

Flame Retardancy and Thermal Properties of Carboxyl-Containing Polysiloxane Derivatives in Polycarbonate

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ABSTRACT: Carboxyl-containing polysiloxane (LCCP) has been successfully applied in the flame retardancy of polycarbonate (PC). The LCCP was synthesized by hydrosilylation and condensation reaction. The presence of carboxyl groups has been demonstrated to be crucial to provide high flame retardant effectiveness. The flame retardancy of LCCP-PC composites is investigated by limiting oxygen index (LOI), vertical burning tests (UL-94). At the mole ratio of diethoxymethyl (1-propionyloxy) silane/diethoxydimethylsilane = 8/100 in LCCP(3), the best flame retardant performance of LCCP-PC composites was obtained. The LOI value of the composites is 38.5 and the UL-94 rating reaches V-0 when the content of LCCP(3) is as low as 0.5 wt %. Evolution of the thermal behaviors of the composites tested by thermogravimetric analysis shows that addition of LCCP(3) in PC can reduce the degradation speed of PC and induce a reduction of the initiated decomposition temperature of PC. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2013, 000, 39814.

KEYWORDS: functionalization of polymers; flame retardance; blends

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INTRODUCTION

Bisphenol A polycarbonate (PC) is an engineering thermoplastic with high impact strength, heat resistance, and excellent electrical properties that are widely used in fields such as electrical and electronics devices, automobiles, and construction. PC by itself belongs to a kind of flame-retardant plastic with a V-2 rating in the UL94 test and ~25% value of the limiting oxygen index (LOI). While as for most electronics devices, which mainly include PC and its derivatives in their housing and part-packaging, a severe flame retardant performance must be required to prevent fire from originating in the electronics devices.^{1,2}

In the past two decades, flame-retardant technologies of PC have been developed extensively.³ With the gradual prohibition of halogen-containing compounds, more efforts have been focused on phosphorus-containing compounds, sulfonate salts, and silicon-containing compounds. Among various phosphorus compounds, some phosphates, such as Triphenyl phosphate (TPP), resorcinol bis(diphenyl phosphate) (RDP), and Bisphenol A bis(diphenyl phosphate) (BDP) are widely used as the flame retardants of PC.^{4,5} However, the relatively high volatility of most phosphate and acids release during processing limit their application in engineering plastics. In addition, sulfonate salts such as potassium perfluorobutane sulfonate, KSS are par-

ticularly effective in flame retardancy of PC even at as low as 0.05–0.1 wt % loading.^{6–8} However, the use of these materials alone is not satisfactory especially in thin walled articles.

Presently, silicon-containing compounds used as the flame retardants of PC have attracted a tremendous amount of attentions owing to their environmental friendliness and processing facility.^{9,10} Since the previous reports by Iji and Serizawa,¹¹ in which a branched structure or a phenyl-rich mixture of phenyl and methyl groups in the chain and methyl groups at the chain terminals were demonstrated effectively in retarding the combustion of PC, more efforts have been exerted to design silicone materials for the flame retardancy of PC and study their flame-retardant mechanism.^{12–17} The general view of the flame retardant mode is that the silicon-containing flame retardant in PC can move to the PC surface during burning process and accumulate on the surface of the polymer, and it further initiates a compact and homogeneous char on the surface. Recent studies demonstrate that silicone compounds can accelerate the isomerization reaction of PC units to form phenyl ether and carboxyl group structures, which subsequently undergo decarboxylation, dehydration, and crosslinking reactions to create a protective barrier.³ It indicates that the presence of carboxyl group probably play an important role in promoting the crosslinking and charring reactions in the PC-silicone system. In addition, it is

well known that silica gel combined with potassium carbonate is an effective flame retardant for a wide variety of common polymers.¹⁸ Similar to the PC-silicone system, the silicon-oxy-carbide (SiOC) groups were detected in the char residues after combustion. It further implies that the carboxyl group might assist the silicon-containing flame retardants with forming the protective char during combustion.

In the present work, we have successfully synthesized a kind of carboxyl-containing polysiloxanes derivatives (LCCP) with different concentration of carboxyl groups. The effects of LCCP on the thermal stabilities and flame retardancy of LCCP-PC composites have been studied.

EXPERIMENTAL

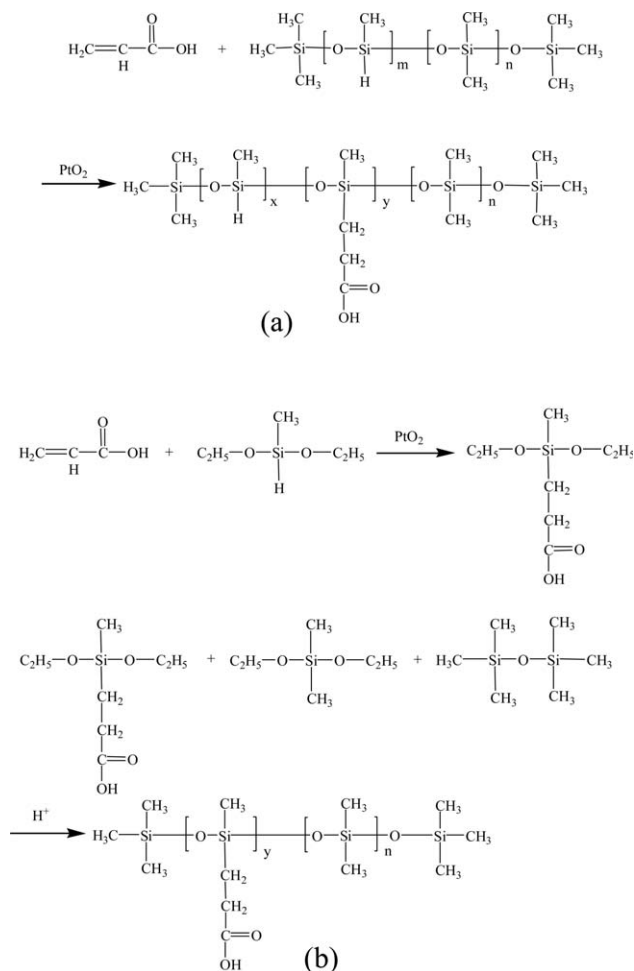
Materials

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, hexamethyldisiloxane, dimethyldiethoxysilane, and methyldiethoxysilane were purchased from Huafeng Organic Silicon, (Jilin, China). The content of hydrogen in silicone oil was 0.18 wt %. Acrylic acid was kindly provided by Guangfu Chemicals Fine Product research institution, (Tianjin, China). Platinum dioxide (PtO₂) was purchased from National Medicines, (China). Toluene was purchased from Fuyu Chemicals Fine Product, (Tianjin, China). Hexamethyldisiloxane, methyldiethoxysilane, and toluene were of analytical-purity grade and hydrogen-containing silicone oil was of industrial grade.

LCCP Synthesis

On the basis of a previous work,^{19,20} the addition of Si—H bond to the unsaturated bond of acrylic acid was catalyzed by PtO₂ catalyst. The synthetic route for LCCP(0) was shown in Scheme 1(a). The mixtures of hydrogen-containing silicone oil and acrylic acid at a certain molar ratio (Si—H in silicone oil: acrylic acid = 1 : 1) were stirred with toluene solvent in a single-necked round-bottom flask under N₂. The PtO₂ (100 ppm equiv) was added, and the flask was heated at 85°C for 20 h. Then the mixture was cooled to room temperature and the PtO₂ was filtered off. After removing the toluene solvent by vacuum distillation, a kind of viscous liquid product was obtained (81% yield).

The synthetic route for LCCP(i) was shown in Scheme 1(b). The hydrosilylation reaction of methyldiethoxysilane and acrylic acid was carried out under the same condition mentioned earlier, but no solvent was used. A monomer product, methyldiethoxy(1-propionic acid)silane, was obtained at about 92% yield. The LCCP(i) was prepared by an acid-catalyzed hydrolytic polycondensation, in which diethoxymethyl(1-propionyloxy) silane, dimethyldiethoxysilane hexamethyldisiloxane, and toluene solvent were added to a 250 mL, three-necked round-bottom flask fitted with a mechanical stirrer and a reflux condenser. Taking into account the probable influences of carboxylic groups on the polycondensation, different amount of 0.1 mol/L hydrochloride was dripped into to keep the same concentration of H⁺ in each solution. The temperature was increased to 80°C for 6 h, during which the ethanol and methanol generated was



Scheme 1. The synthetic route and the structure of LCCP.

removed by evaporating. After cooling to room temperature, the obtained mixture was washed repeatedly to remove acid and the remained alcohol. Finally, the toluene solvent was removed by vacuum distillation, and a viscous liquid product was obtained.

Sample Preparation

The PC was dried in the oven at 120°C for 12 h before being processed to remove moisture, after which the LCCP 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.

Infrared (IR) and NMR Measurement

The infrared spectrum of LCCP was monitored by an Avtar 360 Fourier-transform infrared 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 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-

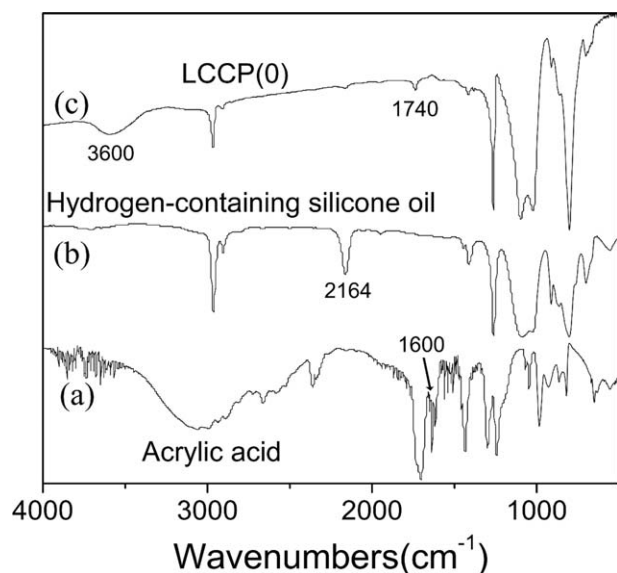


Figure 1. FTIR spectra of (a) acrylic acid, (b) hydrogen-containing silicone oil, and (c) LCCP(0).

spinning (MAS). The spinning rate was set at ca. 5 kHz. The observed frequencies of ^{29}Si nuclei were 99.36 MHz.

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 $130 \times 6.5 \times 3 \text{ mm}^3$. Vertical burning ratings of all samples were measured on a CZF-2 instrument produced by Jiangning Analysis Instrument Factory, China, with the dimensions of $130 \times 13 \times 3 \text{ mm}^3$, where the test results were classified by burning ratings V-0, V-1, or V-2.

Thermogravimetric Analysis (TGA) Tests

All TGA tests were carried out by a Thermal Analyzer (Perkin Elmer Pyris 1) at a linear heating rate of $10^\circ\text{C min}^{-1}$ under air atmosphere within the temperature ranging from 50 to 800°C . The weight of the samples was kept within 2–4 mg.

RESULTS AND DISCUSSION

Spectral Characterization of the LCCP(0)

Figure 1 displays the (a) FTIR spectra of acrylic acid, (b) Hydrogen-containing silicone oil, and (c) the LCCP(0). Curve (a) shows a sharp peak at about 1600 cm^{-1} corresponding to the —C=C 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 almost disappear, which clearly demonstrates the occurrence of the hydrosilylation reaction between the —C=C on the acrylic acid and —Si—H on the hydrogen-containing silicone oil. In addition to those peaks, FTIR spectrum of (c) shows peaks at about 1093 and 1024 cm^{-1} are characteristic vibrations of Si—O—Si , the peak at

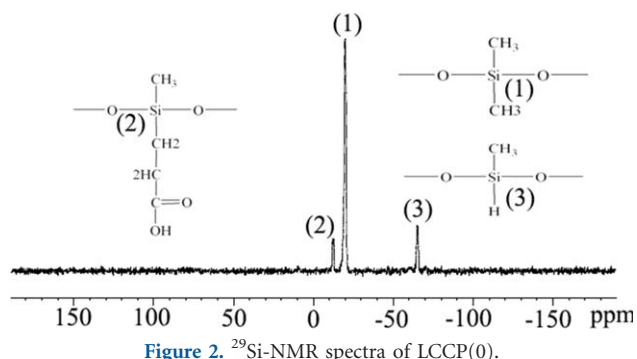


Figure 2. ^{29}Si -NMR spectra of LCCP(0).

3600 belongs to the OH-band and the peak at 2966 cm^{-1} corresponds to characteristic vibrations of —CH_3 .

^{29}Si NMR spectra of LCCP(0) were applied as another evidence to confirm the occurrence of the hydrosilylation reaction between the acrylic acid and the hydrogen-containing silicone oil. As shown in Figure 2, the strong peak at -20.00 ppm belongs to Si atoms in the $\text{—Si(CH}_3)_2\text{—}$. Next to it, a small peak at -15 ppm appears, which is attributed to the Si atoms with methyl and propanoic acid groups. It provides a direct evidence for the occurrence of the hydrosilylation reaction between the acrylic acid and the hydrogen-containing silicone oil. In addition, we still see the peaks near -64.95 ppm , which are due to residual —Si—H groups, indicating that a few amounts of —Si—H groups in hydrogen-containing silicone oil are left.

Flame Retardancy of the LCCP(0)

To investigate the flame retardancy of LCCP(0) applied into PC matrix, combustion tests such as LOI and UL-94 vertical burning tests were employed. 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.⁵ The composition of the flame retarded PC system and combustion test results are summarized in Table I. Pure PC shows a LOI value of 26.5%, and it only exhibits a V-2 rating in the UL-94 test due to some

Table I. Flame Retardancy of PC/LCCP(0) Systems with Different Contents

Samples	LOI (%)	UL-94 (3mm)	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/0.5% LCCP(0)	28.1	V-2	9.2	4.7	13.9	Yes
PC/1.0% LCCP(0)	32.7	V-1	6.1	4.8	10.9	No
PC/1.5% LCCP(0)	31.5	V-2	6.7	3.1	9.8	Yes
PC/2% LCCP(0)	30.1	V-2	5.9	1.5	7.4	Yes
PC/2% silicone oil	26.1		36.2	27.5	63.9	Yes

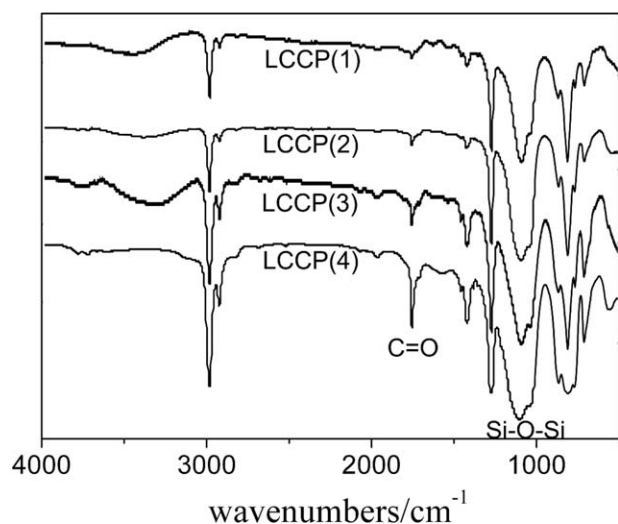


Figure 3. Comparison of the FTIR spectra of LCCP with different carboxyl contents.

dripping existed. By incorporating the LCCP(0) into PC; however, the LOI value sharply goes up, and visible intumescent char is observed. At the same time, the dripping decreases gradually in the UL-94 test. As shown in Table I, when 1.0% LCCP(0) was added, the LOI value was increased from 26.5 to 32.7% and the UL-94 rating was enhanced from V-2 to V-1. Similar with our previous results, further increasing the concentration of LCCP(0) in the PC matrix almost cannot lead to the enhancement of LOI value. 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 of LCCP(0) as low as 0.5 wt % has dropped to 13.9 s. The total combustion time (t_{1+2}) became shorter gradually with the increase of LCCP(0) contents. The samples failed to pass UL-94 V0 rating only because of the presence of dripping.

As a comparison, we blended pure hydrogen-containing silicone oil into PC matrix directly. The flame retardant results in Table I show that the PC composites with the presence of hydrogen-containing silicone oil exhibit a much lower flame retardant performance in relative to pure PC and do not pass any UL-94 ratings. It is evidently confirmed that the presence of carboxyl groups on the LCCP(0) structure is crucial for the high flame retardancy of the LCCP(0)-PC formulations. While the hydrogen-containing silicone oil used in this work belongs to a commercial product, in which the mole content of Si-H is constant. In addition, some of Si-H bond failed to be added during the hydrosilylation reaction, as demonstrated in Figure 2. Thus, it is impossible to adjust artificially the number of carboxyl groups added on the hydrogen-containing silicone oil during the synthesis of LCCP(0). Consequently, it is impossible to discuss the effect of the concentration of carboxyl groups on the flame retardant performance of the LCCP(0) flame retardants in PC matrix. Thus, in the following work, we have synthesized the same type of carboxyl-containing polysiloxane derivatives, in which the content of carboxyl groups can be easily adjusted.

Preparation and Flame Retardancy of the LCCP(i)

Monomer A, i.e., diethoxymethyl (1-propionyloxy) silane, was synthesized through hydrosilylation between acrylic acid and diethoxymethylsilane. Monomer B diethoxydimethylsilane and end capping reagent hexamethyldisiloxane belong to commercial products. After polycondensing between monomer A and monomer B and blocking by hexamethyl disiloxane, a series of carboxyl-containing polysiloxane derivatives were prepared by controlling the mole ratio of monomer A and monomer B, in which LCCP(1) was prepared by the A/B mole ratio = 2/100, LCCP(2) by the A/B mole ratio = 5/100, LCCP(3) by the A/B mole ratio = 8/100 and LCCP(4) by the A/B mole ratio = 11/100. The FTIR spectra were used to characterize this family of carboxyl-containing polysiloxane derivatives. As shown in Figure 3, the peaks at about 1093 and 1024 cm^{-1} existing in all products are characteristic vibrations of Si-O-Si. Since, the molar concentration of Si elements is almost fixed in each LCCP(i), we afford the peak intensity of Si-O-Si stretching as a reference peak. Apparently, the peak intensity of $\text{C}=\text{O}$ stretching in product becomes much stronger with the increase of carboxyl content, indicating that the LCCP(i) with different carboxyl content has been obtained.

The effect of carboxyl content in LCCP(i) on the flame retardancy of the LCCP(i)-PC composites is shown in Table II. LCCP(i) is added in every sample with the same 1 wt % filler loading. It can be seen that LOI of the LCCP(i)-PC samples show an obvious increase relative to pure PC, while the rise in the LOI value seems not to be the same. It is reasonable to conclude that the difference in the LOI values should be attributed to the different carboxyl content in LCCP(i) blended in PC matrix. Indeed, as shown in Table II, LOI values are enhanced with the increase of the carboxyl content at first until a maximum value of 38.1% is reached at the mole ratio of monomer A/monomer B = 8/100 in LCCP(3). However, with further increase of carboxyl mole percent, the LOI values decrease. At the same time, UL-94 test results of the LCCP(i)-PC composites versus the carboxyl mole percent are also given in Table II. Similarly, the best UL-94 result appears at the LCCP(3)-PC sample. In this work, both the LCCP(2)-PC and LCCP(3)-PC samples can pass V-0 rating with an average total after-flame time of 8.9 and 7.4 s, respectively. These results not only further demonstrate that the carboxyl group in LCCP has important effects on

Table II. Flame Retardancy of PC/1 wt %LCCP(i) System with Different Carboxyl Contents

Samples	LOI (%)	UL-94 (3 mm)	t_1 (s)	t_2 (s)	t_{1+2} (s)	Dripping
PC/1% LCCP(1)	32.8	V-2	11.8	6.1	17.9	Yes
PC/1% LCCP(2)	36.9	V-0	5.7	3.2	8.9	No
PC/1% LCCP(3)	38.1	V-0	5.1	2.3	7.4	No
PC/1% LCCP(4)	34.4	V-1	9.9	4.5	14.4	No

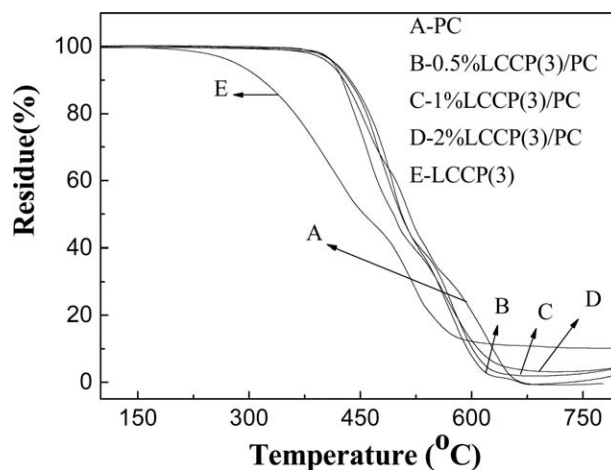
Table III. Flame Retardancy of PC/LCCP(3) Systems with Different Contents

Samples	LOI (%)	UL-94 (3 mm)	t_1 (s)	t_2 (s)	t_{1+2} (s)	Dripping
PC/0.2% LCCP(3)	33.8	V-2	9.8	6.1	15.9	Yes
PC/0.5% LCCP(3)	38.5	V-0	6.1	2.2	8.3	No
PC/1.0% LCCP(3)	38.1	V-0	5.1	2.3	7.4	No
PC/1.5% LCCP(3)	35.9	V-2	5.7	2.0	7.9	yes
PC/2.0% LCCP(3)	33.4	V-2	6.9	1.5	8.4	yes

the flame retardancy of LCCP-PC composites, but also confirm that there is an optimal content of carboxyl group in LCCP for the best flame retardant performance of LCCP. In the following work, the LCCP(3) will be chosen for further flame retardant test.

Effects of the amount of the LCCP(3) in PC on the flame retardancy of LCCP(3)-PC composites are investigated. The composition of LCCP(3)-PC composites and the combustion test results are summarized in Table III. It could be seen that the LOI values increased dramatically with the increase of the loading of LCCP(3) at first, and at a very low loading of 0.5 wt % in PC matrix, a maximum value of 38.5% was reached, after which the LOI values decreased. With the comparison to silicon-containing flame retardants in some previous work,^{12-17,21} the addition of LCCP(3) is more effective to enhance LOI value of PC composites. UL-94 test results of the LCCP(3)-PC composites versus the loading of LCCP(3) are also given in Table III. Interestingly, the best UL-94 test result does not appear at the loading of 0.5 wt %, but 1.0 wt % of LCCP(3). The reduced flame resistance at higher concentrations of flame retardants might due to the increase of total organics content in the system. While the different test environment should be an explanation for the different flame-retardant performance of LCCP(3) between LOI and UL-94 test. In this research, samples for UL-94 test were ignited under ambient atmosphere; however, samples for LOI test were ignited in a sustained, relatively high oxygen concentration circumstance. Generally, samples will combust more sufficiently in LOI test, leading to produce excess heat, which could feedback towards the samples to elevate the temperature of the samples. The results in Table III indicate that the LCCP(3) flame retardant behaves more effectively under the LOI test conditions. At the same time, it also implies that the high flame-retardant effectiveness of LCCP(3) in PC is not only the results of physical barrier action but also the presence of chemical action between the LCCP(3) and PC matrix during combustion.

Turning to the results shown in Table III, it is worth noting that both the LCCP(3)-PC composites with the 0.5 and 1.0 wt % LCCP(3) loading can pass UL-94 V0 rating. Further increasing

**Figure 4.** TG curves of PC/LCCP(3) composites under air atmosphere.

the content of LCCP(3) in PC, the LOI values of composites decline, and the average total after flame time still keeps very low, but dripping occurs. These phenomena are very similar with that of LCCP(0)-PC composites, while it is worth noting that the flame retardant effectiveness of LCCP(3) is more efficient than that of LCCP(0) when used in PC matrix.

Thermal Degradation Behaviors

TGA data under air flow are determined and analyzed to study the thermal stability and decomposition behavior of LCCP(3), PC, and LCCP(3)-PC composites. TGA and DTG curves are presented in Figures 4 and 5. The detailed data for all the composites are given in Table IV, 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°C. The curves of the PC and the LCCP(3)-PC composites show a two-step degradation process. The first stage of mass loss of the pure PC occurs at temperature from 440 to 550°C, following a second slower degradation stage at about 550 to 650°C. The temperature of degradation onset of LCCP(3)-PC is lower than that of pure PC, and decreases gradually with the increase of LCCP loading, possibly because the T_{onset} of LCCP(3) (295°C) is lower than that of pure PC

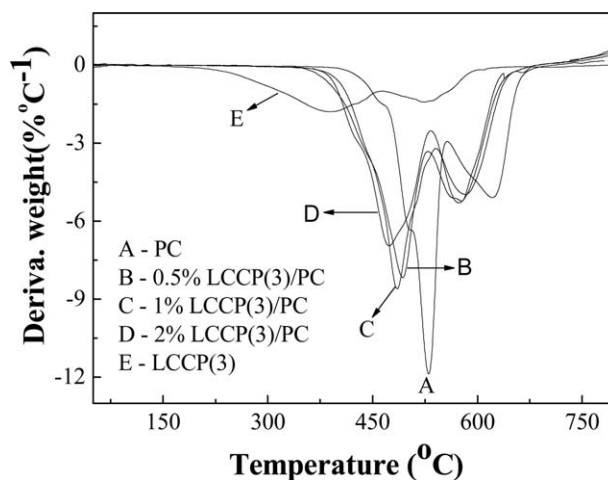
**Figure 5.** DTG curves of PC/LCCP(3) composites under air atmosphere.

Table IV. The Thermal Stability Parameter of the Samples in Air

Sample	Components (%)		TG		
	PC (g)	LCCP(3) (g)	T_{5wt} % (°C)	T_{max} (°C)	Residue wt % 800°C
0	100	0	463	530	0
1	99	0.5	427	492	0.78
2	97	1	416	484	2.48
3	95	2	414	471	3.70
4	0	100	295	390	10.13

(463°C). It should be noted that the thermal stability of flame retardants is slightly lower than processing temperature of PC used (230°C). As shown in Figures 4 and 5, the weight loss is about 1.5% at 230°C. By analyzing the structure of LCCP(3), we attribute the weight loss to a little esterification and dehydration between carboxylic groups. Thus it might not influence the flame retardant performance of LCCP(3) in this research.

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 maximum weight loss rate is close to $12\% \text{ } ^\circ\text{C}^{-1}$; however, the maximum mass loss rates for the LCCP(3)-PC composites are all lower than that of pure PC, as confirmed from DTG plot in Figure 5. It is clear that LCCP(3) may slow the speed of PC degradation and accelerate the formation of carbon layer. The residue of LCCP(3) at 800°C in air atmosphere is 10.13% and there is no char residue for PC at this temperature, while the amount of char residue from LCCP(3)-PC composites is obviously higher than that from pure LCCP(3) under the same level of LCCP(3) condition, as observed from the TG data in Table IV. This shows that addition of LCCP(3) 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. It should be noted that a small weight increase is observed at the final oxidative process of PC-LCCP(3) composites, when temperature is above 675°C on the TGA curves (Figure 4). We estimate that the small weight increase might be due to physisorption.

CONCLUSIONS

A type of novel carboxyl-containing organosilicone flame retardants, i.e., LCCP, has been successfully prepared and applied in this work, and we find that the presence of carboxyl group on the LCCP structures exerts an important influence on the flame retardant performance of LCCP in PC. Specific findings are as follows: comparing with the pure hydrogen-containing silicone oil, its derivatives obtained by the hydrosilylation reaction with acrylic acid have much higher flame retardant effectiveness when used in PC matrix. By adjusting the content of carboxyl group in LCCP, the best flame retardant performance of LCCP-PC composites was achieved in present work. When the mole ratio of diethoxymethyl (1-propionyloxy) silane/diethoxydimethylsilane was 8/100 in LCCP(3), it was surprising to see that the LOI value of composites reached to

38.5% and passed a UL-94 V-0 rating with the filler loading as low as 0.5%. TG and DTG results show that addition of LCCP(3) in PC can reduce the degradation speed of PC and induces a reduction of the initiated decomposition temperature of PC. In future work we plan to further enhance the thermostability of carboxyl-containing organosilicone and examine the flame retardancy of carboxyl-containing organosilicone with the presence of phenyl groups.

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