

SYNTHESIS OF A SILICON-CONTAINING FLAME RETARDANT AND ITS SYNERGISTIC EFFECT WITH POTASSIUM-4-(PHENYLSULFONYL)BENZENESULFONATE (KSS) IN POLYCARBONATE (PC)

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Abstract A novel flame retardant (DAPSiO), containing silicon and nitrogen, was synthesized by using dichlorodiphenylsilane, γ -chloropropyl methyl dimethoxysilane and 1,2-ethanediamine. DAPSiO was used together with potassium-4-(phenylsulfonyl)benzenesulfonate (KSS) to prepare a flame-retardant system for polycarbonate (PC). The structure of DAPSiO was characterized by Fourier transform infrared spectroscopy (FTIR), and ^1H -NMR tests. Flammability and thermal behaviors of PC/KSS/DAPSiO systems were estimated by limited oxygen index (LOI), vertical burning test (UL-94) and thermogravimetric analysis (TGA) tests. The results showed that the flame retardancy and thermal stability of PC/KSS system were improved with the addition of DAPSiO. When 1 wt% DAPSiO and 0.5 wt% KSS were incorporated, the LOI value of PC was found to be 44, and class V-0 of UL-94 test was passed. The scanning electron microscopy (SEM) and FTIR indicated that PC/KSS/DAPSiO system held a more cohesive and denser char structure when compared with pure PC and PC/KSS system.

Keywords: Flame retardant; Thermal properties; Silicon; Polycarbonate.

INTRODUCTION

Polycarbonate (PC) has a wide range of applications for its excellent performances, such as outstanding electrical properties, excellent mechanical properties and high glass transition temperature^[1,2]. However, pure PC shows unsatisfactory flame retardancy during combustion, only UL94-V2 rating is achieved, which restricts its applications in some important fields, particularly in electric or electronic industries^[2–4].

Traditionally, halogenated flame retardants were widely incorporated into PC to improve its flame retardant performance. However, it releases toxic gases and corrosive smoke during combustion^[5,6]. 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.

Recently, silicon-containing compounds used as flame retardant have received more and more attention owing to the environmentally-friendly consideration^[7–10]. 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^[11–13]. Periadurai *et al.*^[14] reported thermal decomposition and flame retardant behaviors of SiO_2 -phenolic nanocomposites. He *et al.*^[15,16] investigated the synergistic effects of polyhedraloligomeric silsesquioxane (POSS) and oligomeric bisphenyl A bis(diphenyl phosphate) (BDP) on thermal and flame retardancy of PC.

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In this paper, a silicon-containing compound (DAPSiO) was synthesized and used together with KSS to prepare a flame-retardant system for PC. The synergistic effect between these two components on flame retardant and thermal properties of PC has been studied.

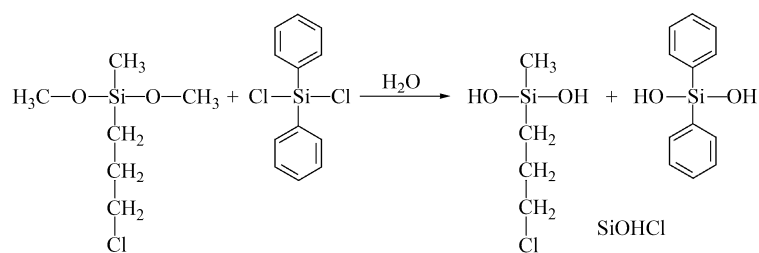
EXPERIMENTAL

Materials

PC (S23001R) was purchased from Mitsubishi Engineering Plastics Corporation (Japan). KSS was supplied by Sloss Industries Corporation (USA). AP. Antioxidizer (1010) was provided by Tianjing Chemical Factory (Tianjing, China). AP. Sodium silicate and 1,2-ethanediamine were both obtained from Chengdu Kelon Chemical Factory (Chengdu, China). AP. Dichlorodiphenylsilane and γ -chloropropyl methyl dimethoxysilane were acquired from Shanghai KangTa Chemical Co., Ltd (Shanghai, China) and Jingzhou jiangnan Fine Chemical Co., Ltd (Jingzhou, China), respectively, AP.

Synthesis of SiOHCl

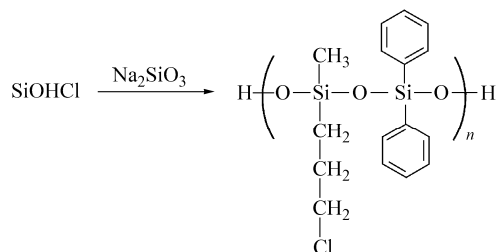
Dichlorodiphenylsilane (12.6 g, 0.05 mol) and toluene (20 mL) were added into a three-neck and round-bottom 250 mL glass flask equipped with a nitrogen inlet, a reflux condenser and a mechanical stirrer. And the mixture was stirred for 10 min. Then distilled water (25 g) was added into the flask. After that, γ -chloropropyl methyl dimethoxysilane (9.1 g, 0.05 mol) was added slowly by drops to the flask within about 30 min and the temperature was kept at 50 °C for 2 h. After being cooled to room temperature, the solution was washed by water until pH = 7. The hydrolysis product (SiOHCl) was obtained. The synthesis route is illustrated in Scheme 1.



Scheme 1 The synthesis route of SiOHCl

Synthesis of PSiOCl

The polymerization was performed in the flask to synthesize PSiOCl. The solution of SiOHCl from the first step and sodium silicate (catalyzer) were added into the flask. Then the flask was heated up to 85 °C and kept refluxed until there was no increase of viscosity for the reaction system. The raw product was washed by water to remove the residual monomer and sodium silicate, then the mixture was washed by ethanol to eliminate toluene and the remaining water. The synthesis route is illustrated in Scheme 2.

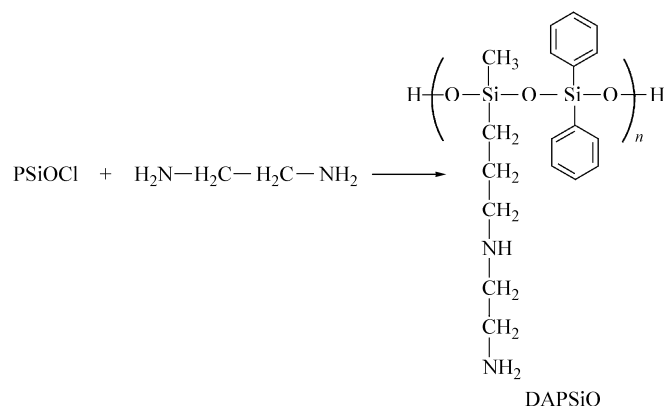


Scheme 2 The synthesis route of PSiOCl

Synthesis of DAPSiO

The synthesized PSiOCl and excess 1,2-ethanediamine were added into the flask with a mechanical stirrer. The reaction was driven to completion by stirring the solution at 40 °C for 3 h. Then the product was washed by

ethanol to eliminate hydrogen chloride and the remaining 1,2-ethanediamine and dried in a vacuum at 80 °C to constant weight. (Product yield: 68%). The synthesis route is illustrated in Scheme 3.



Scheme 3 The synthesis route of DAPSiO

Samples Preparation

PC, dried at 120 °C for 6 h, antioxidant (1010), KSS and DAPSiO were premixed based on a calculated amount of ratio. Then all samples were extruded by a twin-screw extruder (TSSJ-25, Bluestar Chemical Research Institute, Chengdu, China). After the extrudate was pelletized and the blend was dried at 120 °C for 6 h, all test specimens were prepared by an injection-molding machine (PS40E5ASE, Nissei Plastic Industrial Co., Ltd., Japan).

Fourier Transform Infrared (FTIR) Spectrophotometry and ¹H-NMR Test

IR spectroscopy was applied with a Nicolet IS10 FTIR spectrometer using KBr pellets. ¹H-NMR (600 Hz) spectra were recorded on an FT-80A NMR by using CF₃COOD as solvent.

Flame Retardancy Test

The flammability of the flame-retarded PC 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 (China), according to ASTM D2863-77 standard. The dimensions of all samples were 130 mm × 6.5 mm × 3 mm. Vertical burning rates of all samples were measured on a CZF-2 instrument produced by Jiangning Analysis Instrument Factory (China), with sample dimensions of 125 mm × 12.5 mm × 3.2 mm, according to UL-94 test ASTM D635-77.

Thermogravimetry Analysis (TGA)

All thermogravimetry analysis (TGA) tests were performed on a Mettler Toledo TGA/DSC1 instrument thermal analyzer with a heating rate of 10 K/min in the temperature range of 30–800 °C and a pure nitrogen flow of 60 mL/min. The weight of the samples was kept within 8–10 mg.

Analysis of Char Residues by SEM

The surface morphology of the char obtained after LOI test was observed by a scanning electron microscope (INSPECT F). The samples were previously coated with gold to make the surface conductible.

RESULTS AND DISCUSSION

Characterization of DAPSiO

Figure 1 presents the FTIR spectra of SiOHCl, PSiOCl and DAPSiO. The absorption bands at 1667 and 3054 cm⁻¹ corresponded to vibrations of the benzene rings. The peak at 1125 cm⁻¹ was associated with the vibrations of Si—O. The absorptions at 1261 cm⁻¹ was assigned to Si—CH₃. The above peaks appeared in three curves. The main difference among the three curves was above 3100 cm⁻¹. The alcoholic peak appeared in curve

a, but not in curve b. It illustrated that the reactions of steps one and two were successfully carried out and the target product was obtained. Furthermore, the absorption bands at 3357 and 3278 cm^{-1} corresponding to the vibration of N—H appeared in curve c.

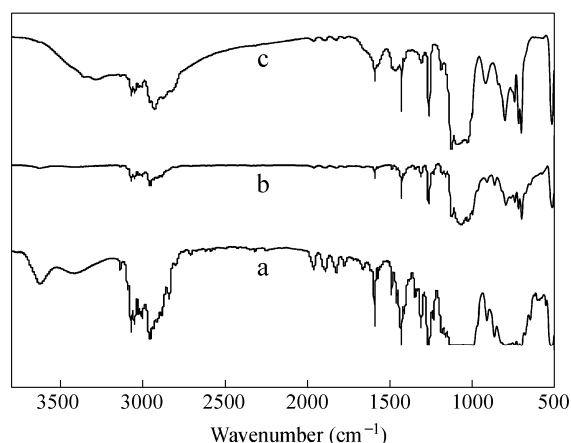


Fig. 1 The FTIR spectra of SiOHCl (a), PSiOCl (b) and DAPSiO (c)

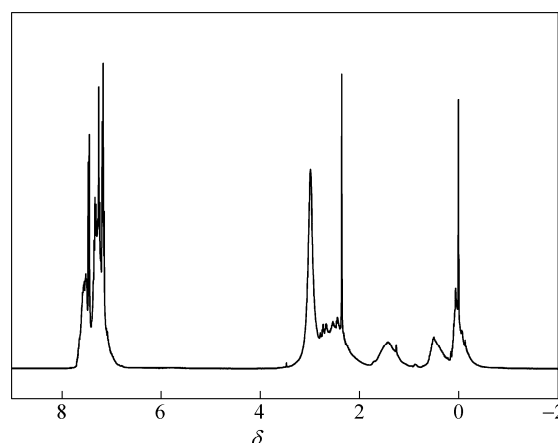


Fig. 2 The ^1H -NMR spectrum of DAPSiO

The ^1H -NMR spectrum of DAPSiO is shown in Fig. 2. The peaks between $\delta = 7$ and 8 were assigned to the proton of benzene ring. The peaks at $\delta = 2.53$ and 2.47 corresponded to $-\text{CH}_2-\text{N}$ protons. The peaks at $\delta = 1.41$ and 0.49 were assigned to the $-\text{C}-\text{CH}_2-\text{C}-$ and $-\text{CH}-\text{Si}$ protons, respectively. Moreover, the peak of $-\text{OCH}-$ disappeared. The information above confirmed that the target product was successfully synthesized.

Flammability

The synergistic effect of DAPSiO and KSS on the flame retardancy of PC was investigated. Table 1 shows the LOI values and vertical burning rates for PC. The addition of either KSS or DAPSiO showed a slight improvement of flame retardancy for PC, the highest LOI value (sample 2) was 38% and just got V-1 class in UL-94 test. This demonstrated that KSS and DAPSiO showed low efficiency in flame retardancy of PC alone. However, when the mixture of KSS and DAPSiO was incorporated into PC, the LOI values was dramatically increased. For example, when 2 wt% DAPSiO and 0.5 wt% KSS were added, the LOI value of PC was found to be 45%, and class V-0 of UL-94 test was passed. Moreover, the flame retardancy of PC through DAPSiO and KSS was not increasing linearly with their content, but favoring small amounts and there was a pronounced

Table 1. Compositions and the flame retardancy of the PC/KSS/DAPSiO systems

Samples	Components (wt%)			LOI (%)	UL-94 (s)
	PC	KSS	DAPSiO		
1	100	—	—	25	V-2 (40.12, dripping)
2	99.5	0.5	—	38	V-1 (26.33, dripping)
3	99.5	—	0.5	27	V-2 (36.21, dripping)
4	99	—	1	28	V-1 (27.67, dripping)
5	98	—	2	29	V-1 (25.10, dripping)
6	97	—	3	31	V-1 (26.55, dripping)
7	99	0.5	0.5	41	V-0 (26.14, no dripping)
8	98.5	0.5	1	44	V-0 (25.48, no dripping)
9	97.5	0.5	2	45	V-0 (24.23, no dripping)
10	96.5	0.5	3	43	V-0 (24.56, no dripping)

synergy of KSS and DAPSiO. Additionally, DAPSiO with excellent flowability can spread to outside from inside during combustion and accumulate on the surface to act as a thermal insulation layer, creating a less flammable material^[17]. Both reasons together resulted in very good LOI and UL-94 performance with very small amount of flame retardant.

Thermogravimetric Analysis (TGA)

Figure 3 shows the TG and DTG curves of DAPSiO. There was a slight degradation peak around 110 °C, which was possibly attributed to the water evolved in the reaction or absorbed in the medium. DAPSiO was thermally stable below 300 °C, then it underwent a rapid weight loss in the range of 310–510 °C. The max degradation temperature ($T_{\max}$) of DAPSiO was 420 °C, which was higher than those of conventional phosphorus-containing flame retardants (BDP, RDP, and TPP) and closed to the onset degradation temperature (T_{onset}) of PC, indicating that DAPSiO may better exert its flame-retardant action before the fast degradation of PC.

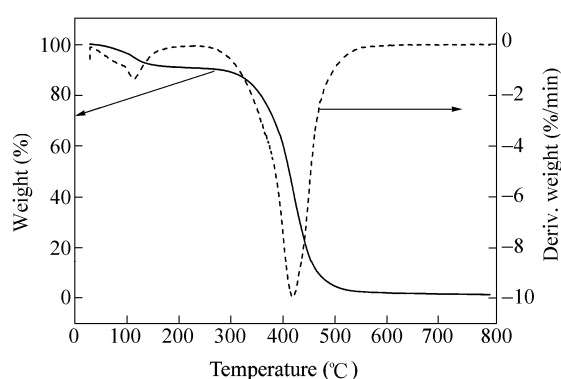


Fig. 3 TG and DTG curves of DAPSiO

The influence of DAPSiO on the thermal properties of PC system was investigated by TGA, as shown in Fig. 4. The main data collected from TG and DTG curves are listed in Table 2. The thermal degradation process of PC exhibited one step in the inert atmosphere. The major degradation of pure PC occurred between 415 °C and 540 °C, T_{onset} was 445 °C, and the $T_{\max}$ was 510 °C. The char residue of pure PC at 800 °C was 15 wt%. From Table 2, the char residue and the $R_{\max}$ of PC/KSS was higher and lower than those of PC, respectively. While, the $T_{\max}$ of PC/KSS was 470 °C, which was much lower than that of PC.

The thermal degradation process of PC/KSS/2 wt% DAPSiO system exhibited one step similar to that of PC/KSS system. T_{onset} of PC/KSS/2 wt% DAPSiO decreased compared with the other two systems, possibly owing to the chemical interaction between KSS and DAPSiO at a relatively low temperature. Also, the char residues above 600 °C was enhanced with the addition of DAPSiO, as listed in Table 2. It was speculated that the formation of silicone-containing groups, participated in the crosslinked carbonization and retarded the decomposition at higher temperature^[18, 19]. Additionally, the $R_{\max}$ of PC/KSS/2 wt% DAPSiO system was 14.5%/min, lower than that of PC/KSS system. These proved that the addition of DAPSiO increased the thermal stability of PC/KSS system at high temperature.

Table 2. TG and DTG data for different systems

Samples	T_{onset} (°C)	$T_{\max}$ (°C)	$R_{\max}$ (%/min)	Char residue (%)		
				600 (°C)	700 (°C)	800 (°C)
1	445	510	17.6	20.0	17.7	15.0
2	424	470	16.3	20.5	18.5	17.5
9	399	511	14.5	22.1	20.0	18.9

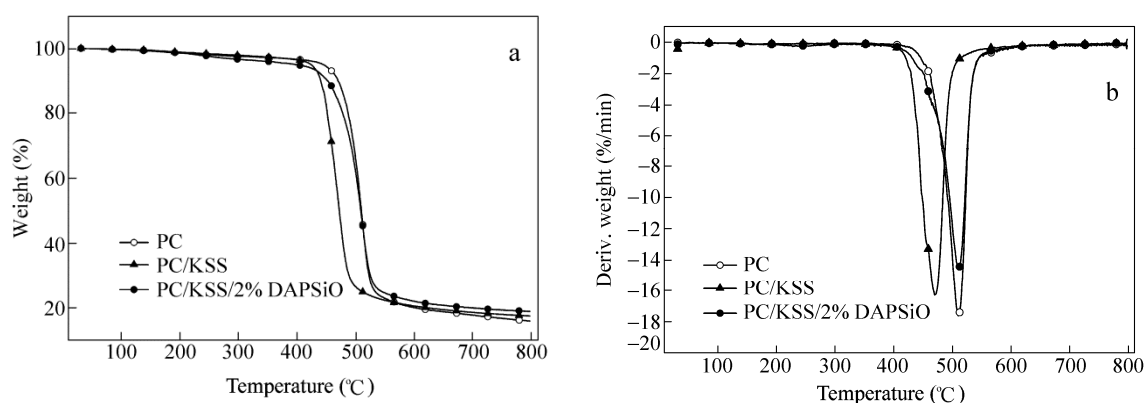


Fig. 4 TG (a) and DTG (b) curves of the PC, PC/KSS and PC/KSS/2 wt% DAPSiO systems

SEM Analysis

The morphology of char residue after LOI tests was further investigated by SEM test. Figure 5 shows the SEM micrographs of char residues of PC (a), PC/KSS (b) and PC/KSS/2 wt% DAPSiO (c) systems. From Fig. 5(a) for PC, the char was alveolate and distributed with lots of big holes on the surface of the residue suggesting a poor char quality. And the structure of char layer for PC/KSS system was loose and interstitial, as shown in Fig. 5(b). The 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. However, the char surface of the PC/KSS/2 wt% DAPSiO system illustrated on Fig. 5(c) was compact and tight, which can effectively prevent the underlying polymer from the heat and combustible gases and was also less susceptible to crack, in agreement with the improvement of flame retardancy.

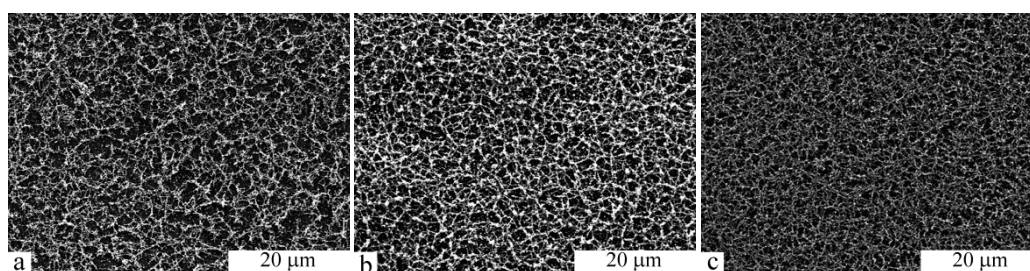


Fig. 5 SEM images of the char residues of PC (a), PC/KSS (b) and PC/KSS/2 wt% DAPSiO (c)

Structural Analysis of Combustion Residue by FTIR

Figure 6 shows the FTIR spectra of the residue obtained from LOI test of PC, PC/KSS, and PC/KSS/2 wt% DAPSiO. The absorption bands at 2921 and 2855 cm^{-1} , which only appeared in curve a, were assigned to the stretching mode of $-\text{CH}_3$ and $-\text{CH}_2-$, respectively. After adding DAPSiO, the peak at 3058 cm^{-1} attributed to aromatic carbon hydrogen structure and the peak around 1100 cm^{-1} for the C—O bond group were observed. Meanwhile, it could be noticed that the absorption bands at 1233 and 1171 cm^{-1} appeared in curve c, attributed to the vibration of Si—C and Si—O, respectively. Based on the observed results, it was proposed that DAPSiO promoted to form a char on the surface during combustion, which was consisted of condensed aromatic compounds and Si—O units.

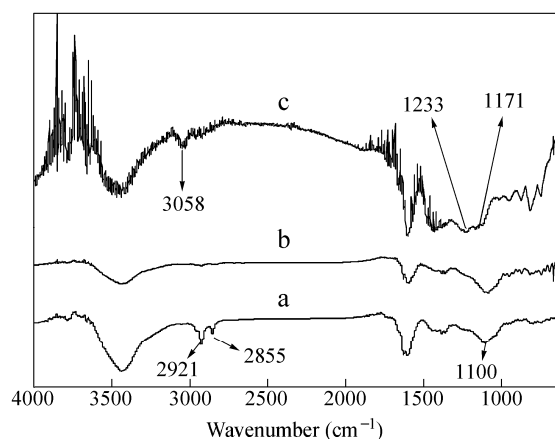


Fig. 6 FTIR spectra of char residues of PC (a), PC/KSS (b) and PC/KSS/2 wt% DAPSiO (c)

CONCLUSIONS

A silicon-containing flame retardant (DAPSiO) was synthesized successfully and characterized by FTIR, ^1H -NMR and TGA tests. The DAPSiO was applied to polycarbonate (PC). The addition of DAPSiO improved the flame retardancy and changed the thermal degradation behavior of the PC/KSS system. When the content of DAPSiO was 1 wt%, the LOI value of PC/0.5 wt% KSS system reached 44% and V-0 rating was obtained. The TG curves demonstrated that DAPSiO increased the thermal stability of PC/KSS system at high temperatures. Moreover, the PC/KSS/DAPSiO system formed excellent char layer containing Si—O structure and condensed aromatic compounds.

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