

Synthesis of a Phenylene Phenyl Phosphine Oligomer and Its Flame Retardancy for Polycarbonate

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ABSTRACT: A novel flame retardant, phenylene phenyl phosphine oligomer (PPPO) was synthesized and its chemical structure was characterized using Fourier transform infrared spectroscopy, ¹H, ¹³C, ³¹P nuclear magnetic resonance spectroscopy and mass spectrometer. PPPO was used to impart flame retardancy to polycarbonate (PC). Combustion behaviors and thermal degradation properties of PC/PPPO system were assayed by limiting oxygen index (LOI), vertical burning test (UL-94), cone calorimeter test, and thermogravimetric analysis. PC/6 wt % PPPO passed UL-94 V-0 rating with 3.0 mm samples and the LOI value was 34.1%, and PC/8 wt % PPPO also passed UL-94 V-0 rating with 1.6 mm samples and the LOI value was 36.3%. Scanning electron microscopy reveals that the char properties had crucial effects on the flame retardancy of PC. Mechanical properties and water resistance of PC/PPPO system were also measured. After water resistance test, PC/6 wt % PPPO with 3.0 mm samples and PC/8 wt % PPPO with 1.6 mm samples kept V-0 rating and mass loss was only 0.2%. The results revealed that PPPO was an efficient flame retardant for PC. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: flame retardant; synthesis; polycarbonate; phosphine oligomer; water resistance

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INTRODUCTION

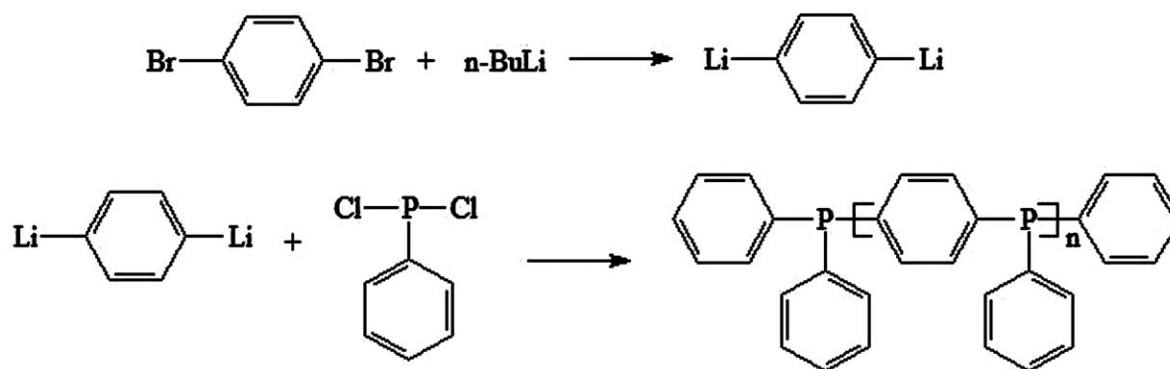
In today's world, polymeric materials are replacing traditional materials like metals and wood for many applications. But polymers are easily flammable and subjected to various mandatory controls for safety reasons.^{1,2} A widely known method to impart flame retardancy is to add a halogen-containing compound to the resin. Although halogenated compounds show good flame retardancy and have been used widely for several decades, their use has been curtailed in many countries because of toxic and corrosive fumes released during combustion.^{3,4} Environmental concerns about halogenated flame retardants are the driving forces behind the development of cost effective, halogen-free alternatives. In this race, organo-phosphorus flame retardants are among the leading contenders.^{5,6} Various phosphorus compounds, such as phosphines, phosphine oxides, phosphonates, red phosphorus, phosphites, and phosphates, are used as flame retardants.^{7–12}

Polycarbonate (PC), a widely used engineering plastic, has outstanding properties, including good stiffness, impact strength,

transparency, dimensional stability, and thermal stability. Therefore, it is widely used in the fields of optical equipment, construction, automobiles, electronic and electric devices, etc.^{6,13–15} Because of its relatively high tendency to charring, PC by itself shows a limiting oxygen index (LOI) of ~ 28% and a V-2 rating in the vertical burning test (UL-94). However, more stringent flame retardancy is often required in certain applications.^{14,15}

In order to improve the flame retardancy of PC, various phosphorus compounds, such as triphenyl phosphate (TPP), resorcinol *bis*(diphenyl phosphate) (RDP), and bisphenol A *bis*(diphenyl phosphate) (BDP) are widely used.^{6,15–17} However, these phosphates have disadvantage. The high volatility of TPP limits its application in engineering plastics, which usually require high processing temperatures. BDP and RDP suffer from proceeding problem due to their resin state.¹⁴ In addition, phosphates hydrolyze easily and have poor resistance to acid and base, which limit their application range. A possible way to improve flame retardancy of PC would be the use of stable flame retardants.¹⁸

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Scheme 1. Synthesis of PPPO.

Of the various phosphorus containing compounds, the P-C bonds containing compounds are preferred as flame retardant.^{19–21} They can promote char formation, have high efficiency at low phosphorus concentration, and have good thermal stability and resistance to acid and base.^{20–22} The action of the compounds can take place in the vapor phase by a radical mechanism to interrupt the exothermic processes and to suppress combustion. In this case, PO, P, and P₂ species are likely to react with H and OH radicals to form HPO.¹ On the other hand, they can also act in the condensed phase. The compounds incorporated in polymer materials act like acid precursors and the acids participate in char formation.^{14–16} Then, a protective layer formed to stop the propagation of heat and oxygen to melt polymer matrix during combustion. Therefore, it prevents the polymer from further burning. Some P-C containing compounds have been synthesized and used to enhanced flame retardancy to polymer materials, such as phosphine, phosphine oxide and phosphonate.^{19,22–25} So far, using phosphine oligomer to improve flame retardancy of PC has not been reported.

In this study, phenylene phenyl phosphine oligomer (PPPO) was synthesized and characterized. The effects of PPPO on

flame retardancy, thermal degradation, mechanical properties, and water resistance of PC were assessed.

EXPERIMENTAL

Materials

N,N,N',N'-tetramethylethylenediamine (TMEDA), anhydrous ethyl ether, methanol, and tetrahydrofuran (THF) of analytical grade were purchased from Kermel Chemical Reagents Development Center. (Tianjin, China). *p*-Dibromobenzene of analytical grade was purchased from Sinopharm Chemical Reagent (Shanghai, China). *n*-Butyllithium in hexane (technical grade) was obtained from Hualun Chemical (Zhejiang, China). Dichlorophenyl phosphine (DCPP) of technical grade was supplied by Lida Chemicals Industry (Guangdong, China). PC 2805 was provided by Bayer Germany and was dried in the oven at 120°C for 6 h before use.

Synthesis of Phenylene Phenyl Phosphine Oligomer

In a 500-mL four-neck flask, *p*-dibromobenzene (0.12 mol, 28.3 g) and ethyl ether (150 mL) were mixed under argon atmosphere. The reaction flask was cooled to –78°C and *n*-butyllithium in hexane (2.5 M, 0.24 mol, 96 mL) was added

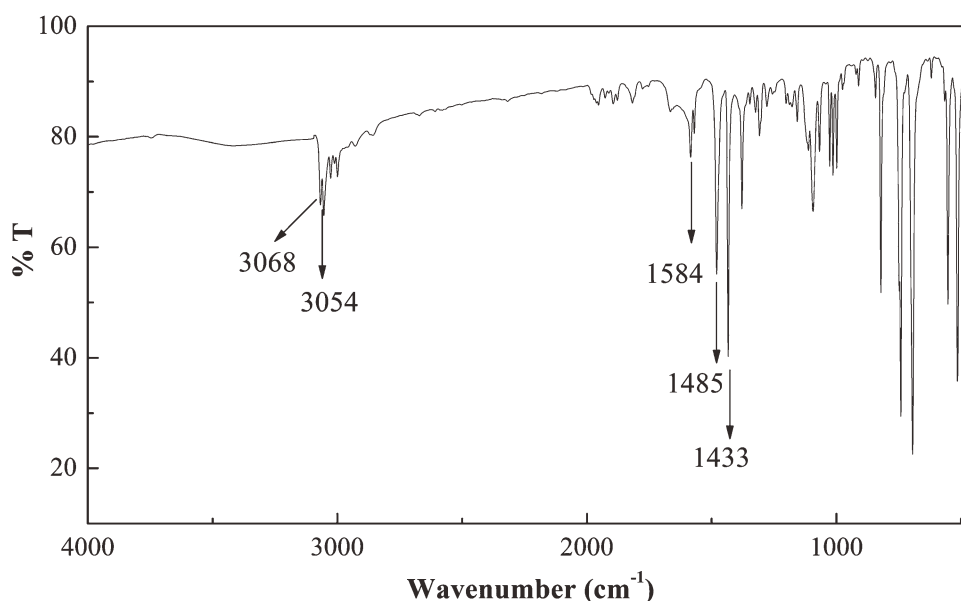


Figure 1. FTIR spectrum of PPPO.

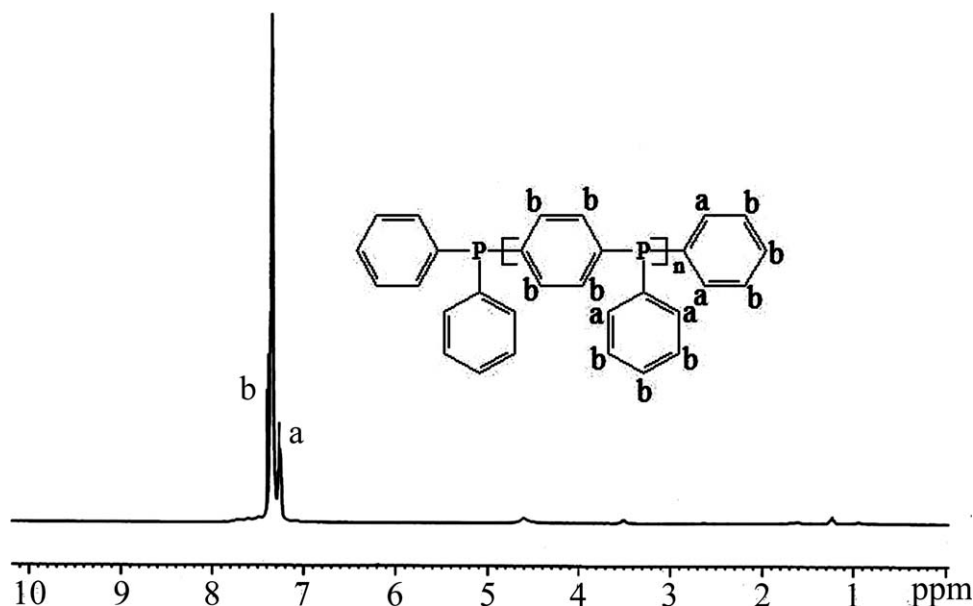


Figure 2. ^1H NMR spectrum of PPPO.

dropwise via an addition funnel. The mixture spontaneously warmed up, and TMEDA (7.2 mmol, 0.83 g) was dripped. Then the mixture was gradually increased to room temperature and stirred for 10 min. After cooling, DCCP (0.1 mol, 17.9 g) was added to the reaction mixture which was held at less than 3°C during the addition. The contents were warmed to room temperature and stirred for 12 h. And then, the reaction was quenched with methanol and stirred. The solvents were removed at reduced pressure and solid residue was washed with methanol and with water. The crude product was reprecipitated in THF/ methanol. The off-white solid powder was obtained and dried under vacuum at 80°C for 8 h (yield 12 g, 59.8%). The synthesis reactions of PPPO are shown in Scheme 1.

Characterization of PPPO

Fourier transform infrared (FTIR) spectra were obtained using potassium bromide discs and Perkin Elmer 400 spectrometer (USA). Nuclear magnetic resonance (NMR) spectra were

obtained using 10–25% solutions in deuteriochloroform and Bruker 300 NMR (300 MHz) spectrometer (Germany). Proton and carbon chemical shifts were reported with respect to tetramethylsilane (TMS) as internal reference. Phosphorus chemical shifts were reported with respect to 85% aqueous phosphoric acid solution as external reference. Mass spectra (MS) were obtained using an Agilent Q-TOF 2105-6520 (USA).

Preparation of Samples

PC and PPPO were mixed in a RM-200A rheometer (HAPRO, Harbin, China) at a temperature of 250°C and a rotor speed of 50 rpm for 8 min. The samples were pressed on a curing machine at 190°C for 3 min into sheets of suitable thickness and size.

Flame Retardancy Tests

The LOI values were measured at room temperature on a JF-3 oxygen index meter (Jiangning Analysis Instrument Company,

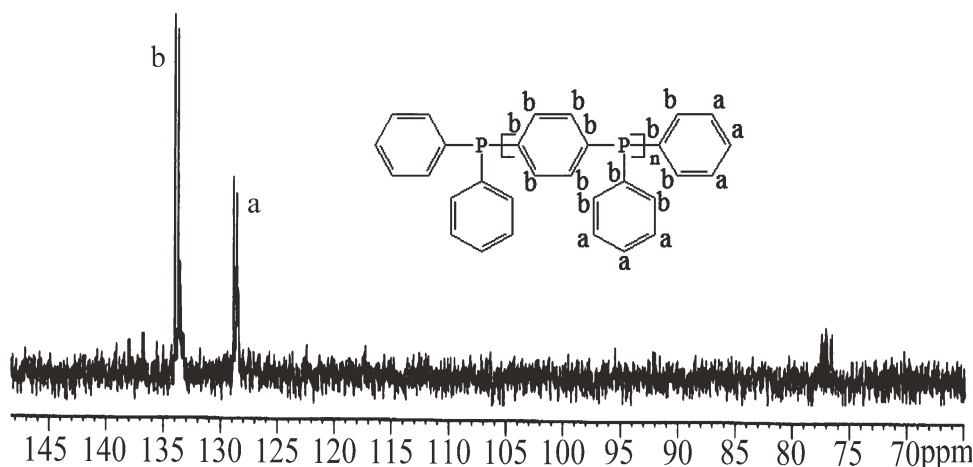


Figure 3. ^{13}C NMR spectrum of PPPO.

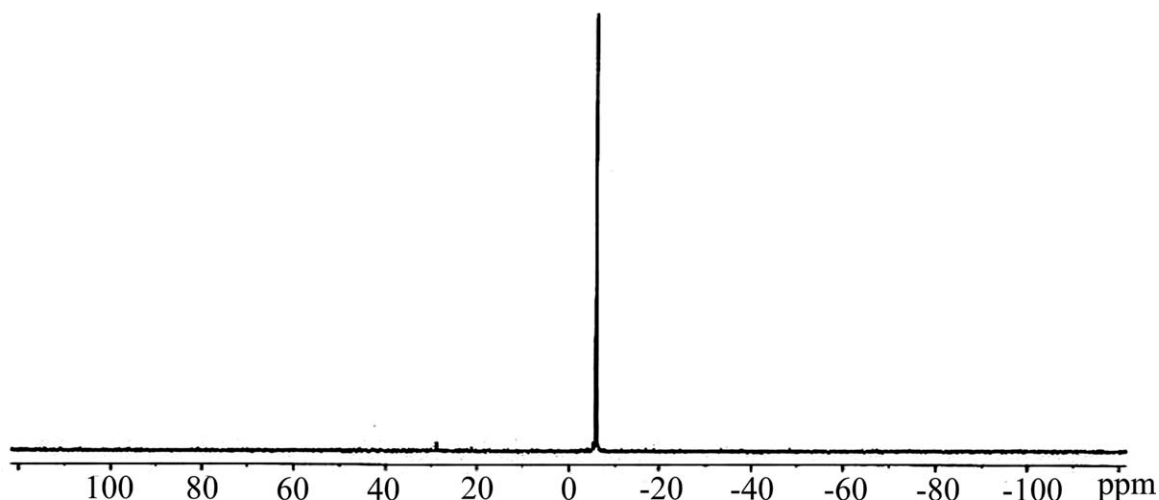


Figure 4. ^{31}P NMR spectrum of PPPO.

China) according to ISO4589-1984 standard. Dimensions of all samples were $130 \times 6.5 \times 3 \text{ mm}^3$.

Vertical burning (UL-94) tests were carried out on a CZF-2-type instrument (Jiangning Analysis Instrument, China) with the dimension of $130 \times 13 \times 3 \text{ mm}^3$ and $130 \times 13 \times 1.6 \text{ mm}^3$ according to UL-94 test standard. UL-94 testing results were carried out for burning ratings V-0, V-1, or V-2. V-0 rating corresponds to the best flame retardancy of polymeric materials.

Cone Calorimetry

The combustion behavior under ventilated conditions was measured using a Fire Testing Technology cone calorimeter

(West Sussex, UK), in conformance with ISO 5660-1 standard. The samples were firstly backed with aluminium foil and then mounted in the frame. Finally, the grid was put on the surface of the sample. Samples with size of $100 \times 100 \times 3 \text{ mm}^3$ were exposed to cone at a heat flux of 50 kW m^{-2} .

Scanning Electron Microscopy

Morphological studies on the residual chars were conducted using a FEI QUANTA-200 (Eindhoven, Netherlands) scanning electron microscopy (SEM) at an acceleration voltage of 15 kV. The chars were adhered to a copper plate, and then coated with gold for imaging.

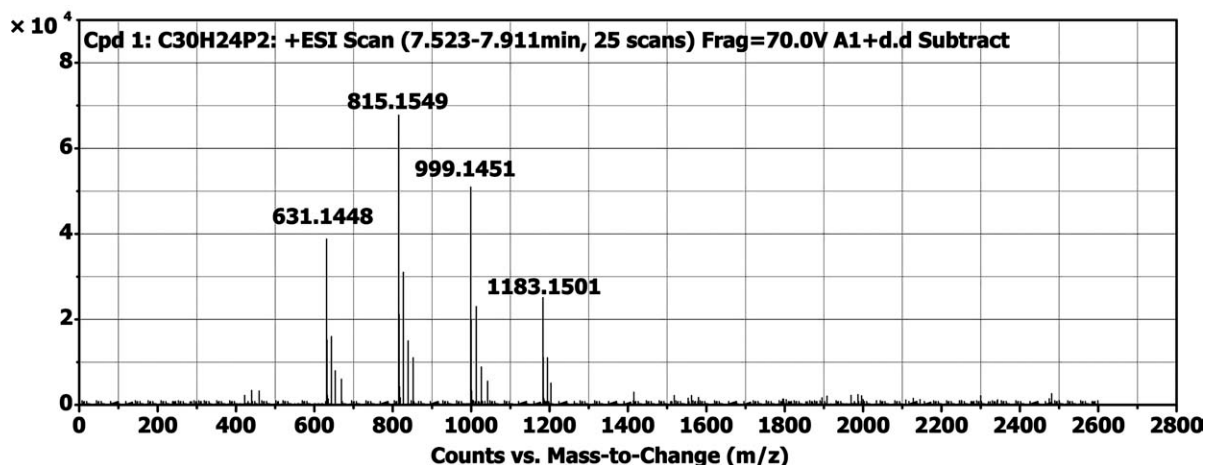
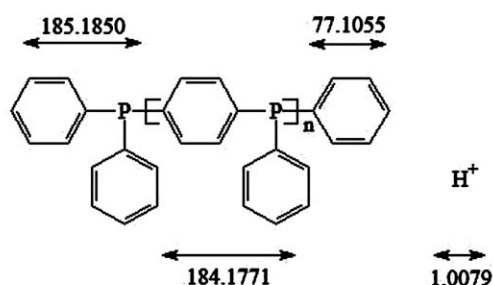


Figure 5. MS of PPPO.

Table I. Results of Flame Retardancy Test for PC and PC/PPPO System

Samples	LOI (%)	UL-94 rating			
		3.0 mm	Dripping	1.6 mm	Dripping
PC	28.1	V-2	Yes	No rating	Yes
PC/1 wt % PPPO	28.6	V-2	Yes	No rating	Yes
PC/3 wt % PPPO	30.2	V-2	Yes	V-2	Yes
PC/5 wt % PPPO	32.4	V-2	Yes	V-2	Yes
PC/6 wt % PPPO	34.1	V-0	No	V-2	Yes
PC/8 wt % PPPO	36.3	V-0	No	V-0	No

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) data were obtained using a Perkin Elmer Pyris 1 thermal analyzer (Massachusetts, USA). A heating rate of $10^{\circ}\text{C min}^{-1}$ was used. Samples (2–4 mg) were placed in a standard platinum pan and heated from 50 to 800°C . The sample compartment was purged with N_2 and air at 20 mL min^{-1} during analysis. All thermal degradation data were obtained from the TGA and derivative thermogravimetric analysis (DTG) curves.

Mechanical Properties Test

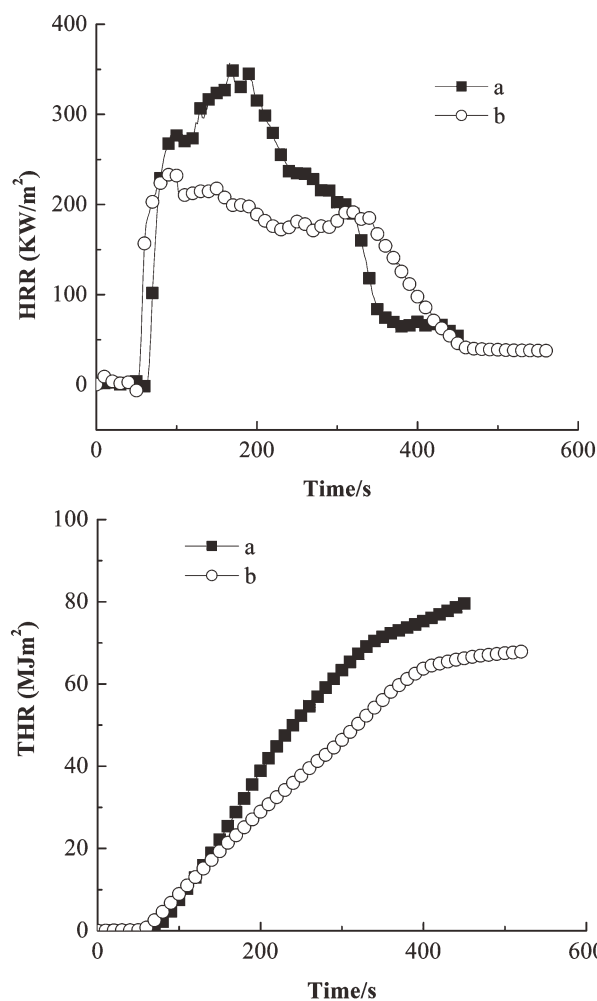
Tests of tensile strength, flexural strength and Izod impact of all samples were performed by Regeer computer controlled mechanical instrument (Shenzhen, China) and Notched Izod impact instrument (Chengde, China), respectively, according to ASTM standards. Dimensions of samples were $150 \times 10 \times 4 \text{ mm}^3$. At least five specimens were tested for each sample and the average values were reported.

Water Resistance Test

Samples of PC and PC/PPPO were kept in 70°C water and the time lasted 1 to 7 days. Then the samples were dried at 80°C for 3 days. The water resistance was monitored in terms of mass loss, flame retardancy and mechanical properties. Mass loss was tested with the dimensions of $50 \times 50 \times 1 \text{ mm}^3$. Dimensions of samples for flame retardancy and mechanical properties tests were the same to that of above tests.

Table II. Cone Calorimetric Data Obtained with a Heat Flux of 50 kW m^{-2}

Sample	PC	PC/6 wt % PPPO
TTI (s)	58	52
PHRR (kW m^{-2})	356.9	234.8
THR (MJ m^{-2})	79.8	68.3
t_{PHRR} (s)	166	98
ASEA ($\text{m}^2 \text{ kg}^{-1}$)	751.7	678.5
AMLR (g s^{-1})	0.093	0.067

**Figure 6.** HRR and THR curves of PC and PC/6 wt % PPPO: (a) PC and (b) PC/6 wt % PPPO.

RESULTS AND DISCUSSION

Synthesis and Structure Characterization of Phenylene Phenyl Phosphine Oligomer

As indicated above, under argon gas atmosphere, PPPO was prepared in two steps with a yield of 59.8%. First, 1, 4-dibromobenzene was reacted with *n*-butyl lithium to give dilithium benzene. It was a process of lithium-halogen exchange. In the second step, dilithium agent, as nucleophiles, was reacted with dichlorophenyl phosphine to give PPPO.

Chemical structure of PPPO was characterized with FTIR, ^1H , ^{13}C , and ^{31}P NMR and MS analysis. In Figure 1, the infrared spectrum contains characteristic absorptions at 3067 and 3054 cm^{-1} for the aromatic C-H stretching, 1584 and 1485 cm^{-1} for the phenyl nucleus, 1433 cm^{-1} for the P-C stretching vibration.

The ^1H NMR spectrum of PPPO is shown in Figure 2. The Peaks between 7.21 and 7.26 ppm corresponded to the protons (a) of the benzene ring. The signal from 7.31 to 7.33 ppm was attributed to protons (b) of the benzene ring. Figure 3 presented the ^{13}C NMR spectrum of PPPO. The peaks at 128.5 – 128.8 ppm and 133.5 – 134.0 ppm were presented carbon atoms

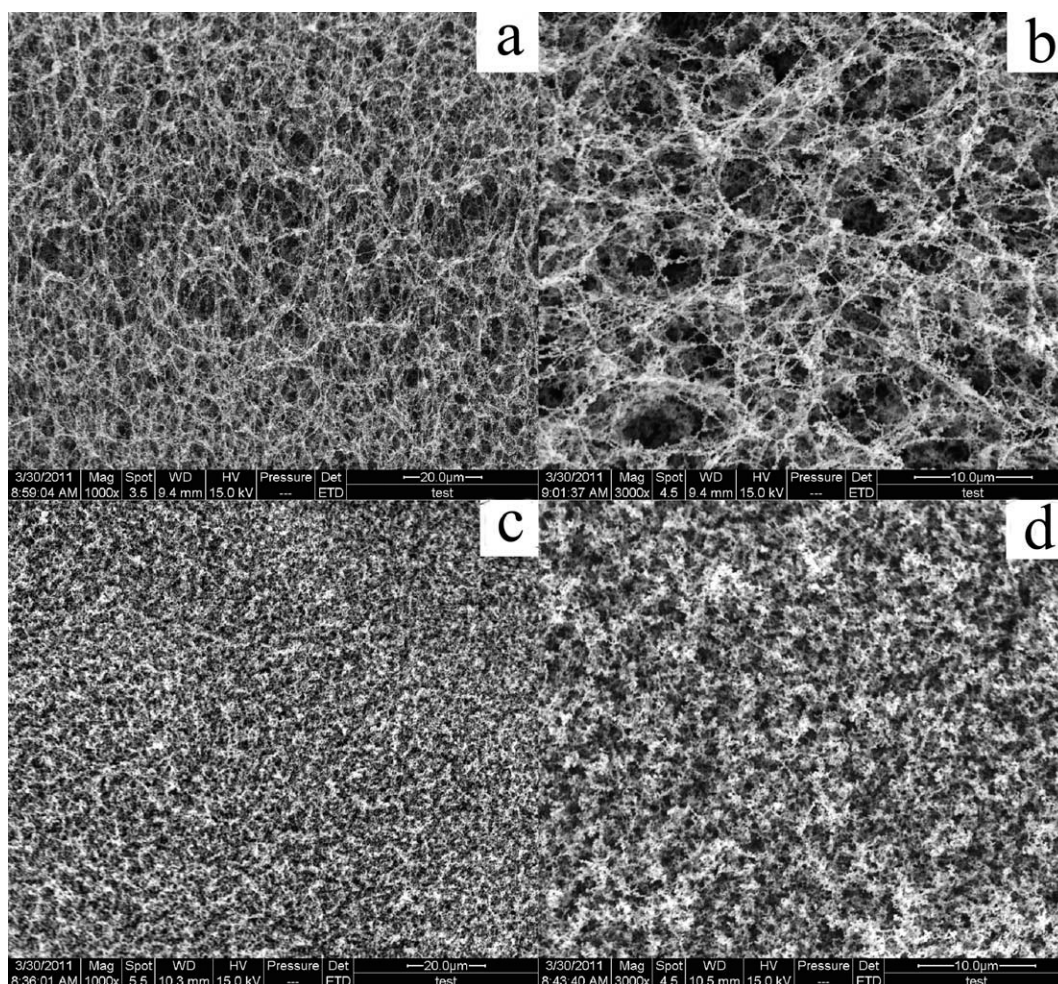


Figure 7. SEM of the char layer from combustion: (a) PC magnified 1000 times, (b) PC magnified 3000 times, (c) PC/6 wt % PPPO magnified 1000 times, and (d) PC/6 wt % PPPO magnified 3000 times.

(a) and (b) in the benzene rings, respectively. As shown in Figure 4, the ^{31}P NMR spectrum contained a single resonance at -5.2 ppm suggesting that the environment was similar for most of the P nuclei.

The mass spectrum of the compound is displayed in Figure 5. It can be seen that $m/z = 631.1, 815.1, 999.1,$ and 1183.1 corresponded to $M_n H^+$, where M_n is oligomer molecular weight with different degree of polymerization. All the information above was consistent with the expected molecular structure.

Flame Retardancy

Results of the flame retardancy tests for PC and PC/PPPO system are presented in Table I. The LOI value of PC was 28.1%. With increase of PPPO contents the LOI values increased for PC/PPPO system. For example, when PPPO was increased to 5 wt %, the LOI value increased to 32.4%. The LOI value of PC/6 wt % PPPO was 34.1%. PC/6 wt % PPPO passed the vertical burning test (UL-94) V-0 rating with 3.0 mm sample, but it merely passed V-2 rating when the sample thickness was decreased to 1.6 mm. When the PPPO loading increased to 8 wt %, the LOI value reached 36.3%, and the samples with 1.6 and 3.0 mm thickness can successfully pass V-0 rating. To date,

numerous phosphorus compounds has been used to improve the flame retardancy of PC.^{16,18,26,27} For example, Liu et al. reported that PC/10 wt % RDP system can pass the V-0 rating with 3.0 mm sample; PC/8 wt % S-BDP/0.4%

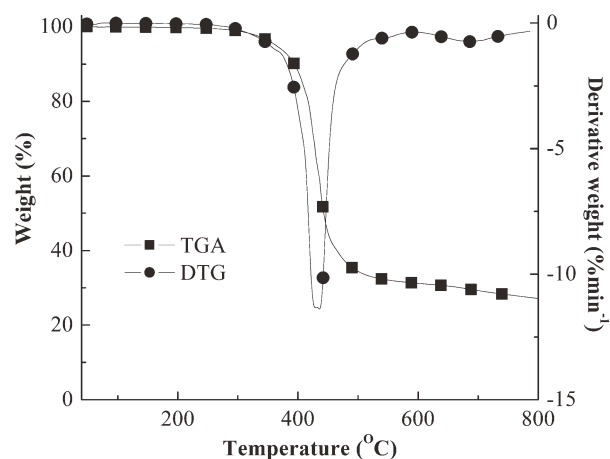


Figure 8. TGA and DTG curves of PPPO in N_2 .

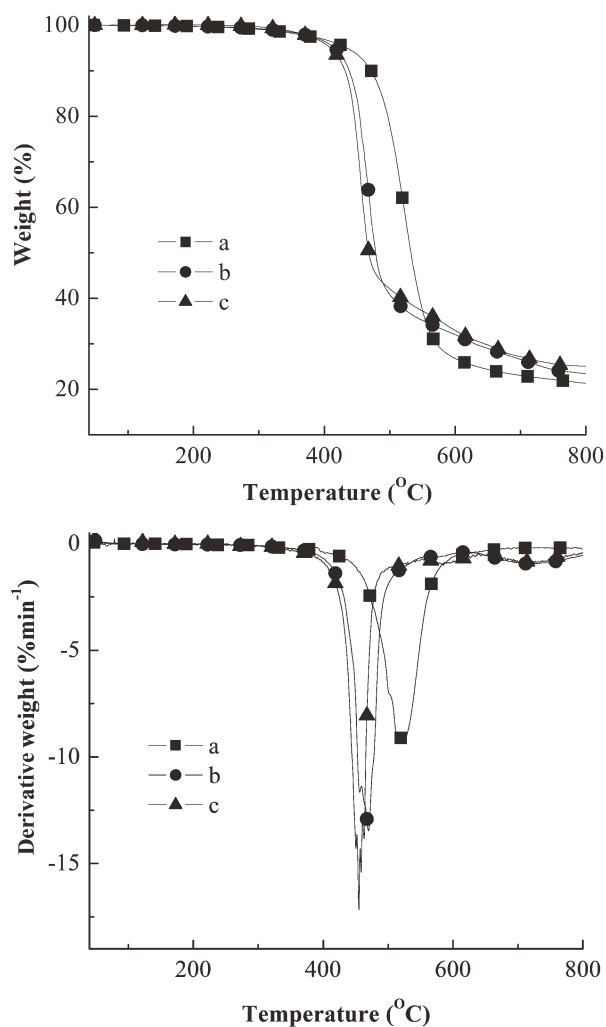


Figure 9. TGA and DTG curves of PC and PC/PPPO system in N_2 : (a) PC, (b) PC/6 wt % PPPO, and (c) PC/8 wt % PPPO.

polytetrafluoroethylene system material can pass the V-0 rating with 3.0 mm sample, which has been established by Feng et al.; Jang et al. reported that PC/12 wt % triphenylphosphate can pass the V-0 rating with 3.0 mm sample and Hoang et al. reported that PC/7.5 wt % pentaerythritol bis(phenyl phosphonate) can pass the V-0 rating with 3.0 mm sample. However, the previous research on the flame retarded PC with phosphorus compounds showed high loading and low efficiency of flame retardancy. Compared with the reported results, our synthesized PPPO is a high efficient flame retardant, when the loading of PPPO is only 6 wt %, the PC sample with 3.0 mm could pass the V-0 rating.

Although small-scale tests such as LOI and UL-94 are useful in highlighting and ranking flame retardancy in polymers, they are not reliable indicators of likely performance in a real fire. For this type of analysis, cone calorimeter is becoming the method of choice. Some parameters provided by cone calorimeter such as time to ignition (TTI), heat release rate (HRR), total heat released (THR), peak heat release rate (PHRR), time of peak heat release rate (t_{PHRR}), average mass loss rate (AMLR), and

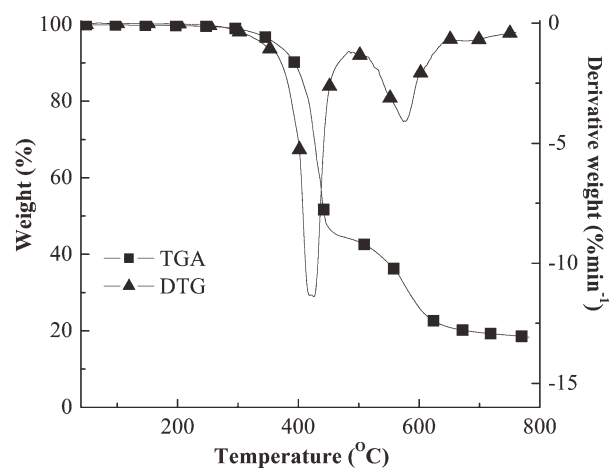


Figure 10. TGA and DTG curves of PPPO in air.

average specific extinction area (ASEA, a measure of smoke) were summarized in Table II and Figure 6.

As shown in Table II, TTI was shorter compared to that of PC for PC/6 wt % PPPO. This may be the fact that PPPO decomposes in air and forms phosphoric and polyphosphoric acids, which may accelerate the thermal decomposition of PC. Meanwhile, ASEA and AMLR reduced.

Figure 6 shows that the HRR of PC increased rapidly for the initial 100 s, after which the rate of increase was somewhat slower. The 356.9 kW m^{-2} PHRR of PC occurred at 166 s. Subsequently, the HRR decreased until 450 s. The initial HRR of PC/6 wt % PPPO increased at a fast rate. PHRR occurred in a shorter time than did that of PC. PHRR and t_{PHRR} of PC/6 wt % PPPO were 234.8 kW m^{-2} and 98 s, respectively. The reduction of PHRR indicated that a cohesive char layer was formed during combustion which acted as an insulating barrier between the fire and PC.^{28,29} It is observed from Figure 6 that at the end of the test, PC released a total heat of 79.8 MJ m^{-2} , whereas PC/6 wt % PPPO released 68.3 MJ m^{-2} . The lower THR values indicated that a part of PC/6 wt % PPPO had not completely combusted, possibly undergoing a char-forming process. It is believed that lower HRR and THR related to condensed phase and contributed to better flame retardancy.

Figure 7 shows SEM images of the char layers after cone calorimeter test. A loose, porous structure formed on the surface of PC [Figure 7(a, b)]. This structure cannot provide a good barrier to the transfer of heat and prevent the underlying PC from degradation and combustion. A very distinct difference in

Table III. TGA Data of PC/PPPO System in N_2

Samples	T_{initial} ($^{\circ}\text{C}$)	T_{max} ($^{\circ}\text{C}$)	Char residues at 800°C (%)
PPPO	363.2	435.7	27.2
PC	433.9	523.9	21.3
PC/6 wt % PPPO	415.3	456.3	23.4
PC/8 wt % PPPO	409.1	455.1	25.1

Table IV. TGA Data of PC/PPPO System in Air

Samples	T_{initial} (°C)	T_{max1} (°C)	T_{max2} (°C)	Char residues at 800°C (%)
PPPO	379.2	425.5	577.3	18.2
PC	428.2	500.6	591.7	0
PC/6 wt % PPPO	406.1	455.6	611.6	8.9
PC/6 wt % PPPO calculated	423.7	494.9	585.2	1.1
PC/8 wt % PPPO	398.1	443.1	628.3	10.1
PC/8 wt % PPPO calculated	420.7	496.3	588.7	1.4

appearance was observed for the charred samples of PC/6 wt % PPPO. The surfaces of the samples were covered by a continuous and dense char layer [shown as Figure 7(c, d)]. A high-quality char can effectively form a protective layer to stop the propagation of heat and oxygen to melt and polymer matrix during combustion.

Thermal Degradation Properties

In order to investigate effect of PPPO on thermal degradation property of PC during combustion, TGA in N_2 and air is tested. TGA and DTG curves for PPPO and PC/PPPO systems are shown in Figures 8–10 and 12. T_{initial} is defined as the temperature at which 5% weight loss occurs and T_{max} is defined as the temperature at maximum weight loss rate. The thermal decomposition data are presented in Tables III and IV.

PPPO decomposition occurred in one step under N_2 atmosphere. As shown in Figure 8, PPPO did not show any significant weight loss at temperatures below 360°C. However, it occurred with rapid weight loss between 380 and 480°C. T_{initial} and T_{max} of PPPO were 363.2 and 435.7°C, respectively. The residue of PPPO at 800°C in N_2 atmosphere was 27.2%, indicating that PPPO itself possessed excellent charring ability.

The thermal decomposition of PC, PC/6 wt % PPPO and PC/8 wt % PPPO system occurred in one step in N_2 , as revealed in Figure 9. T_{initial} and T_{max} of PC were 433.9 and 523.9°C, respectively. The char residue at 800°C was 21.3%. The addition of PPPO effectively influenced the thermal degradation of PC. When the loading of PPPO was 6 wt %, T_{initial} and T_{max} decreased to 415.3 and 456.3°C, respectively, but the residual char yield increased to 23.4%. Similarly, T_{initial} and T_{max} of PC/8 wt % PPPO dropped to 409.1 and 455.1°C, respectively, but the residual char yield increased to 25.1%.

Unlike under N_2 atmosphere, PPPO decomposition occurred in two distinct steps in air. As shown in Figure 10, PPPO did not show any significant weight loss at temperatures below 350°C. However, it underwent rapid weight loss between 400 and 500°C. T_{initial} , T_{max1} , and T_{max2} of PPPO were 379.2, 425.5, and 577.3°C, respectively. Lower T_{initial} may be attributed to the fact that the P-C bond is less stable than the C-C bond. Typical bond energies of the P-C and the C-C bond are 260 and 347 kJ mol⁻¹, respectively. P-C bonds breaks firstly, then C-C bonds disconnects at high temperatures. The residue of PPPO at 800°C in air atmosphere was 18.2%, indicating that PPPO had

very effective charring ability. The FTIR spectra of the residual char for PPPO following the thermal degradation in air from room temperature to 530°C are given in Figure 11. The absorption band at 1433 cm⁻¹ decreased and disappeared from 370 to 450°C. This confirmed that P-C bond breaks. At the same time, the broad peaks at 3400, 1200, and 980 cm⁻¹ appeared. The peaks at 3400 and 980 cm⁻¹ were attributed to the stretching vibration of P-OH groups and the peak at 1200 cm⁻¹ was attributed to P=O.³⁰ It is a process of thermo-oxidative decomposition. The FTIR spectra provided positive evidence that PPPO produced phosphoric and polyphosphoric acids during thermal degradation in air, which served as the dehydration agents and driving force for the formation of the char layer by carbonization. The previous research on phosphorus containing flame retardants showed low thermal stability under air atmosphere. For example, Bright et al. reported that TGA data of triphenyl phosphate and resorcinol bis(diphenyl phosphate) were tested in air, and T_{initial} of them were only 219 and 299°C, respectively.³¹ PPPO has two degradation stages: the first stage occurred from 370 to 450°C, and the second stage occurred from 450 to 600°C, as revealed in Figure 10. As shown in Figure 11 of the FTIR spectra, when the temperature reached to 370°C, the peak of P=O absorption appeared at 1200 cm⁻¹. Combined with the results of TGA and FTIR spectra, we can deduce that PPPO remained as a phosphine and did not occur any decomposition before 370°C. The T_{initial} of the synthesized PPPO was

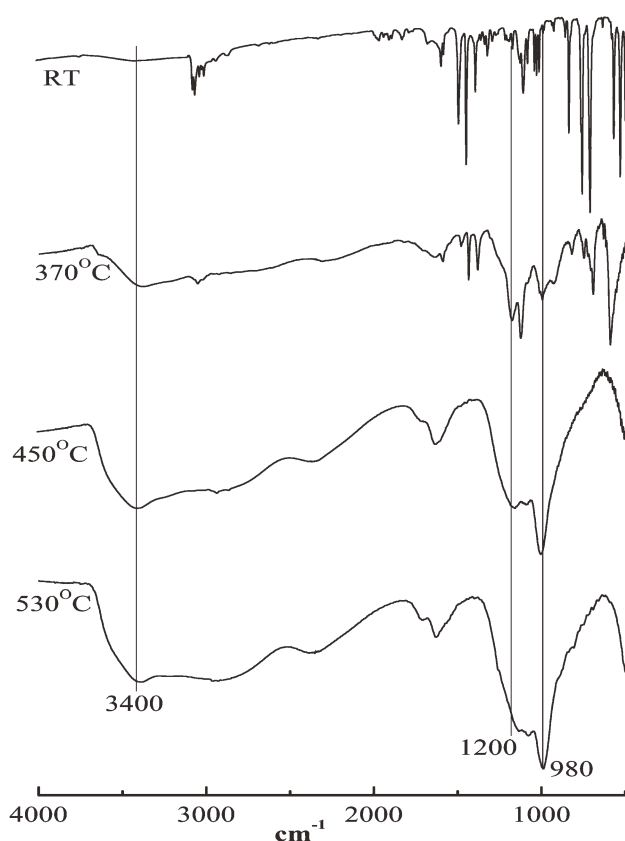


Figure 11. FTIR spectra of PPPO during the thermal degradation in air from room temperature to 530°C.

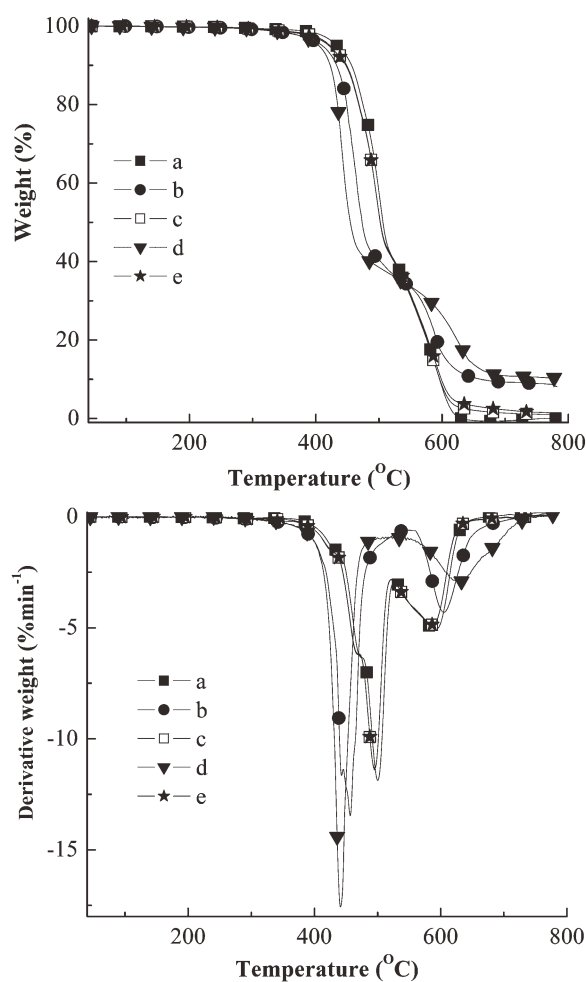


Figure 12. TGA and DTG curves of PC and PC/PPPO system in air: (a) PC, (b) PC/6 wt % PPPO, (c) PC/6 wt % PPPO calculated, (d) PC/8 wt % PPPO, and (e) PC/8 wt % PPPO calculated.

379.2°C. Compared with the reported results, PPPO possessed high thermal stability in air.

As shown in Figure 12, the thermal decomposition of all the samples occurred in two steps. As reported,^{4,32} the first step corresponds to oxidative decomposition of the polymer, while the second step corresponds to oxidative decomposition of the char formed in the first step. T_{initial} , T_{max1} , and T_{max2} of PC were 428.2, 500.6, and 591.7°C, respectively, remaining no char residue at 800°C.

The addition of PPPO influenced the thermal degradation of PC effectively. When 6 wt % PPPO was added, T_{initial} and T_{max1} decreased to 406.1 and 455.6°C, respectively, but the residual char yield increased to 8.9%. The shift in degradation temperatures may be because the PPPO could undergo thermo-oxidative degradation and form phosphoric and polyphosphoric acids at lower temperature. The acids accelerated the decomposition of PC. This phenomenon was reported when tri-*n*-butylphosphine oxide and triphenyl phosphine were used as flame retardant additives for poly (methyl methacrylate) and epoxy resins, respectively, and TGA data were tested in air.^{33,34} T_{max2}

increased to 611.6°C. This reflected that the thermal stability of the char layer formed during oxidative degradation is enhanced. PC/8 wt % PPPO exhibits a similar behavior in air. T_{initial} and T_{max1} drops to 398.1 and 443.1°C, respectively, but T_{max2} and the residual char yield increased to 628.3°C and 10.1%, respectively. The thermal decomposition of PC, PC/6 wt % PPPO, and PC/8 wt % PPPO system occurred in one step in N_2 , and the char yields were 21.3, 23.4, and 25.1%, respectively. However, PC, PC/6 wt % PPPO and PC/8 wt % PPPO system decomposed in two steps under air. First, PPPO occurred thermo-oxidative degradation and formed phosphoric and polyphosphoric acids at lower temperature. The acids promoted the decomposition of PC and char-forming. Secondly, the char layer occurred during oxidative degradation. The residual char yields of PC, PC/6 wt % PPPO, and PC/8 wt % PPPO system were only 0, 8.9, and 10.1%, respectively, due to the existence of air.

The calculated TGA and DTG curves of PC/6 wt % PPPO and PC/8 wt % PPPO in air are also illustrated in Figure 12. Both of the calculated curves were similar. The Differences between experimental and calculated curves can be detected clearly. The experimental curves were below the calculated curves from 250 to 540°C. Thus PC/6 wt % PPPO and PC/8 wt % PPPO decomposed more quickly than a simple sum of each ingredient. The experimental curves were above the calculated curves since 540°C. It revealed that the char layer formed during oxidative degradation decomposes more slowly than that of a simple sum of each ingredient. Therefore, it demonstrated that the interactions between PC and PPPO occurred in oxidative decomposition, and the interactions were rather positive for the promotion of decomposition and char-forming.

Mechanical Properties

Table V summarizes the mechanical properties of the PC and PC/PPPO systems. The tensile, flexural, and Izod impact strength of PC were 59.1 MPa, 74.9 MPa, and 14.1 kJ m², respectively. The addition of PPPO showed a slight impact on the tensile and the Izod impact strength of PC. When PPPO content increased, the tensile and the Izod impact strength decreased, which attributed to the poor compatibility between PPPO and PC, and resulting in macromolecular chains of PC broken. So the tensile and the Izod impact strength of PC/PPPO systems decreased. This phenomenon was also reported by Liu et al., in which the mechanical properties of flame

Table V. Mechanical Properties of PC and PC/PPPO Systems

Samples	Mechanical properties		
	Tensile strength (MPa)	Flexual strength (MPa)	Izod IMPACT Strength (kJ m ²)
PC	59.1 ± 0.2	74.9 ± 0.1	14.1 ± 0.3
PC/1 wt % PPPO	58.8 ± 0.1	75.0 ± 0.3	13.9 ± 0.3
PC/3 wt % PPPO	58.2 ± 0.2	75.8 ± 0.2	13.5 ± 0.2
PC/5 wt % PPPO	57.1 ± 0.4	76.9 ± 0.3	12.1 ± 0.3
PC/6 wt % PPPO	56.7 ± 0.1	77.2 ± 0.2	11.9 ± 0.1
PC/8 wt % PPPO	55.3 ± 0.1	78.9 ± 0.2	10.5 ± 0.1

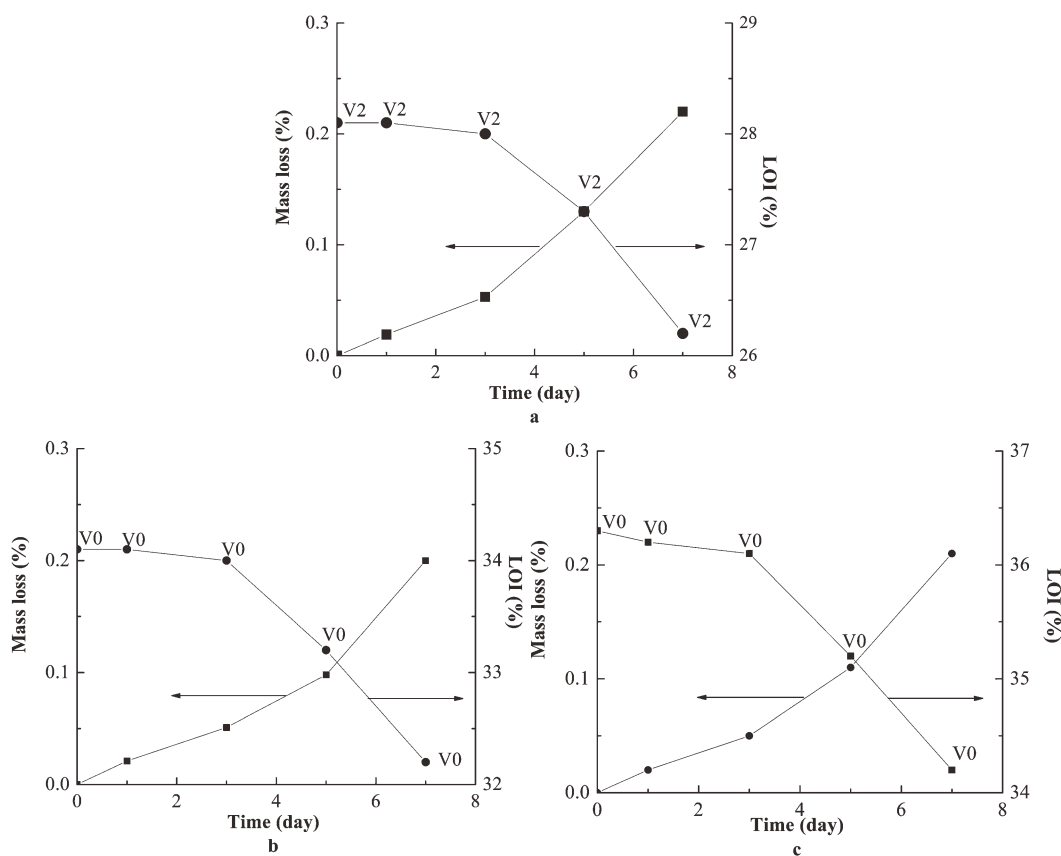


Figure 13. Effect of the time on mass loss and flame retardancy of PC/PPPO system during water resistance test: (a) PC, (b) PC/6 wt % PPPO, (c) PC/8 wt % PPPO, vertical burning tests: (a,b) with 3.0 mm samples and (c) with 1.6 mm samples.

retarded PC was tested.¹⁶ The decrease of the tensile and the Izod impact strength was marginal when PPPO was added from 1 to 3 wt %. With increasing PPPO content to 6 wt %, the tensile and the Izod impact strength of PC slightly decreased to 56.7 MPa and 11.9 kJ m², respectively. For PC/8 wt % PPPO, the tensile and the Izod impact strength were 55.3 MPa and 10.5 kJ m², respectively.

The addition of PPPO showed a positive impact on the flexural strength. When PPPO content increased, the flexural strength enhanced. For example, with increasing PPPO content to 6 wt %, the flexural strength of PC increased to 77.2 MPa. The flexural strength of PC increased to 78.9 MPa in the presence of 8 wt % PPPO. The addition of PPPO could increase the rigidity of PC, which resulting in the flexural strength of PC increased.

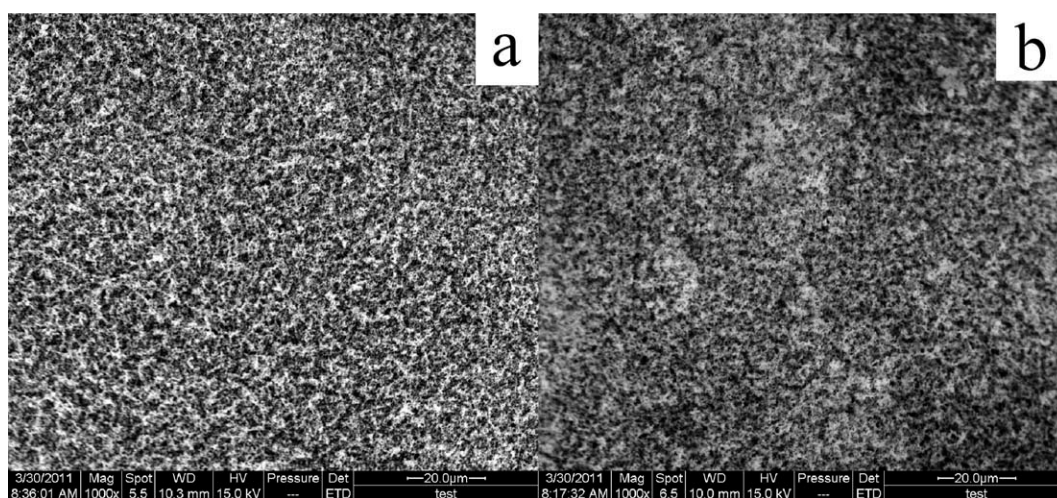


Figure 14. SEM of the char layer of PC/6 wt % PPPO from combustion before and after water resistance test: (a) before test and (b) after test.

Table VI. Mechanical Properties of PC and PC/PPPO System During Water Resistance Test

Samples	Time (days)	Mechanical properties		
		Tensile strength (MPa)	Flexural strength (MPa)	Izod impact strength (kJ m ⁻²)
PC	0	59.1 ± 0.2	74.9 ± 0.1	14.1 ± 0.3
	1	59.1 ± 0.1	74.7 ± 0.2	14.1 ± 0.2
	3	58.8 ± 0.1	74.7 ± 0.2	13.9 ± 0.3
	5	58.1 ± 0.2	73.9 ± 0.1	13.3 ± 0.2
	7	56.7 ± 0.1	72.7 ± 0.3	12.1 ± 0.1
PC/6 wt % PPPO	0	56.7 ± 0.4	77.2 ± 0.3	11.9 ± 0.3
	1	56.7 ± 0.3	77.1 ± 0.1	11.9 ± 0.1
	3	56.6 ± 0.2	77.0 ± 0.2	11.8 ± 0.1
	5	55.3 ± 0.1	76.1 ± 0.2	11.1 ± 0.2
	7	54.5 ± 0.2	75.0 ± 0.3	10.2 ± 0.3
PC/8 wt % PPPO	0	55.3 ± 0.1	78.9 ± 0.2	10.5 ± 0.1
	1	55.3 ± 0.1	78.8 ± 0.1	10.5 ± 0.1
	3	55.3 ± 0.2	78.7 ± 0.2	10.3 ± 0.3
	5	54.5 ± 0.3	77.8 ± 0.2	9.8 ± 0.2
	7	53.1 ± 0.1	76.5 ± 0.4	8.8 ± 0.2

This phenomenon was also reported by Liu et al. when the mechanical properties of flame retarded PC was tested.¹⁶ The previous research on the flame retarded PC with phosphorus compounds showed high loading, which deteriorate the mechanical properties of polymer matrix. For example, Liu et al. reported that the Izod impact strength of PC/10 wt % RDP system decreased by 78.7%, compared to that of PC.¹⁶ However, the Izod impact strength of PC/8 wt % PPPO only decreased by 25.5% in our present work. It is demonstrated that PPPO possessed excellent compatibility with PC and resulted slightly harmful effect on the mechanical properties of PC.

Water Resistance

Water resistance of engineering resins flame retarded with additives is of some concern because of exudation. Exudation of the additive most likely deteriorates its flame retardancy and mechanical properties because of greater exposure to the moisture condition.^{35,36}

Figure 13 shows effect of the time on mass loss and flame retardancy of PC, PC/6 wt % PPPO and PC/8 wt % PPPO. In time of 3 days, the mass loss was marginal and had not effect on its flame retardancy for all the samples. After 7 days of the test, mass loss of PC was 0.2% and the LOI value dropped by 5.8%. The reduction was similar to that of PC/6 wt % PPPO and PC/8 wt % PPPO. For example, after the test, the mass loss of PC/6 wt % PPPO was 0.2% and the LOI value dropped by 5.9%. Although the LOI value decreased, PC/6 wt % PPPO with 3.0 mm samples and PC/8 wt % PPPO with 1.6 mm samples kept V-0 rating during test. Figure 14 shows SEM of the char layer of PC/6 wt % PPPO from combustion before and af-

ter water resistance test. The char layer kept continuous and dense. It indicated that the water resistance test did not seriously deteriorate the char layer formed after combustion. So the sample kept good flame retardancy after the test.

Table VI lists effect of the time on mechanical properties of PC, PC/6 wt % PPPO, and PC/8 wt % PPPO. It is clearly that the mechanical properties decreased with the extension of time. After 7 days, the tensile, flexural, and izod impact strength of PC reduced by 4.1, 3.0, and 14.2%, respectively. The reduction was similar to that of PC/6 wt % PPPO and PC/8 wt % PPPO. For example, after the test, the tensile, flexural, and izod impact strength of PC/6 wt % PPPO reduced by 3.9, 2.8, and 14.3%, respectively.

Up to now, the water resistance of flame retarded PC has never been reported. In this study, results of the test indicated that the deterioration of the flame retardancy and mechanical properties were attributed to PC itself. PC could hydrolyze and be aging during long time test.³⁶ So PPPO possesses excellent water resistance in PC.

CONCLUSION

A novel phosphorus-containing flame retardant, PPPO, was successfully synthesized and the chemical structure was well confirmed by Fourier transform infrared spectroscopy, ¹H, ¹³C, ³¹P nuclear magnetic resonance spectroscopy, and mass spectrometer. PPPO was used as flame retardant for PC. The LOI value of PC/PPPO system increased with the increasing of the loading amount of PPPO. The LOI value of PC/6 wt % PPPO reached 34.1%, and the sample with the thickness of 3.0 mm can pass vertical burning test V-0 rating. When the loading amount of PPPO increased to 8 wt %, the LOI value reached 36.3%, and the samples with 3.0 and 1.6 mm both successfully passed V-0 rating. TGA data revealed that PPPO possessed excellent ability of char forming and it accelerated decomposition and char forming of PC. A rich char layer could be observed through SEM micrographs, which can prevent the transfer of heat and oxygen into melt polymer matrix. The result of mechanical properties test indicated that the negative effects of PPPO on the tensile and Izod impact strength of PC were slight. Especially, the flexural strength of PC increased due to the addition of PPPO. The PC/PPPO system possessed excellent water resistance, and still remained with excellent flame retardancy and mechanical properties after water resistance testing.

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