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Study on the Synthesis and Application in the Polycarbonat of Silicone-Cyclophosphazene Flame Retardant

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Abstract: Silicone-cyclophosphazene (SCP) as a flame retardant was synthesized using hydroxyl terminated polydime thylsiloxane(PDMS-OH) and hexa cyclophosphazene silicone oil and phosphonitrilic chloride trimer(HCCTP) as the precursors, The properties of SCP-modified polycarbonat(PC) such as thermal stability, flame retardant properties and carbon layer after combustion were analyzed. It was found that the target product was SCP, as evidenced by infra-red spectrum (IR)and nuclear magnetic resonance(31P-NMR) spectra results. The PC/SCP composite had higher thermal stability, with higher amount of carbon residue at both initial degradation temperature and 800 oC. When the addition of SCP was 10 wt.% in the PC/SCP composite, the oxygen index increased from 28 to 34%, and a V-0 level was achieved on UL – 94 test. Also, a compact structure of the residue carbon layer after combustion was observed.

Keywords: SCP, Flame retardant, PC, Thermal stability, Carbon layer morphology.

1. INTRODUCTION

Organic silicone flame retardant molecules have high thermal stability due to the high dissociation energies of Si-O bond [1]. However, the efficiency of the single flame retardant is usually not high, thus much attention has been paid on the combination of silicone flame retardants and other compounds [2]. For example, Pen *et al*. synthesized phosphorus-silicon flame retardants using dichloromethyl vinylsilane and dimethyl phosphite as the precursors, which could be cross-linked on fabric and have advantages such as high efficiency and halogen-free [3]. Zheng *et al*. and Zhou *et al*. synthesized phosphorus - nitrogen - silicone flame retardants [4, 5]. Matsumoto *et al*. synthesized poly silicon borane flame retardants with a three-dimensional cross-linked structure, the polymer has at least one aromatic ring in the R groups, which further improved its flame retardant performance [6]. Polyphosphazene compounds consist of alternative nitrogen-phosphine single bond and double bond as the skeleton [7]. These compounds have excellent thermal stability and flame retardancy, which could be directly added to the polymer, or modified to the main chain or side chain of the polymer.

One of the most commonly approaches is the modification of polycarbonate (PC) flame retardant is the addition of halogenated flame retardants. However, disadvantages of such systems are the formation of smoke and corrosive/toxic gases during combustion, which are detrimental to the environment.

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Thus, in this work, we synthesized a novel silicone-cyclophosphazene (SCP) compound with hydroxyl silicone oil and Phosphonitrilic chloride trimer as the precursors, which could possibly possess the advantages of the organic silicone and phosphorus nitriles flame retardants. Thermal properties, flame retardant properties,carbon structure and the flame retardant mechanism of this system was also investigated.

2. EXPERIMENT SECTION

2.1. Reagent and Instrument

Reagent: PDMS-OH (OH Value=8%,M=2000), HCCTP (purity 99.9%), triethylamine (AR), tetrahydrofuran (CP), PC(The Dow Chemical Company, melt index:30g/10min, density:1.2g/cm^3)

Instrument: Constant Temperature Magnetic Stirrer(DF-101S), Thermogravimetric analyzer (Pyris1 TGA), Nuclear magnetic resonance spectrometer (CMX - 500 MHz), Fourier transform infrared spectroscopy (NICOLET 5700), Torque Rheometer (XSS-300), Oxygen index analyzer (JF-3), Micro hybrid molding machine (HAAKE MiniJet II), Vulcanizing machine (GT-7014-A50C), Scanning electron microscopy (Xl30E SEM).

2.2. The Synthetic Route of SCP

The synthetic route is shown as below:

Synthesis process:

Certain quantities of PDMS-OH, HCCTP, tetrahydrofuran were added to a three-neck flask under N_2 atomsphere and vigorous stirring. Then triethylamine was drop-wise added to

the mixture and reacted for 48 h at 70 °C. The resulting product was cooled down to room temperature, followed by the removal of ammonium salt *via* decompression filtration. Then it was vacuum filtrated and washed with n-hexane for several times. After the evaporation of the residual n-hexane, a yellow liquid was obtained as the final product. The Fig. (**1**) as shown in the figure below.

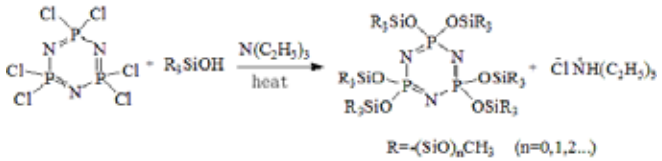

Fig. (1). Synthetic route of SCP.

2.3. Preparation of PC/SCP Composite

The SCP was mixed with different amount of PC and various additives, and blended at 230 °C in a torque rheometer for at least 10 min to obtain the modified PC/SCP composite materials, which were made into standard spline according to the test requirement.

2.4. The Thermal Performance Analysis

The thermal stabilities of the PC/SCP composites were performed in nitrogen or air environment with a temperature range of 50 ~ 800 °C at different heating rates.

2.5. Flame retardant performance analysis

According to GB/T 2406, made the PC/SCP composites into standard spline with the size of 150mm× 10mm× 4mm. Determination of the limiting oxygen index of the sample(LOI)Vertical Burn(VB)test, evaluated for flame retardant according to standard UL-94.

2.6. Char Layers Morphology and Structure Analysis

The morphologies of the char layers was analyzed with a scanning electron microscopy (SEM), operated at 20 kV polycarbonat.

The carbon layer structure of the sample was analyzed using a Fourier infrared spectroscopy（FTIR).

3. RESULTS AND DISCUSSION

3.1. Characterization of Synthetic Products

The synthetic products was obtained: HCCTP: 1.93x 10^{-3}mol, PDMS-OH: 6.67x10^{-3} mol, triethylamine: 0.03 mol, tetrahydrofuran 150ml, T= 70 °C Time=48 h.

3.1.1. IR Characterization

The IR spectra of synthetic products shows as Fig. (**2**).

Fig. (**2**) shows, the spectrum absorption peak at 2959 cm^{-1} means to the Si-CH_3, near 1089 cm^{-1} and its wide absorption peak are the vibration absorption band of Si-O-C. The absorption peak of 1257 cm^{-1}, 798 cm^{-1} are P=N, P-N-P respectively, the results show that the hydroxyl silicone oil has mostly replaced chlorine of HCCTP, and formed the SCP. But the absorption peak of 587 cm^{-1}, 526 cm^{-1} of show remains P- Cl, this is due to the steric hindrance was stronger after the replacement, and kept on replacing on the same phosphorus becoming so difficult.

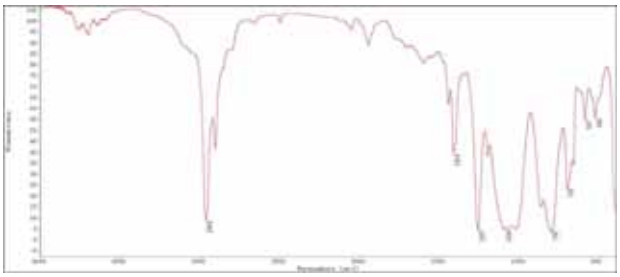

Fig. (2). IR spectra of synthetic product.

3.1.2. 31P- NMR Characterization

The Fig. (**3**) was the ^{31}P- NMR spectra of synthetic products.

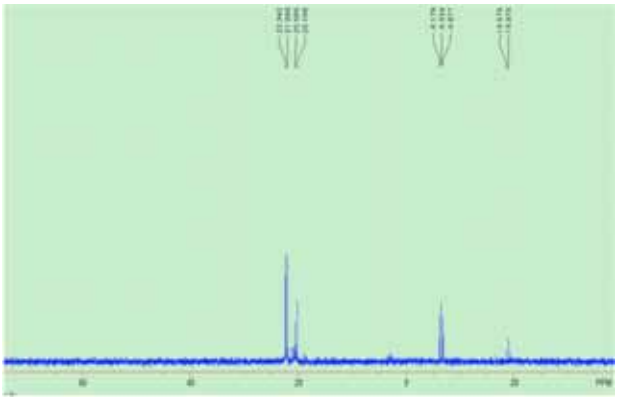

Fig. (3). ^{31}P- NMR spectra of synthetic products.

As the spectra shows, the chemical shift at -6.178 ppm, -6.542 ppm, -6.877 ppm suggest the Si-O group have beening accessed to the products, this means the chlorine of Phosphonitrilic chloride trimer has beening replaced the -OH of organic silicon , and form the SCP. And the chemical shift at 22.432 ppm, 21.998 ppm, 22.432 ppm, 20.168 ppm shows that the product still being P-Cl keys, means the chlorine of HCCTP molecules is not completely replaced, consistent with the results of the IR .

3.1.3. The Thermal Performance Analysis

The test conditions: 50~800 °C, heating rate:10 °C /min, nitrogen atmosphere. The Fig. (**4**) was Thermal weight loss(TGA) of material and product.

Contrast the TGA of th e material ang the product, the product has good thermal stability. The temperature of 5% weight loss is about 300 °C, and the HCCTP and PDMS-OH was only about 150 °C. This suggests that the product has good thermal stability, could be used as flame retardant.

3.2. The Thermal Performance of PC/SCP

3.2.1. TGA Characterization

The data of the TGA tests for PC, PC/SCP and SCP in N_2 environment (heating rate is: 10 °C / min) are given in Table **1**.

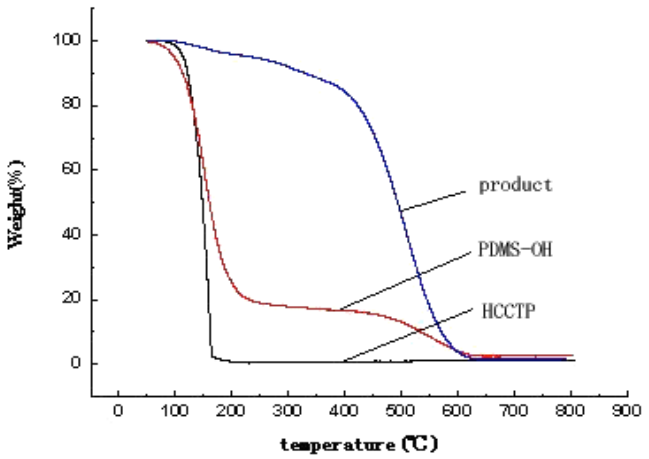

Fig. (4). TGA of the material and the product**.**

It can be seen from Table **1**, the initial degradation temperature(IDT) of PC is 389 ^{o}C, however the PC/SCP is raised to 420 ^{o}C. Because of SCP can degrade to silane free radicals or siloxane derivatives at low temperature, which can promote the crosslinking reaction of PC/SCP system, and prevent degradation of polymer further, so as to improve the thermal stability of the PC/SCP, such as the maximum TGA temperature(T_{max}) and amount of carbon residue.

3.2.2. The Degradation Districts Characterization

The test conditions of degradation districts: in air , heating rate : 5 ^{o}C /min、10 ^{o}C /min、15 ^{o}C /min、20 ^{o}C /min、25 ^{o}C /min, the result shows as Fig. (**5**).

Fig. (**5**) dashed parts show the decomposition of PC. From the experimental data, it can be seen that stage a and b move to the high temperature area, decomposition interval of stage a is smaller, and weightlessness decreases, and stage b decomposition peak has strengthened, in the meantime stage

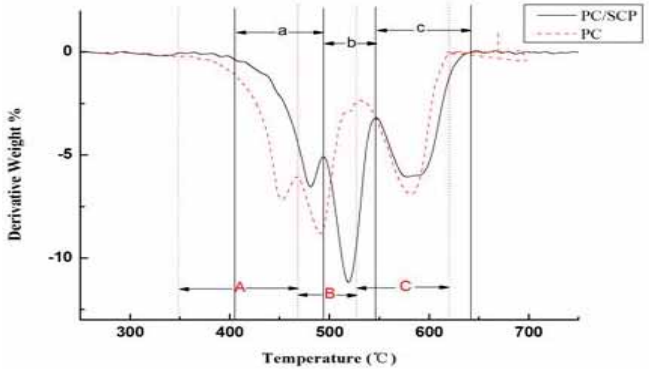

Fig. (5). Degradation districts of PC and PC/SCP.

c decomposition peak has reduced. The reasons may be: (1) Silica groups are easy to transfer and enrichment in the PC/SCP surface layer, and forming a carbonized layer, preventing thermal decomposition, making its A and B stage to move to high temperature area. (2) Due to the weightlessness of the silicone-cyclophosphazene reaches a maximum around 500 ^{o}C, the b decomposition peak has strengthened; (3) The phosphazene can break down to form phosphate structure at high temperature, and crosslink with siloxane through esterification further, to improve the thermal stability of the carbon layer, thus c stage of the degradation speed is smaller. Finally the thermal stability and flame retardancy of the PC/SCP are improved through the three stages.

3.3. The LOI and UL-94 Characterization

The SCP is added to the PC according to the different proportion to prepare the samples, and test their.The data are given in Table **2**.

It can be seen from these datas, early the LOI index is only 28% of the PC, with the addition increasing the LOI value is increasing significantly, When the addition of SCP

Table 1. TGA data of PC, PC/SCP and SCP in N_2.

Sample No.	Compositions of composites (wt. %)	Temperature (^{o}C)				Residue at 800 ^{o}C (%)
		IDT*	5 % Mass loss	50 % Mass loss	Max. Mass loss	
1	PC	389	440	505	498	19.6
2	PC/SCP	420	475	524	515	23.1
3	SCP	---	239	502	508	1.7

IDT*: The temperature corresponding the weight loss of 1 wt%

Table 2. Effect of the amount of SCP on the combustion properties of PC.

Sample No.	Compositions of composites (wt. %)	LOI (%)	ΔLOI (%)	UL-94（4mm）
1	PC	28.0	0	V-2
2	97.5 % PC+2.5 % SCP	30.5	8.9	V-1
3	95 % PC+5 % SCP	31.5	12.5	V-1
4	92.5 % PC+7.5 % SCP	33.0	17.9	V-0
5	90 % PC+10 % SCP	34.0	21.4	V-0

reaches 10wt% the oxygen index value of PC/SCP composites increases from 28% to 34%,the increased LOI value is 21.4%. And it rated up from V-2 to V-0 on UL-94 test. PC/SCP composite materials can self-extinguish quickly, and there is no drop. But due to the large relative molecular weight and the network structureof SCP, The miscibility of the system become worse when the amount of SCP flame retardants has been increased, so we are not able to continue the experiments with increasing the SCP addition.

3.4. Flame Retardant Performance

3.4.1. Char Layers Morphology

The samples of PC and PC/SCP composites (95% PC+5%SCP) were put into the muffle furnace at 400 ^{o}C for 45 min, where they would be carbonized into dark matter. Their morphology after thermally treated is shown in Fig. (**6**).

Fig. (6). Photo of the PC and the PC/SCP after thermally treated.

After thermally treated, the crucible of PC is tan, while the other crucible almost has no change, that means the effects of smoke suppression are obvious. Mean while, the volume of the PC/SCP is larger expansion after thermally treated. The surface of char layers are smooth, compact, uniform and thick relatively, but the surface of PC char layers are rough, has ravines and cracking phenomenon in local area. So the addition of SCP improves the morphology of char layers,

Fig. (**7**) are the SEM of char layers surface of PC and PC/SCP after thermally treated.

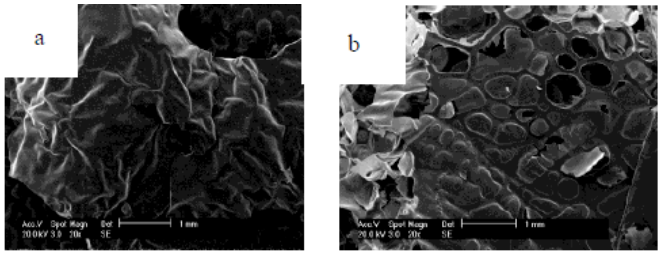

Fig. (7). SEM spectrum of the surface of PC/SCP after thermally treated（**a:**PC, **b:** PC/SCP）.

The SEM show that the char layer surface of the PC is folds and uneven (Fig. **7a**), and the PC/SCP is a relatively dense bubbling structure as shown in figure b, this structure can prevent the small molecules of combustible gas escaping, and the molecules are diluted by CO_2 and N_2 formed in the internal, prevent the spread of the combustion and to prevent the heat transmission under char layer.

3.4.2. Char Layers Structure

The char layers above-mentioned were studied by IR spectrometry, Fig. (**8**) is the infrared spectrum.

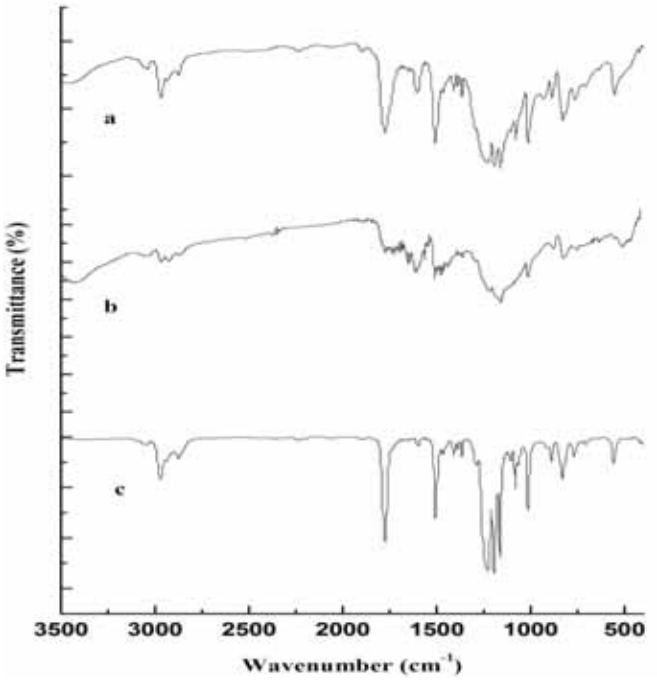

Fig. (8). IR spectra of the PC (**a**) after thermally treated at 400 °C. (**b**) and PC/SCP (**c**) and the degradation residues of PC.

From comparison and analysis of the Fig. (**8**): In the spectrogram of modified PC, there are still strong absorption peaks at 1770 cm^{-1}, 1150 cm^{-1} and 1020 cm^{-1}, and wide absorption peak at 1200 cm^{-1}, which are the characteristic absorption peaks of the PC. and there are not obvious absorption peaks for PC residue after thermally treated. Thus it can be showed that the SCP has good improvement for flame retardant performance of PC material.

CONCLUSION

(1) The charatcterization by IR and ^{31}P- NMR shows that the products were SCP, which has good thermal stability, could be used as flame retardant.

(2) SCP modified PC, which can obviously increase IDT and the carbon residue amountion under 800 ^{o}C, and make it of better thermal stability. When the addition of SCP reaches 10wt.% the oxygen index value of PC/SCP composites increases from 28% to 34%, and it rated up from V-2 to V-0 on UL-94.

(3) The SCP promoted the effects of smoke suppression The surface of char layers with dense bubbling structure is smooth, compact, uniform, and thick relatively. The results of FT-IR demonstrated that the characteristic absorption peaks of the PC still exists in the thermally treated residue of the modified PC, so that shows, the

SCP increases the flame retardant performance of PC/SCP composite.

CONFLICT OF INTEREST

The author confirms that this article content has no conflict of interest.

ACKNOWLEDGEMENTS

Declared none.

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