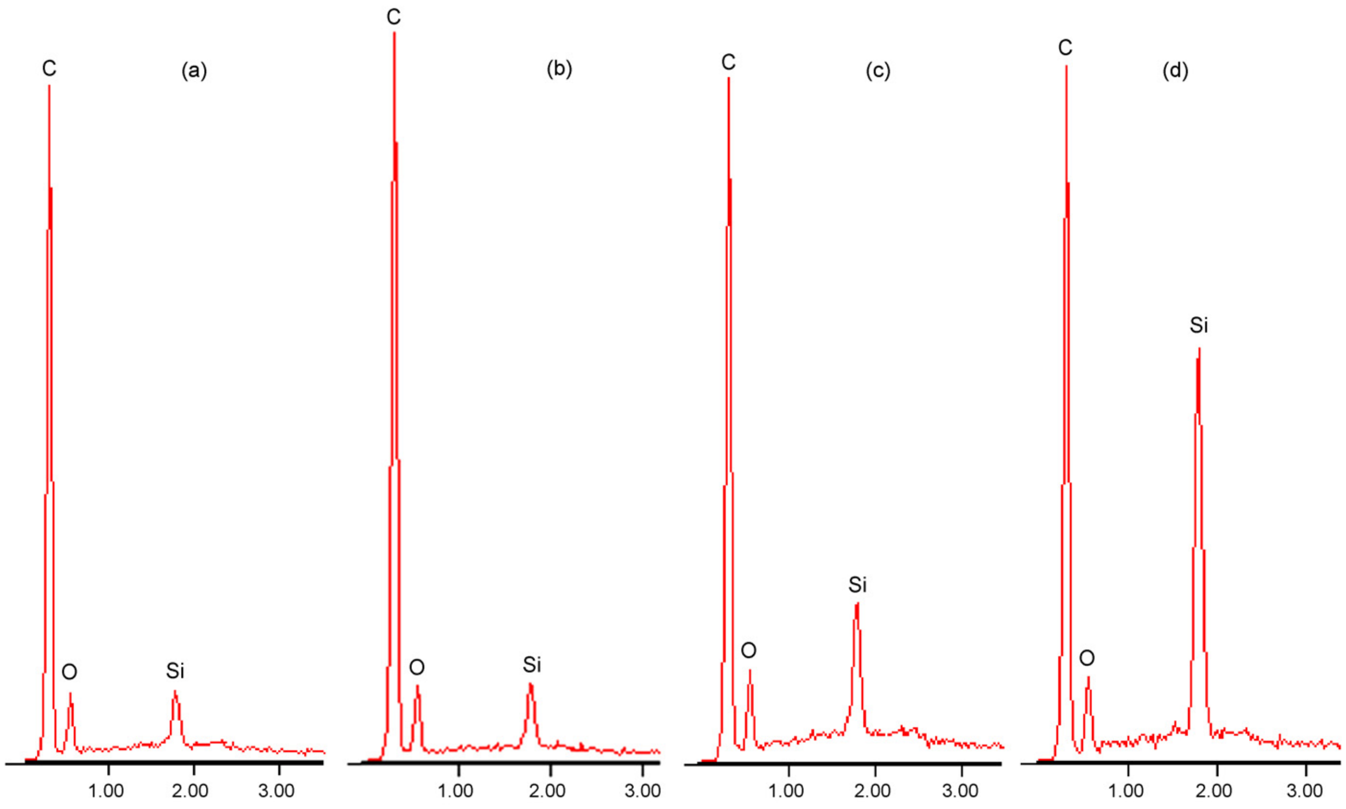

Fig. 5. EDX analysis of the SFR-PC: (a) before combustion, (b) combustion for 5 s, (c) combustion for 15 s and (d) combustion completely.

Table 4
Elemental composition of the surface of the SFR-PC by EDX measurement

The SFR-PC samples	Si (wt.%)	C (wt.%)	O (wt.%)
Before combustion	2.25	83.48	14.27
Combustion for 5 s	2.13	82.88	14.98
Combustion for 15 s	4.02	81.22	14.76
Combustion completely	8.95	80.68	10.37

of the surface of the SFR-PC increased with the combustion going on. The silicon content increased to 8.95 wt.% when the SFR-PC burnt completely. During the initial process of combustion, the Si–O bond scission of the silicone has produced the volatile products containing silicon, which resulted in a decrease for the surface silicon content of the SFR-PC. After burning several seconds, the thermo-oxidative degradation of PC became faster, and the degradation of silicone was slower than that of PC. Simultaneously, the silicone moved to the PC surface, and silicon accumulated on the surface of the polymer to form a barrier to mass transport and to protect the underlying polymer from the flame.

To clarify the structure of the flame resistant barrier on the surface, the SFR-PC was analyzed before and after combustion by infrared (IR) measurement. The IR spectra of the SFR-PC are shown in Fig. 6. The bonds in a region of the 2800–3200 cm^{-1} are for C–H stretching. Aromatic carbon hydrogen and sp^3 carbon hydrogen stretching are above and below 3000 cm^{-1}, respectively. sp^3 carbon hydrogen peaks decreased while aromatic carbon hydrogen peaks almost remained unchanged when the polymer had burnt for 5 s. These peaks were almost not observed when the SFR-PC combusted completely. The alcoholic peak at 3440 cm^{-1} appeared in the three spectra, and the intensity of the peak increased after the SFR-PC combustion. This indicated the presence of a considerable amount of alcohol groups in the char. The peak at 1074 cm^{-1} was still observed in Fig. 6(c), which was attributed to Si–O bond [24]. The peaks at 798 and 1618 cm^{-1} appeared in Fig. 6(b), which might be the condensed aromatic bonds, and the intensities of these two peaks increased when the SFR-PC combusted completely. During the combustion of the SFR-PC, the dehydrogenation among phenyl of the silicone took place and the condensed aromatic structure formed. The hydroxyl of the degradation products of the PC attacked the carbon silicon bond in silicone to form cross-linking structure at high temperature. The formation of the condensed aromatic structure and the cross-linking process were illustrated in Figs. 7 and 8. With the combustion going on, the extent of cross-linking increased, therefore the structure of the char became more complicated and compact.

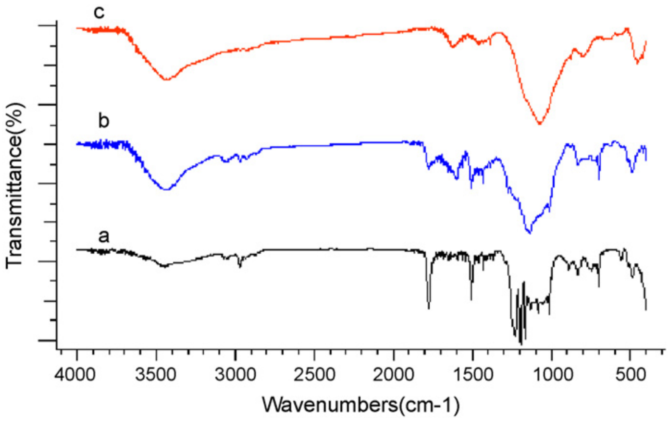

Fig. 6. IR spectra of the SFR-PC: (a) before combustion, (b) combustion for 5 s and (c) combustion completely.

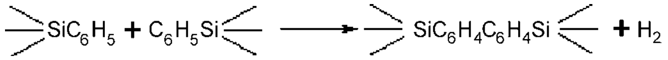

Fig. 7. Pathway of dehydrogenation among phenyl of the silicone.

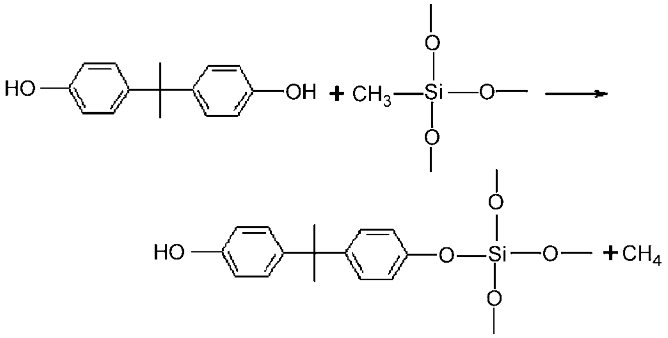

Fig. 8. Cross-linking pathway of the SFR-PC.

Based on the observed results for the SFR-PC, it was proposed that the methylphenyl-silicone with branched structure induced cross-linking reactions and promoted to form a char on the surface of the SFR-PC during combustion, which was of cross-linking structure and consisted of condensed aromatic compounds and siloxane units. The char acts as a good insulating barrier, which reduces radiant heat of flame, suppresses the thermal degradation of the polymers, and also restrains the diffusion of flammable degradation products into the combustion zone.

4. Conclusions

The degradation residue of polycarbonate containing methylphenyl-silicone with branched structure (SFR-PC) at 800 °C in air atmosphere is obviously higher than that of the PC. The decomposition activation energy of the SFR-PC is also considerable higher than that of the PC. The addition of the silicone enhances the thermal stability of the PC and promotes the formation of char. The methylphenyl-silicone is effective in flame retarding for the PC. The superior flame retarding effect of the silicone is proposed from a result of the formation of the cross-linking structured char, which consists of condensed aromatic compounds and siloxane units on the SFR-PC surface during combustion. The char acts as an insulating barrier to reduce both radiant heat of flame and the diffusion of flammable degradation products into the combustion zone.

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