

# Thermal Degradation Behavior of Low-Halogen Flame Retardant PC/PPFBS/PDMS

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Received 22 December 2008; accepted 26 October 2009

DOI 10.1002/app.31695

Published online 13 September 2010 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** Flame retardant polycarbonate (FRPC) with 0.2 wt % additives of potassium perfluorobutane sulfonate and polydimethylsiloxane was found to achieve V-0 rate at 1.6 mm thickness without significantly affecting the mechanical properties of PC. Condensed aromatic bonds with a small amount of Si—O bonds were found in the UL-94 burning residues tested by FTIR spectra. A compact char layer with cavities inside was formed on the surface of the sample during the rapid decomposition of FRPC, and the concentration of Si was

found to be much higher inside the surface of the char layer than that outside the surface analyzed by SEM-EDX, which was related to the synergistic effects of the two flame retardants of PPFBS and PDMS. A schematic diagram was designed to describe the mechanism of the FRPC. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2730–2736, 2011

**Key words:** polycarbonate; nonhalogen flame retard mechanism; TGA; EDX; char structure

## INTRODUCTION

Bisphenol A type polycarbonate (PC) shows the limited oxygen index at about 26 accompanied with both good physical and chemical properties, and it can be used for electronic devices. Flame retardants containing halogen such as brominated aromatic compounds are used in Flame retardant Polycarbonate (FRPC), but halogen-containing compounds might release highly toxic and potentially carcinogenic substances during combustion. Attempts have been made to replace them with non-halogen flame retardants. Since a patent<sup>1</sup> published by GE in 1976 showed that addition of a small amount of sulfonate together with siloxane could improve the flame retardancy of PC greatly. Many studies focused on the process of the thermal degradation of the FRPC containing one of the aforementioned flame retardants.<sup>2–14</sup>

Ballistreri et al.<sup>3</sup> indicated that the thermal decomposition process of PC was influenced by adding potassium trichlorobenzene sulfonate and the char layer formation was prone to form. Potassium perfluorobutane sulfonate (PPFBS) was widely investigated because of its effective improvement on the flame retardancy of PC in the amount of only 0.1 wt %.<sup>5</sup> Ishikawa et al.<sup>6</sup>

believed that the degradation process included different scission routes and PC showed excellent flame retardancy resulted from perfluoroalkane sulfonic acid potassium salts. Nodera and Kanai<sup>7</sup> indicated that potassium sulfonate accelerated the degradation of PC as a catalyst, and facilitated the char formation. Huang et al.<sup>8</sup> showed that the release of CO<sub>2</sub> could be accelerated by addition of PPFBS, and a majority of the flame retardant reactions were found to take place in the condensed phase.

It is difficult to mix a silicone derivative into PC because of their poor compatibility. However, the addition of PDMS with reactive groups (alkoxy, vinyl, etc) and some organic metal compounds (magnesium stearate, etc.) could improve the flame retardancy of resin greatly.<sup>10</sup> Iji and Serizawa<sup>11</sup> found that a special silicone compound with branched chain structure was effective in retarding the combustion of PC. Ohtani and coworkers<sup>12</sup> indicated that the formation of the crosslinking structure between PC and phenyl silicone-based additives might play an important role in the good flame retardancy of PC. Zhou and Yangzref<sup>13</sup> showed that after degradation at 800°C in the air atmosphere, the residue of modified PC contained 5 wt % of methyl phenyl-silicone with branched structure was obviously higher than that of pure PC.

Few publications were concerned about the flame retardant process of PC with the addition of the synergistic flame retardant PPFBS/PDMS. In this study, the thermal behavior and flame-retardant mechanism of PC/PPFBS/PDMS were studied. Some new evidences, which supported the synergistic effects of

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Contract grant sponsor: Shanghai Postdoctoral Scientific Research Project Fund; contract grant number: BR110001.

Contract grant sponsor: Shanghai Leading Academic Discipline Project; contract grant number: B202.

TABLE I  
UL-94 Test Data and the LOI Data of PC and PC/PPFBS/(PDMS)

Samples	$t_1$ (S)	$t_2$ (S)	Phenomena	LOI (%)	UL-94
PC (3.2 mm)	25	7	Easy to melt, dripping	26.0	–
PC/PPFBS (3.2 mm)	1	4	Strong char, lean to dripping	28.5	V-0
PC/PPFBS/PDMS (1.6 mm)	1	0	Strong char, no dripping	30.5	V-0

$t_1$ , the max after-flame time for the first burning;  $t_2$ , the max after-flame time for the second burning.

the two flame retardants were also discussed. A schematic diagram was designed to describe the flame retardant mechanism of the FRPC.

## EXPERIMENTAL

### Materials

PC 201-15, a bisphenol A type PC, was produced by LG DOW Polycarbonate Co., PPFBS, FR-2025, was produced by 3M Co. PDMS, Tegomer E525, was produced by Degussa Co. PC was dried at 120°C for 4 h before processing. PC/PPFBS/PDMS sample was obtained by melt mixing at a weight ratio of 100/0.1/0.1 using a twin-screw extruder, Berstorff ZE25, at 250°C and a screw speed of 200 rpm.

### Measurements

TGA was carried out at the heating rate of 20°C/min, under nitrogen on a TGA Q5000 thermal analyzer (TA Instruments). The thermal oxidation behavior of PC and PC/PPFBS/(PDMS) was tested under oxygen on TGA Q5000 at a heating rate of 10°C/min.

The exterior surfaces of the char layer of PC and PC/PPFBS/(PDMS) were observed by scanning electron microscope (SEM, Hitachi-2000) and field emission scanning electron microscope (FESEM, Fei Sirion 200). The weight ratio of C/O/Si on the surface of the char layer was determined by energy dispersive X-ray (EDX, Oxford).

Limited oxygen index (LOI) and UL-94 rate were measured according to ISO 4589-1984 and UL-94, respectively. The condensed residues were collected and kept in a drier for two days, and then analyzed by FTIR (Paragon 1000).

Tensile properties were tested according to ASTM 638 on a tensile test instrument (Instron 4456). The notched Izod impact strength was measured according to ASTM D 256 on a Ray-Ran pendulum impact tester.

## RESULTS AND DISCUSSION

### Synergistic effects of flame retardants on PCs

Table I and II show the flame retardancy and mechanical properties of PC and modified PCs. The

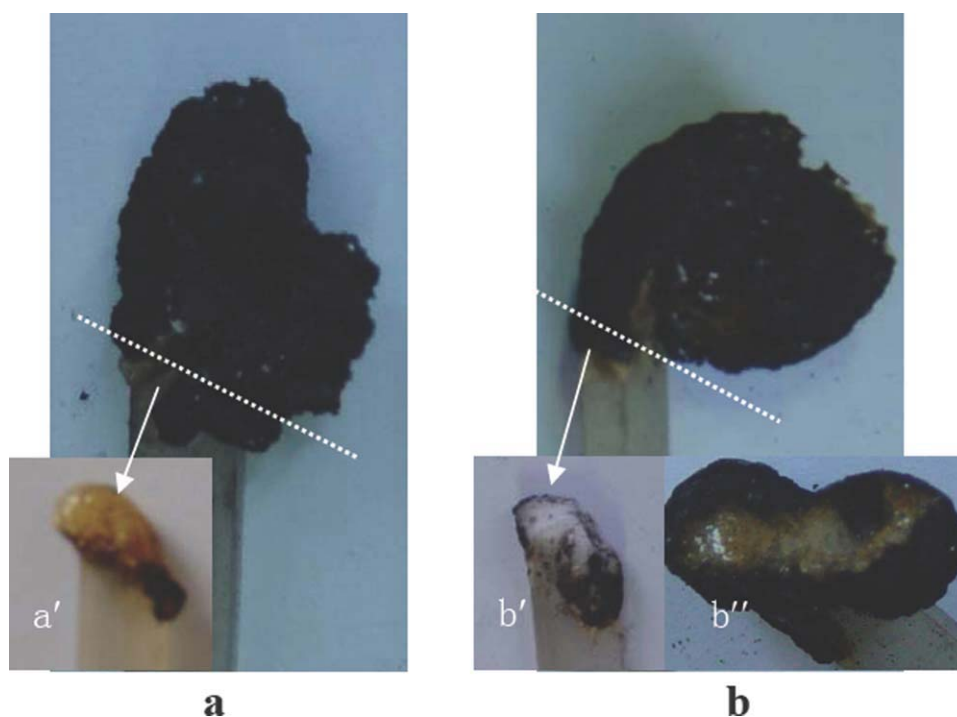
addition of 0.1% of PPFBS and 0.1% of PDMS in PC increased the LOI and the flame retardancy rate of UL-94 test without significantly affecting the mechanical properties of PC. As to PC/PPFBS, the burning time decreased significantly, i.e., from 25 s to only 1 s for  $t_1$ , and the sample reached V-0 rate of the UL-94 test at 3.2 mm thickness. PDMS and PPFBS increased the LOI and the flame retardancy rate. PC/PPFBS/PDMS (100/0.1/0.1) had the LOI of 30.5, 17.3%, which is higher than that of PC. PC/PPFBS/PDMS sample of 1.6 mm thickness reached the UL-94 V-0 rate. PC/PPFBS/PDMS had the shortest burning time, with  $t_2$  being close to zero. This indicates the char generated on the surface during the first combustion restrained the extension of fire effectively.

### Morphology of the char residue after combustion

Nodera and Kanai<sup>7</sup> compared the char formation of PC and modified PC by adding a small amount of PPFBS, and found that the char layer was formed only on the surface. The material under the char layer was not carbonized when PC with PPFBS was burned. A similar phenomenon appeared in our study. Apart from that, the material even inside the intumescent char layer was not carbonized when PC/PPFBS/PDMS was burned. Figure 1 shows the photos of the char residue of PC/PPFBS and PC/PPFBS/PDMS. The intumescent char residue of PC/PPFBS was loose and the char layer could be peeled off from the substrate easily. The interface between the char layer and substrate (Fig. 1a') was also loose. But the intumescent char residue of PC/PPFBS/

TABLE II  
Mechanical Properties of PC and PC/PPFBS/(PDMS) Before Combustion

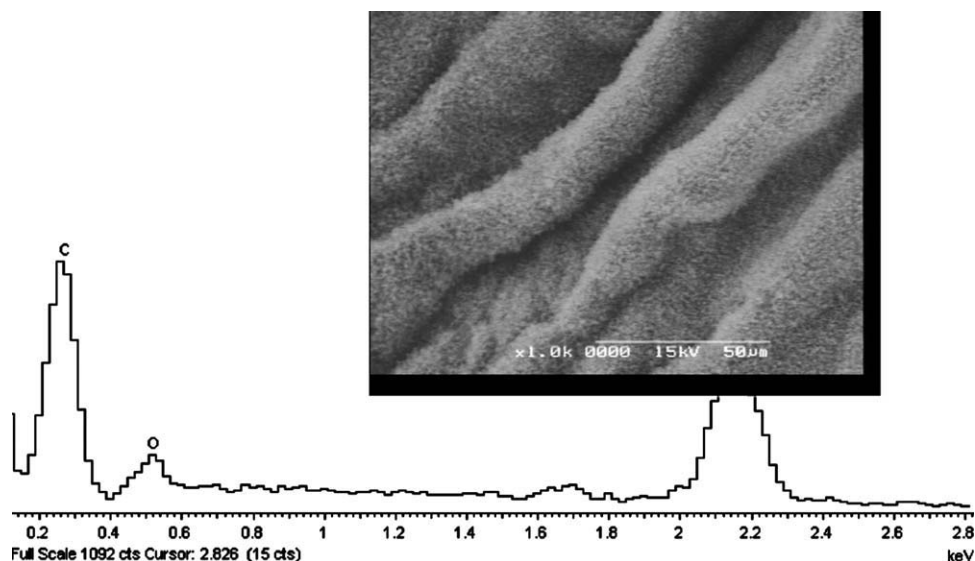
Properties	PC	PC/PPFBS	PC/PPFBS/PDMS
Tensile strength (MPa)	59.1	59.0	61.4
Elongation at break (%)	100	65.0	110
Flexible strength (MPa)	95.3	96.7	98.2
Flexible modulus (MPa)	2410	2506	2578
Notched izod impact strength (J/m)	822	856	895
$T_g$ (°C)	148.8	148.0	149.6



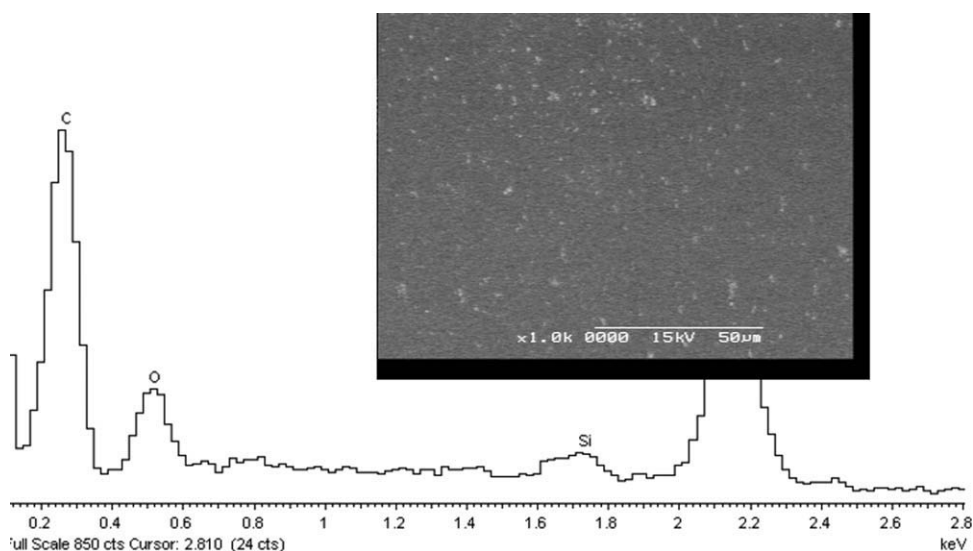
**Figure 1** Char of the burned (a) PC/PPFBS and (b) PC/PPFBS/PDMS after LOI test; (a') burned PC/PPFBS completely peeling char layer, (b') burned PC/PPFBS/PDMS completely peeling char layer, (b'') burned PC/PPFBS/PDMS peeling part of the char layer. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)].

PDMS, containing a large cavity (Fig. 1b''), was compact and the char layer could hardly be peeled off from the substrate. The cross section between the char layer and substrate was stress-whitening as shown in Figure 1b'. This indicates that PC/PPFBS/PDMS was easy to form compact char layer to prevent more heat and fire outside when flame occurs and thus the material inside the char layer could not

be carbonized. And the material under the char layer might crosslinked due to PDMS,<sup>7</sup> which could help the material release heat without bearing extremely high temperature. The inside cavity of the char layer might formed by the evolved inert gas,<sup>2</sup> which expanded the char layer during the degradation of the material. The LOI result of PC/PPFBS was 28.5 and that of PC/PPFBS/PDMS was 30.5 as



**Figure 2** SEM with EDX result of the exterior surface of the char layer of PC/PPFBS/PDMS (the weight ratio of C/O is about 85.7 : 14.3) (the peak of Si at ca 1.670 KeV was not be detected) (the tested sample were gold sprayed, the peak at ~ 2.154 KeV is Au).



**Figure 3** SEM with EDX result of the interior surface of the char layer of PC/PPFBS/PDMS (the weight ratio of C/O/Si is about 70.7 : 22.5 : 6.81) (the peak of Si is at  $\sim 1.670$  KeV) (the tested sample were gold sprayed, the peak at  $\sim 2.154$  KeV is Au).

shown in Table I. This could be related to the synergistic effect of the two flame retardants of PPFBS and PDMS.

#### Distribution of silicon element

The interior surface of the char layer of the burned PC/PPFBS/PDMS is different from its exterior surface, as depicted in Figures 2 and 3. SEM equipped with EDX analyzer was used to observe the gold-sprayed surfaces of the char layer and to detect the distribution of Si element (Figs. 2 and 3). The ratio of C/O/Si on the interior surface of the char layer was found to be about 70.7 : 22.5 : 6.8, while there was no Si element detected on the exterior surface. This result assured that the enrichment of Si element on the interior surface belonged to the polymer rather than the char, as the average weight ratio of C/O/Si was about 82.6 : 17.0 : 0.09 according to the composition of PC/PPFBS/PDMS, and the ratio of C/O/Si on the surface, detected by EDX, was 72.3 : 23.4 : 0.36 before combustion because of the incombustibility of silicon. Such enrichment of Si element should have contributed to the better flame retardant performance of PC/PPFBS/PDMS.

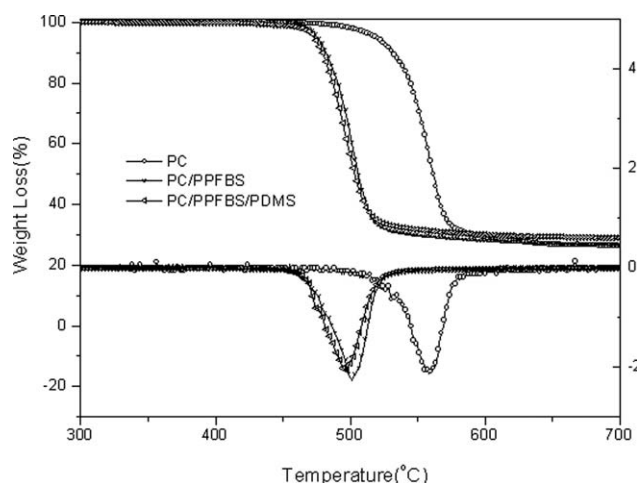
#### Thermal behavior of PC and PC/PPFBS/(PDMS)

Thermogravimetric analysis under  $N_2$

According to the literatures,<sup>7,15</sup> the degradation and char formation of polymers during combustion were generated in non-oxygen atmosphere. Therefore, TGA analysis was carried out under nitrogen.

The TGA and DTG curves in Figure 4 are summarized in Table III. The presence of PPFBS could

accelerate the thermal degradation of PC. The initial decomposition temperature (IDT) is defined as the temperature at the weight loss of 5 wt %.  $T_{max}$  is the temperature at the highest weight loss rate. As shown in Table III, PC/PPFBS had lower IDT and  $T_{max}$  than PC. It is especially noticeable that although PC/PPFBS/PDMS showed the lowest IDT and the lowest temperatures at 50 and 60% weight loss among the three samples, it showed the highest temperature at 70% weight loss. In addition, the residue at 700°C were almost the same for PC and PC/PPFBS, while the residue of PC/PPFBS/PDMS was higher. These results imply that the flame retardancy was not entirely dependent on the char residue, but mainly on the rate of the weight loss during the early stage of combustion. Because the weight loss



**Figure 4** TGA/DTG curves of PC and PC/PPFBS/(PDMS) at the heating rate of 20°C/min under  $N_2$ .



TABLE III  
The Thermal Parameters of PC and PC/PPFBS/(PDMS) Under N<sub>2</sub>

Samples	IDT (°C)	T <sub>50%</sub> (°C)	T <sub>60%</sub> (°C)	T <sub>70%</sub> (°C)	T <sub>max</sub> (°C)	Residue at 700°C (wt %)
PC	519	561	567	590	559	26.4
PC/PPFBS	475	507	511	544	501	26.5
PC/PPFBS/PDMS	473	501	510	597	497	28.9

rate of PC/PPFBS/PDMS at 60% is the fastest as shown in Table III. The combustion at the weight loss of 70% became difficult as the temperature was higher (597°C) than those of the other two. Such conclusion is based on the viewpoint that char formation during combustion is generated in anoxic atmosphere, and thus TGA under nitrogen could be used to describe the burning process.

#### Thermogravimetric analysis under O<sub>2</sub>

Krevelen<sup>16</sup> stated: For a better insight into flame resistance and flame extinction, it is useful to split the combustion process into its constituent elements. It then appears that the thermal decomposition is the fundamental link in a series of reactions. In terms of this viewpoint, assumption of the result of the sample by the TGA under O<sub>2</sub> could be used to conceptually and qualitatively prove the process in the zone, which was influenced by thermal oxidation without burning. To observe the process more detaildly, the TGA curves and data at the heating rate of 10°C/min are depicted in Figure 5 and Table IV, respectively.

Compared the data in Table III with Table IV, it could be seen that the temperatures at a given weight loss under oxygen were lower than those under nitrogen. Such a difference is reasonable, because the thermal oxydation decomposition must be easier and faster than that under N<sub>2</sub>. The TGA curves in Figure 5 implies that the thermal oxidation behavior of the PC and PC/PPFBS/(PDMS) is more complex than that under nitrogen. During the early stage of thermal oxidation decomposition, the weight loss rate of PC/PPFBS/(PDMS) was much higher than that of PC. But during the later stage, the situation became reversed, especially for PC/PPFBS/PDMS. Below the burning temperature of PC (about 600°C), the TGA curves showed a two-stage degradation process as mentioned under oxygen. The behavior during the early stage of degradation was similar comparing to that under nitrogen, But during the later stage the behavior associated with char oxidation. Consequently, little residue could be found, as shown in Table IV. This indicates that more stable char formed in PC/PPFBS/PDMS due to PDMS during the early stage of accelerated thermal oxidation decomposition. This could still con-

tributed to better flame retardant performance of PC/PPFBS/PDMS.

#### FTIR of the residue of PC and PC/PPFBS/(PDMS)

The composition and the amount of the residues after UL-94 test were different from those after the TGA test under N<sub>2</sub>. The content of the char residue obtained under nitrogen and oxygen should be different, The FTIR was used to analysis the content of the char residue of PC and FRPCs after TGA test and UL-94 test, respectively.

#### FTIR of the residue after TGA test under N<sub>2</sub>

The FTIR spectra of the residue of PC and PC/PPFBS/(PDMS) obtained at 800°C under N<sub>2</sub> are shown in Figure 6. The band at 750 cm<sup>-1</sup>, characteristic band of condensed aromatic structure as the precursor of char,<sup>15</sup> could be observed in the FTIR spectra of PC/PPFBS/PDMS. And the band at 1110 cm<sup>-1</sup> was found to be broadened in the FTIR spectra of PC/PPFBS/PDMS compared to that of PC and PC/PPFBS, whose characteristic bands of Si—O or Si—O—C. PC/PPFBS/PDMS showed the characteristic band at 750 cm<sup>-1</sup> and 1110 cm<sup>-1</sup>, thus could effectively restrain the diffusion of fire by forming char layer as the barrier of the flame.

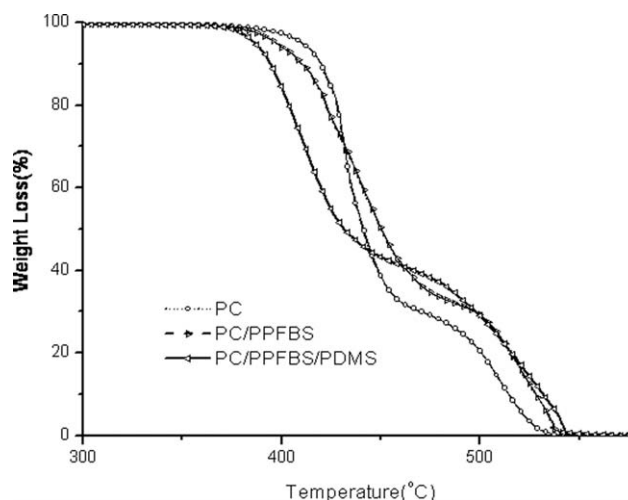


Figure 5 TGA curves under O<sub>2</sub> at the heating rate of 10°C/min.

TABLE IV  
TGA Data Under O<sub>2</sub> at the Heating Rate of 10°C/min

Samples	IDT (°C)	T <sub>50%</sub> (°C)	T <sub>60%</sub> (°C)	T <sub>70%</sub> (°C)	T <sub>80%</sub> (°C)	T <sub>max1</sub> (°C)	T <sub>max2</sub> (°C)	Residue at 600°C (wt %)
PC	410	450	448	470	500	417	532	0
PC/PPFBS	397	441	467	497	515	434	527	0
PC/PPFBS/PDMS	386	431	463	498	516	431	511	0.06

FTIR analysis of the residue after UL-94 test

The FTIR spectra of the burned PC and PC/PPFBS/(PDMS) after UL-94 test are shown in Figure 7. The burned PC/PPFBS/PDMS had a wide peak absorption of alcoholic groups (3440 cm<sup>-1</sup>), a small wide peak of Si—O bond (1074 cm<sup>-1</sup>) and two peaks of condensed aromatic bonds (1618 and 760 cm<sup>-1</sup>).<sup>13</sup> The band at 1760 cm<sup>-1</sup> might represent the hydrogen bonding between the carbonate moiety and alcohol.<sup>17</sup>

Comparing the spectra of PC/PPFBS(PDMS) with the spectrum of PC/PPFBS/PDMS in Figure 7, some

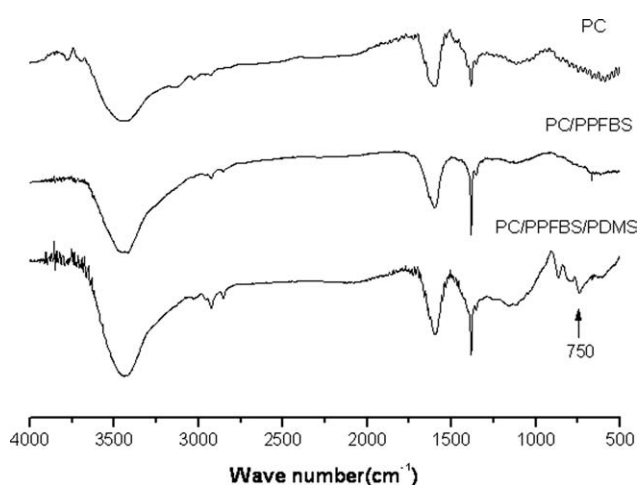


Figure 6 FTIR spectra of the residue after TGA test under N<sub>2</sub>.

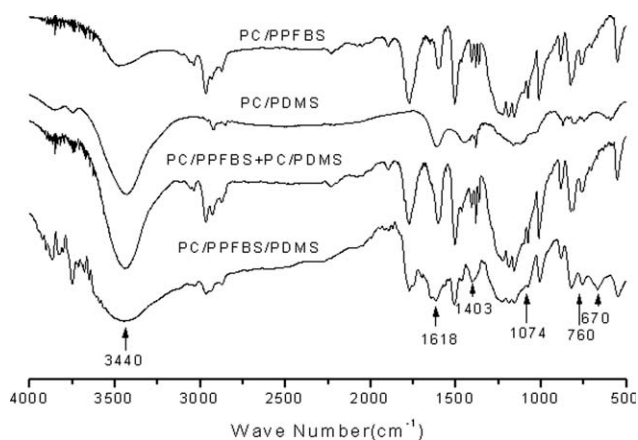


Figure 7 FTIR spectra of the residue after UL-94 test.

differences could be found. Two new peaks at 1403 and 670 cm<sup>-1</sup> appeared, while they were not found in the superposition FTIR spectrum of PC/PPFBS or PC/PDMS. Such difference should be related to the synergistic effects of the two flame retardants in this study.

#### Schematic diagram of flame retardancy mechanism of PC/PPFBS/PDMS

Based on the earlier results and discussion, the flame retardant mechanism of PC/PPFBS/PDMS is shown in Figure 8. FRPC with PPFBS and PDMS would degrade greatly when flame arises (about 380°C), releasing a large amount of inert gas and producing aromatic fragment, which could form condensed residue with Si concentrates. The char residue could loose with alveolate pores, through which inert gas could escape if there is no PDMS in PC. It would make the char residue pile up loosely. The intumescent char residue of FRPC was compact and hard without any apertures with both PPFBS and PDMS, which became the first barrier for the FRPC to stop the CO<sub>2</sub> and H<sub>2</sub>O escaping when flaming. Those inert gas expanded and formed inner cavum, which also became the second barrier for FRPC to stop the heat transmitting into the material matrix. But the

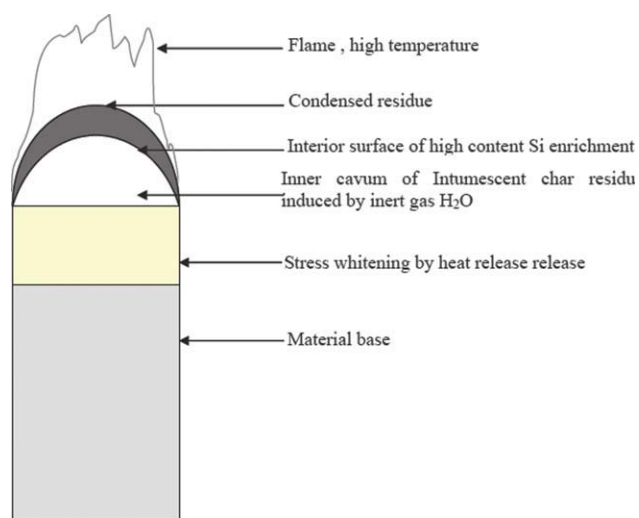


Figure 8 Schematic diagram of flame retardant mechanism of PC/PPFBS/PDMS. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

temperature near the material matrix was so high that stress whitening happened. It became the third barrier of the FRPC help the heat dissipation, and stopped further melting fluid so that the dropping was prevented.

### CONCLUSIONS

FRPC was prepared by melt-compounding of PC with potassium perfluorbutane sulfonate and polydimethylsiloxane. The FRPC PC/PPFBS/PDMS(100/0.1/0.1) could meet V-0 rate at 1.6 mm thickness, without significantly affecting the mechanical properties of PC. The flame retardant technology of PC by the organic metal salt as PPFBS is thought to be the flame-retardant system that control the decomposition and activation of the salt and could be effective for extinguishing the small initial flame.<sup>7</sup> But the yield of char for PC/PPFBS is insignificant relative to PC itself.<sup>8</sup> As shown in this study, the addition of PDMS to the PC/PPFBS system change the flame retardant technology of PC/PPFBS to some extent. The distribution of Si on the char layers was tested. A compact char layer formed on the surface of sample during the rapid decomposition of the FRPC could account for the excellent flame retardancy. The enrichment of Si in the interior interface of the char layer also explained the improved flame retardancy. Condensed aromatic

bond with a small amount of Si—O bond were found in the residue after TGA test under N<sub>2</sub> and after UL-94 test by FTIR, which was related to the synergistic effect of PPFBS/PDMS.

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