

An Easy-To-Obtain Silicone-Containing Flame Retardant and its Effects on the Combustion of Polycarbonate

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ABSTRACT: A novel silicone-containing flame retardant (HSOBA) synthesized from hydrogen-containing silicone oil and Bisphenol A via a simple approach has been incorporated into polycarbonate (PC) matrix to study its effects on the flame retardancy. The flame retardancy of PC/HSOBA composites is investigated by limiting oxygen index (LOI), vertical burning tests (UL-94), and cone calorimeter measurement. The LOI value of the composites is 31.7 and the UL-94 rating reaches V-0, when the content of HSOBA is 3 wt %. Cone calorimeter data confirm that the HSOBA acts as an effective additive

functioning both as flame retardants and as smoke suppressant. Evolution of the thermal behaviors of the composites tested by TGA, the morphological structures, and the constituent of char residue after LOI tests characterized by scanning electronic microscopy-energy-dispersive X-ray analysis were used to explain the possible flame-retardant mode. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: polycarbonate; flame retardancy; silicone-containing flame retardant

INTRODUCTION

Bisphenol A polycarbonate (PC), commonly used as a high-performance amorphous engineering thermoplastic, has a high degree of thermal stability, a V-2 rating in the UL-94 tests and the limiting oxygen index (LOI) of typical pure PC is about 25%. Despite this, more stringent flame retardant performance is often required for electronic and electrical applications.^{1,2}

Most halogen-containing flame retardants with high flame-resistant efficiency in the case of PC have been forbidden gradually^{3,4} owing to the environmental concerns. Phosphorus-containing compounds (such as triphenyl phosphate [TPP], resorcinol *bis*(diphenyl phosphate) [RDP], and Bisphenol A *bis*(diphenyl phosphate) [BDP]) have been developed as the flame retardants for PC and its blends.^{5,6} However, the heat distortion temperature of PC composites will decrease sharply with TPP, RDP, or BDP loading; furthermore, the viscous liquid phosphates may lead to some problems in processing.

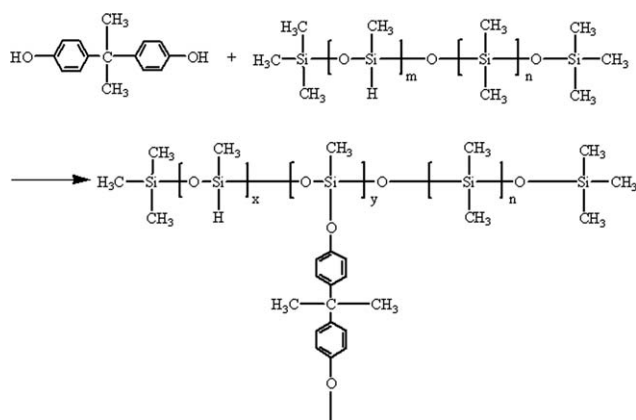
Recently, silicon-containing compounds used as polymer additives have received more and more

attentions owing to their environmental friendliness and processing facility.^{7,8} Iji and Serizawa previously studied some silicone derivatives as flame retardants for PC and its derivatives⁹ in which 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 was found to be effective in retarding the combustion of PC. After that, more and more silicone flame retardants have been synthesized and even commercially produced.^{10–15} However, the preparation of these silicone compounds usually requires complicated synthesis steps in which huge amount of solvent and acid–base solution is needed. Owing to the multiple steps involved in these procedures and additional costs associated with the use and the removal of solvents and/or reducing reagents, the flame retardants containing silicon are generally very high in cost relative to other flame retardants, which becomes a main reason for the lower utilization rate of silicon-containing compounds as flame retardants in plastic. Thus, a more rational synthesized processing or a novel flame retardant containing silicone with lower production cost should be developed.

Here, we report a rational yet simple synthetic approach for synthesizing a novel silicone-containing flame retardant (HSOBA), where a condensation directly takes place between the hydrogen-containing silicon oil and Bisphenol A without any reagents acting as solvents. Experimental results demonstrate

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Scheme 1 The synthetic route and the structure of HSOBA.

that the HSOBA effectively improves the flame retardancy of PC at relatively lower loading.

EXPERIMENTAL

Materials

PC (2805, melt flow rate, 10.0 g/10 min) purchased from Bayer Chemicals (Germany) was dried in the oven at 120°C for 12 h prior to blending. Hydrogen-containing silicone oil was purchased from Huafeng Organic Silicon (Jilin, China). The content of hydrogen in silicone oil was 0.18 wt %. Bisphenol A was purchased from Guangfu Chemicals Fine Product Research Institution (Tianjin, China). Stannous Octoate was purchased from National Medicines (China). Diethyl ether was purchased from Fuyu Chemicals Fine Product (Tianjin, China). Bisphenol A, Stannous Octoate, and Diethyl Ether were of analytical purity grade and hydrogen-containing silicone oil was of industrial grade.

HSOBA synthesis

The synthetic route for HSOBA is shown in Scheme 1. The mixtures of hydrogen-containing silicone oil and Bisphenol A at a certain molar ratio (Si–H in silicone oil : hydroxyl in Bisphenol A = 1 : 1) were added to a 250 mL, three-necked round-bottom flask fitted with a mechanical stirrer and a reflux condenser. The condensation reaction between them was catalyzed by Stannous Octoate (Stannous Octoate : silicone oil = 51/10,000 by weight). The temperature was held at 85°C for 6 h. It was worth mentioning that no solution was used in this reaction, which will effectively simplify the prepared processing and purification steps. The resulting product was obtained as a white powder after washing with diethyl ether to remove the raw material¹⁶ (yield, 92%).

Sample preparation

The PC was dried in the oven at 120°C for 12 h before being processed to remove moisture, after which the HSOBA was mixed into the PC matrix using a RM-200A Haake Record made in Habo Electrical Appliance manufacturing company at a temperature of 230°C and a rotor speed of 50 rpm for 10 min. The mixtures were compression molded into the sheets with 3 mm thickness and cut into standard testing bars to test the LOI value and UL-94 rating. The mixtures were compression molded into sheets of 100 mm × 100 mm × 3 mm for cone calorimeter tests.

Infrared and nuclear magnetic resonance measurement

The infrared spectrum of HSOBA was monitored by an Avatar 360 Fourier transform infrared (FTIR) spectroscopy. The transmittance was recorded in the wave number range of 500–4000 cm⁻¹. All samples were thoroughly mixed with KBr and pressed into flakes. Solid ²⁹Si and ¹³C nuclear magnetic resonance (NMR) spectra were obtained with a BRUKER AVANCE III 500 spectrometer at room temperature. Samples were inserted into a cylindrical rotor made of zirconia. Line narrowing was achieved by high-power ¹H decoupling and magic-angle spinning (MAS). The spinning rate was set at ca. 5 kHz. The observed frequencies of ²⁹Si and ¹³C nuclei were 99.36 and 125.77 MHz, respectively. For the measurements with spin-lock cross-polarization sequence (CP/MAS), the following conditions were used: contact time, 2 ms; repetition time, 5 s; spectral width, 37 kHz; data point, 8192. Spectra were accumulated for 2048 times to achieve a reasonable signal-to-noise ratio.

LOI and UL-94 tests

The flame retardancy of all samples was characterized by LOI and UL-94 tests. LOI denotes the lowest volume concentration of oxygen sustaining candle burning of materials in a mixture of nitrogen and oxygen. LOI data of all samples were obtained at room temperature on an oxygen index instrument (JF-3) produced by Jiangning Analysis Instrument Factory, China, according to GB/T2406.1-2008 standard. The dimensions of all samples were 130 mm × 6.5 mm × 3 mm. Vertical burning ratings of all samples were measured on a CZF-2 instrument produced by Jiangning Analysis Instrument Factory, China, with the dimensions of 130 mm × 13 mm × 3 mm, where the test results were classified by burning ratings V-0, V-1, or V-2.

Cone calorimeter tests

The flammability of the sample was measured with a cone calorimeter device of FTT Company, British, according to ISO-5660-1 standard. The samples with

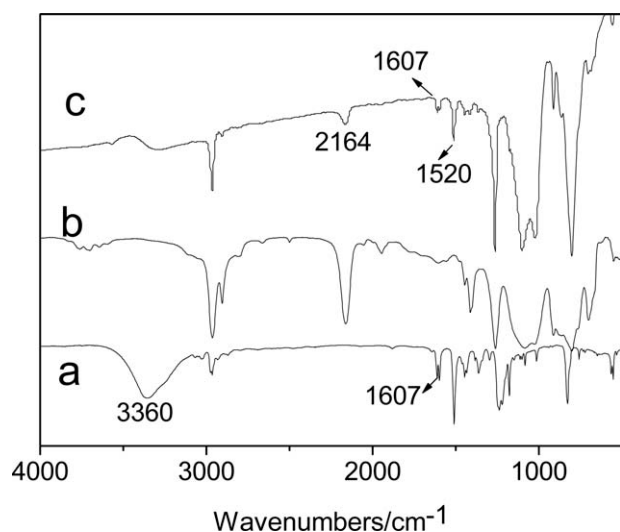


Figure 1 FTIR spectra of Bisphenol A (a), hydrogen-containing silicone oil (b) and HSOBA(c).

a size of 100 mm × 100 mm × 3 mm were exposed to a radiant cone at 50 kW/m².

Mechanical property tests

Determination of tensile strength and flexural strength of all samples was performed by Regeer computer-controlled mechanical instrument according to ASTM standards.

Thermogravimetry analysis tests

All Thermogravimetry analysis (TGA) tests were carried out by a Thermal Analyser (PerkinElmer Pyris 1) at a linear heating rate of 10°C min⁻¹ under air atmosphere within the temperature ranging from 50 to 800°C. The weight of the samples was kept within 2–4 mg. All data can be obtained from TG and DTG curves.

Scanning electronic microscopy observation and energy-dispersive X-ray analysis

Scanning electronic microscopy (SEM) (FEI Quanta 200, USA) was used to investigate the surface of char residues of the flame-retardant PC after the LOI tests. SEM graphs of the char residues were recorded after gold-coating surface treatment and an accelerating voltage of 15 kV. SEM was equipped with an X-ray detector for energy-dispersive X-ray analysis (EDX). Si atom content on the surface after LOI tests was analyzed by EDX.

RESULTS AND DISCUSSION

Characterization of the structure of HSOBA

Figure 1 shows the FTIR spectra of Bisphenol A (a), hydrogen-containing silicone oil (b), and the HSOBA

(c). Curve (a) shows a stronger peak at about 3360 cm⁻¹ corresponding to the —O—H stretching, and (b) shows a stronger peak at about 2164 cm⁻¹ corresponding to the —Si—H stretching. But in the product (c) the two stronger peaks disappear and weaken, respectively, which clearly demonstrates the occurrence of the condensation reaction between —O—H on the Bisphenol A and —Si—H on the hydrogen-containing silicone oil. In addition to those peaks, FTIR spectrum of (c) shows peaks at about 1607 and 1520 cm⁻¹ corresponding to the phenyl vibrations which also appear in (a). The peaks at about 1093 and 1024 cm⁻¹ are characteristic vibrations of Si—O—Si and the peak at 2966 cm⁻¹ corresponds to characteristic vibrations of =CH₃.

¹³C- and ²⁹Si-NMR spectra of HSOBA were applied as another evidence to confirm the occurrence of the condensation reaction between the Bisphenol A and the hydrogen-containing silicone oil. As shown in Figure 2(b), the peak at -2.54 ppm belongs to methyl groups in the —Si(CH₃)₃; the absorption of methyl groups in —Si(CH₃)₂— units occurs at 0.87 ppm; the peaks near 31 and 41 ppm are the absorption of methyl groups and C atom of =C(CH₃)₂— units in the Bisphenol A; the small multiple peaks at 118.99–127.92 ppm are attributed to the absorption of C atoms of phenyl group. Figure 2(a) shows the solid-state ²⁹Si-NMR spectrum of the HSOBA. The big peak at -20.00 ppm belongs to Si atoms in the —Si(CH₃)₂—. The small peaks at -36.72 and -37.23 ppm are owing to residual —Si—H groups. The peaks near -64.95 ppm belong to Si atoms of three groups —SiO_{1.5}, which provides a direct evidence for the occurrence of condensation

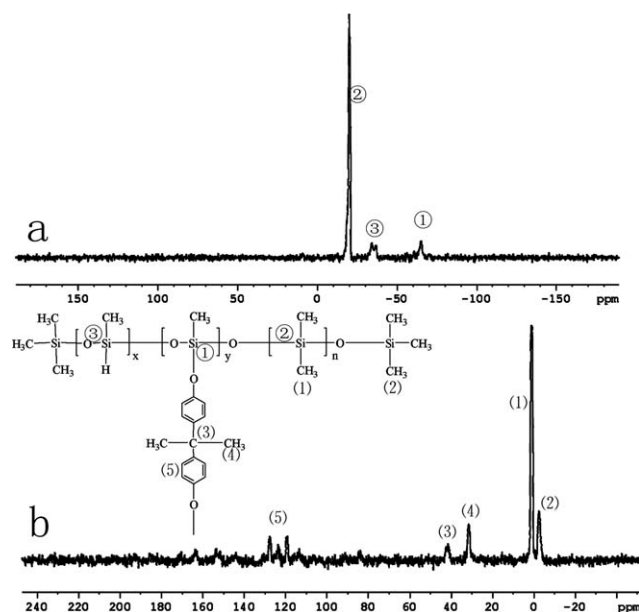


Figure 2 ²⁹Si-NMR (a) and ¹³C-NMR (b) spectra of HSOBA.



Figure 3 Char layer of the samples after LOI tests (a) pure PC, (b) PC/5 wt % HSOBA.

reaction between hydrogen-containing silicone oil and Bisphenol A. Thus, based on above ^{13}C , ^{29}Si -NMR and FTIR results, it is demonstrated that the Bisphenol A molecules have been reacted with the hydrogen-containing silicone oil via condensation reaction and it is reasonable to propose that the obtained HSOBA has a crosslinking structure. It is clear that the HSOBA structure prepared in this study is similar with that of branched silicones which have been demonstrated effectively in promoting the flame retardancy and thermal stability of PC much better than the "line" type silicones.^{5,15}

LOI value and UL-94 rating

To investigate the flame-retardant effectiveness of HSOBA, the LOI value and UL-94 rating of PC mixed with different HSOBA loadings are examined (Table I). In the UL-94 tests, the burning time after first ignition (t_1), the burning time after second ignition (t_2), and total combustion time (t_{1+2}) were recorded as the average burning time of the five samples.⁶ The results summarized in Table I show that the LOI value of pure PC is 26.5% and the UL-94 rating passes V-2. However, the LOI value was significantly increased by the incorporation of HSOBA in PC until the content of HSOBA reached 3 wt %. As summarized in

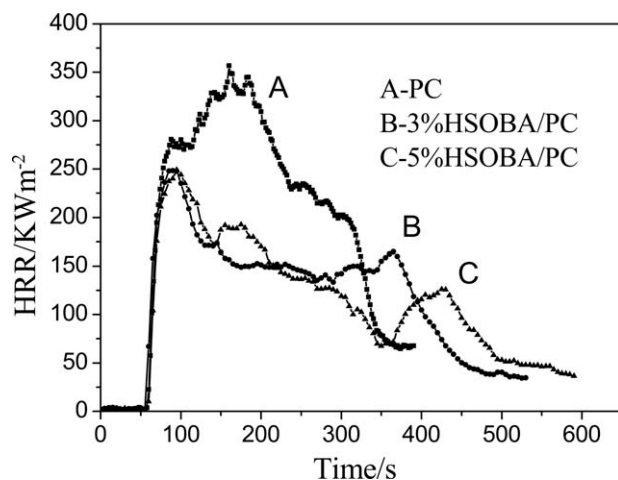


Figure 4 HRR of PC and PC/HSOBA composites at 50 kW/m².

Table I, the LOI value was increased from 26.5 to 31.7% and the UL-94 rating was enhanced from V-2 to V-0. The LOI value of PC was enhanced slightly when we further increase the content of HSOBA. A V-0 rating was achieved by the addition of the HSOBA at respective 3–7 wt % loading and the total combustion time (t_{1+2}) became shorter gradually with the increase of HSOBA contents. It is important to point out that comparing with the total combustion time of pure PC ($t_{1+2} = 47.6$ s), the total combustion time of the PC at loading as low as 1 wt % has dropped to 6.9 s. In a word, the results obtained from LOI and UL-94 rating measurements indicate that the HSOBA is very effective in flame retarding PC, especially in promoting the UL-94 rating of PC.

The video images of the samples after LOI tests are shown in Figure 3. Comparing the char morphologies for the pure PC (a) with PC/3 wt % HSOBA composites (b), it is clear that a big difference is induced by the presence of HSOBA. In case of PC/HSOBA composites, larger volume of char residues with a continuous and inflated layer is formed by the presence of HSOBA, which provides a direct evidence for verifying the flame retardancy of PC/HSOBA composites, because it can effectively inhibit mass transfer and energy transfer between polymer and flame. This is in contrast with pure PC which produces lower amounts of char residues with a discontinuous layer after LOI tests.

TABLE I
Flame Retardancy of PC/HSOBA System with Different Contents

Samples	LOI (%)	UL-94 (3 mm)	t_1 (s)	t_2 (s)	t_{1+2} (s)	Dripping
Pure PC	26.5	V-2	30.6	17.0	47.6	Yes
PC/1% HSOBA	29.1	V-2	2.2	4.7	6.9	Yes
PC/3% HSOBA	31.7	V-0	2.1	4.3	6.4	No
PC/5% HSOBA	31.9	V-0	1.7	3.2	4.9	No
PC/7% HSOBA	32.1	V-0	1.9	2.5	4.4	No

TABLE II
Cone Calorimetric Data Obtained with a Heat Flux of 50 kW/m²

Sample	Pure PC	3% HSOBA/PC	5% HSOBA/PC
TTI(s)	58	57	58
PHRR (kW/m ²)	357	249	248
THR (MJ/m ²)	74.54	66.24	61.63
TSR(MJ/m ²)	2681.94	2510.32	2484.32

Cone calorimeter studies

Cone calorimetry is an effective approach for fire safety engineers and researchers who are interested in quantitative material flammability analysis to investigate materials flammability by different parameters, such as the heat release rate (HRR), the peak heat release rate (PHRR), the total heat release (THR), and the total smoking release (TSR). Table II and Figure 4 report the results for PC, PC/3% HSOBA and PC/5% HSOBA in the cone calorimeter test. The HRR is a very important parameter to quantitatively express the intensity of fire. An efficient flame-retardant system normally gives a lower HRR value. As shown in Figure 4 and Table II, it can be clearly seen that both composites exhibit much lower PHRR (249 and 248 kW/m², respectively) compared with that of pure PC (357 kW/m²), whereas three samples show almost the same TTI at about 58 s. It is worth mentioning that in the cases of the samples containing HSOBA, there are two PHRR in the HRR plots which means that the combustion behavior of PC has been changed besides the PHRR values. This behavior is similar to some thermally thick charring materials, such as intumescent flame-retardant systems and wood,¹⁷⁻²¹ which tend to show the first HRR peak at the beginning prior to charring, and the second HRR peak in the middle of the measurements induced by cracking

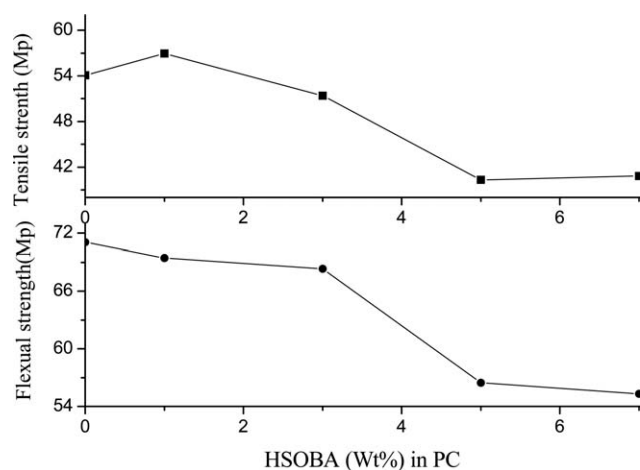


Figure 5 Effect of HSOBA on tensile strength and flexural strength of PC/HSOBA composites.

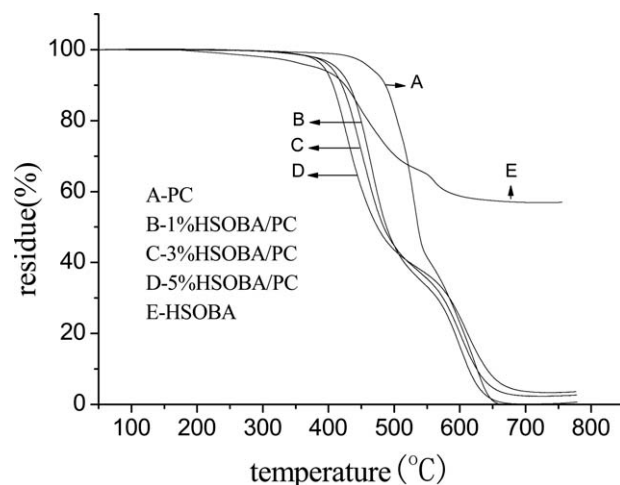


Figure 6 TG curves of PC/HSOBA composites under air atmosphere.

char or increasing the effective pyrolysis, as observed in the thick charring materials. At the same time, a comparison of the THR and the TSR data between PC and HSOBA/PC composites is summarized in Table II, showing that the values of THR and TSR for HSOBA/PC composites are much lower than pure PC at the same combustion time in cone. Thus, based on the above results, it is confirmed that the presence of HSOBA in PC matrix can effectively enhance the flame retardancy of PC and suppress the smoke production.

Mechanical properties

The mechanical properties of the PC/HSOBA composites are shown in Figure 5 for a range of HSOBA mass fractions. Compared with pure PC, addition of HSOBA clearly affects the mechanical properties of PC matrix by the decrease in the tensile and flexural

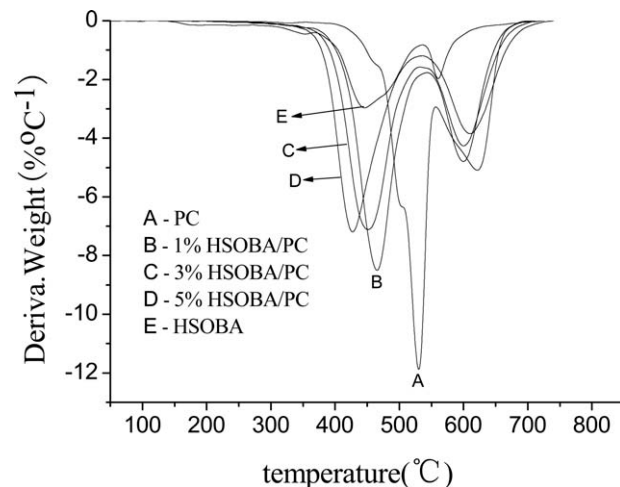


Figure 7 DTG curves of PC/HSOBA composites under air atmosphere.

TABLE III
The Thermal Stability Parameter of the Samples in Air Atmosphere

Sample	Components (%)		TG		
	PC	HSOBA	$T_{\text{onset}}/^{\circ}\text{C}$	$T_{\text{max}}/^{\circ}\text{C}$	Residue/%(800 $^{\circ}\text{C}$)
0	100	0	463	530	0
1	99	1	412	464	0.7
2	97	3	404	452	2.6
3	95	5	393	428	3.6
4	0	100	381	450	56.9

strength. However, the effects of HSOBA mass fractions on the tensile and flexural strength are obviously different. As shown in Figure 5, with low loading of HSOBA (i.e., 1 and 3%), the tensile and flexural strength properties decrease slowly, whereas a significant decrease in the tensile and flexural strength is observed for the PC/HSOBA (5%) and PC/HSOBA (7%) composites. Thus, we suggest that the mass fraction of HSOBA should not surpass 5% in PC matrix.

Thermogravimetric analysis

TGA data under air flow are determined and analyzed to study the thermal stability and decomposition behavior of HSOBA, PC, and PC/HSOBA composites. TGA and DTG curves are shown in Figures 6 and 7. The detailed data for all composites are summarized in Table III, including the T_{onset} defined as the temperature at which 5% weight loss occurs, the T_{max} , defined as the temperature at maximum weight loss rate and the char residues at 800 $^{\circ}\text{C}$. The curves of the PC and the PC/HSOBA composites show a two-step degradation process. The first stage of mass loss of the pure PC occurs at temperature from 440C to 550 $^{\circ}\text{C}$, following a slower second degradation stage at about 550–650 $^{\circ}\text{C}$. The temperature of degradation onset of PC/HSOBA is lower than that of pure PC, and decreases gradually with the increase of HSOBA loading, possibly owing to that the T_{onset} of HSOBA (381 $^{\circ}\text{C}$) is lower than that of pure PC (463 $^{\circ}\text{C}$). It is speculated that the lower T_{onset} of the silicone may be beneficial to form an insulating carbon layer on the surface which inhibits mass transfer and heat transfer between the flame zone and the burning substrate.⁶ The pure PC

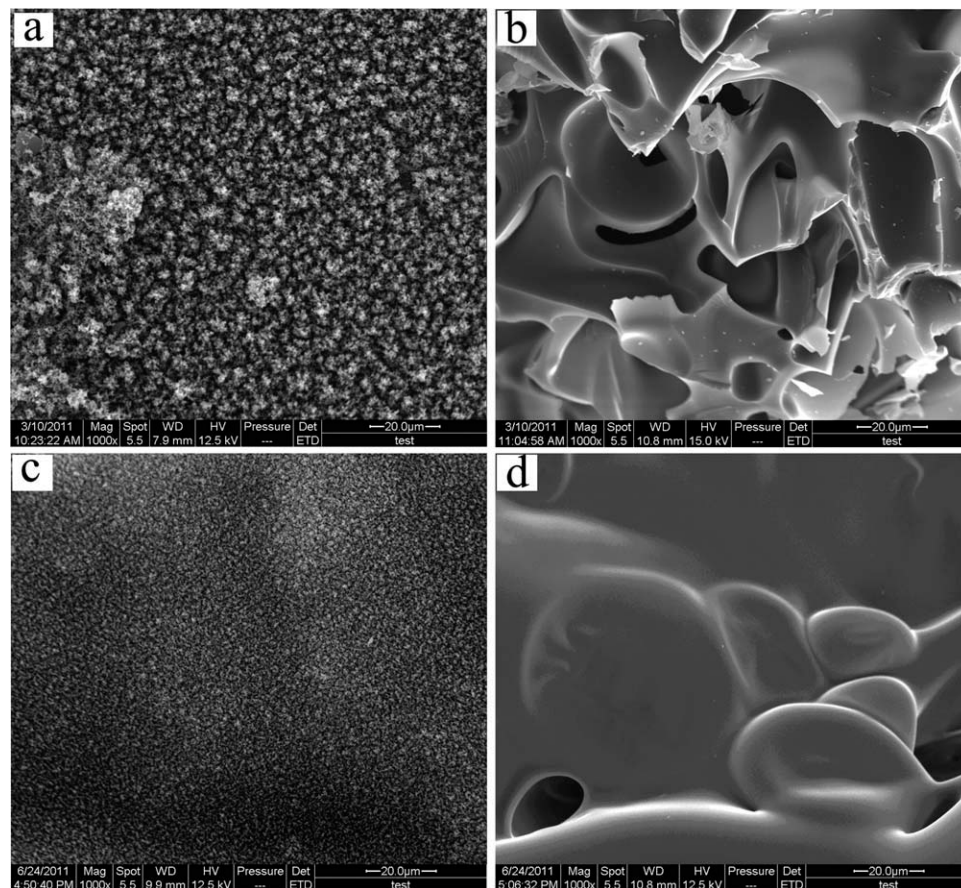


Figure 8 SEM micrographs of outer and inner surface char residue of pure PC (a, b), PC/5 wt % HSOBA (c, d) after LOI tests.

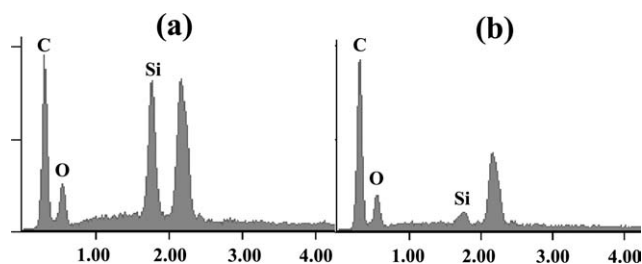


Figure 9 EDX of outside surface (a) and inside surface (b) after LOI tests.

maximum weight loss rate is close to $12\%^{\circ}\text{C}^{-1}$; however, the maximum mass loss rates for the PC/HSOBA composites are all lower than that of pure PC, as confirmed from DTG plot in Figure 7. It is clear that HSOBA may slow the speed of PC degradation and accelerate the formation of carbon layer. The residue of HSOBA at 800°C in air atmosphere is 56.9% and there is no char residue for PC at this temperature, whereas the amount of char residue from PC/HSOBA composites is obviously higher than that of pure HSOBA under the same level of HSOBA condition, as observed from the TG data in Table III. This shows that addition of HSOBA in PC slows the speed of PC degradation and accelerates the formation of carbon layer, whereas induces the reduction of the initiated decomposition temperature of PC.

EDX and SEM observation

The SEM micrographs in Figure 8 show the microstructures of the outer (a) and inner (b) char of pure PC after the LOI tests. The char residue of the pure PC presents a porous char layer with many micro-size pores. This means that the rapid volatilization has happened in the PC matrix because of the heat. The same observation of morphological structures of the outer (c) and inner (d) char of PC/5% HSOBA after the LOI tests is shown in Figure 8. Obviously, the char layer of PC/5% HSOBA with a swollen inner structure as well as a close and compact outer surface can provide an effective barrier to resist the transfer of heat and oxygen during combustion.

It is believed that the mechanism of silicon-containing flame retardant is correlated to the low-surface energy of silicon, which moves to the surface and acts as protective layers. In the present study, it is further confirmed from the EDX results of char from the PC/5% HSOBA after LOI tests. Results in Figure 9 show that the silicon content of inside surface of char is 2.06% after LOI tests; however, the silicon content of the outside surface of the char increases to 15.64%, which is in agreement with the phenomenon in some previous reports.^{6,15} Thus, a similar proposal is given: during the burning process, the silicone moves to the

PC surface, and silicon accumulates on the surface of the polymer to form a barrier which reduces the speed of PC degradation and takes part in the formation of carbon layer.

CONCLUSIONS

A novel silicone-containing flame retardant for PC has been successfully synthesized in this study. The findings are as follows:

1. The HSOBA with a reticular structure was directly synthesized by the condensation reaction between hydrogen-containing silicone oil and Bisphenol A and its structure had been characterized by the FTIR spectra and the solid ^{13}C -NMR and ^{29}Si -NMR spectra.
2. The superior flame retardancy of PC was obtained by the addition of the HSOBA, where the LOI value of PC/HSOBA composites reached to 31.7 and passed a UL-94 V-0 rating when the HSOBA loading was above 3 wt %. Cone results further confirmed that HSOBA acted as an effective additive functioning both as flame retardant and as smoke suppressant. At the same time, the mechanical properties of the PC/HSOBA composites indicated that the mass fraction of HSOBA should not surpass 5% in PC matrix.
3. TG and DTG results show that addition of HSOBA in PC can reduce the degradation speed of PC and accelerate the formation of carbon layer, whereas induces a slight reduction of the initiated decomposition temperature of PC. The SEM-EDX results for the char residue after LOI tests confirm that the HSOBA in PC can move to the PC surface during burning process and accumulate on the surface of the polymer, initiating a compact and homogeneous char on the surface, which turns out to be most important for the flame retardant performance.

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