Effect of Talc on Thermal Stability and Flame Retardancy of Polycarbonate/PSBPBP Composite

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ABSTRACT: A novel flame retardant poly(3-aminopropyl methylsiloxane bis(3-hydroxy phenyl spirocyclic pentaerythritol bisphosphate)) (PSBPBP) in combination with talc was blended into polycarbonate (PC) by melt compounding. The flame retardancy and thermal stability of PC/PSBPBP/talc composites were investigated by limiting oxygen index (LOI) test, UL-94 rating test, thermogravimetric analysis (TGA), Raman spectroscopy (RS), and scanning electron microscope (SEM). The mechanical properties were also measured in this work. Increasing talc content leads to observed improvement on flame retardancy of PC composites. LOI value of PC/PSBPBP/10 wt % talc system was 34, and this system passed V0 rating in the UL-94 test. The char yield at 700°C was 28.2% and the onset decomposition temperature shifted up to 540°C for PC/10% PSBPBP/10% talc system in TGA. In the Raman measure, the R value and G linewidth of PC/PSBPBP with 10 wt % talc composite increased to 1.41 and 65 cm^{-1} from 1.12 and 43 cm^{-1} of pure PC, respectively. The Raman results suggest that the char residue of PC/PSBPBP with talc composites was denser and had better barrier property, which is agreement with the SEM results. Besides, talc had no remarkable influence on the mechanical properties of PC/PSBPBP composites. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 3167–3174, 2012

Key words: polycarbonates; flame retardancy; thermal properties; Raman spectroscopy

INTRODUCTION

Polycarbonate (PC) has been widely used in electronic appliance, aeronautics and astronautics, mechanics, and automobile industries due to its high optical clarity, high heat deformation temperature, toughness, electrical insulation, and weathering resistance. However, the flame retardancy of pure PC was not enough for its further application.[1,2]

There are some methods of improving flame retardancy of PC, including halogenated and halogen-free flame retardants (FRs). Among these, halogenated FRs have environmental limitations, because they may generate toxic substances such as dioxin derivatives during combustion.[3] Organophosphorus compounds show good ability as FRs by forming char layers, which acts as a physical barrier to heat transfer from flame to polymer and retards the release of combustible gases.[4,5] Triphenyl phosphate (TPP), resorcinol bis(biphenyl phosphate) (RDP), and bisphenol A bis(biphenyl phosphate) (BDP) are common phosphorus FRs.[6] The inorganic FR additives, such as talc, magnesium hydrate (Mg(OH)$_2$), and zinc borate (ZB) have been proved to be effective synergetic FRs in many reports as they are halogen-free, nontoxic, nonvolatile, with good stability and environmental protection.[7,8] Talc is the major constituent of rocks known as soapstone or steatite.[9] Its major ingredient is a hydrated magnesium silicate mineral. Kim found that the flame retardancy induced by Mg(OH)$_2$ can be effectively enhanced by the addition of zinc borate and talc.[10] Longerey reported that talc could significantly delay the ignition of these samples.[11] The unique features of talc are softness, lubricity, and oleophilicity with excellent wetting and dispersion in plastics and other organics. In plastics, the addition of talc improves their heat distortion temperature, dimensional stability, scratch resistance, and impact resistance.[12] Durin reported that talc could build a layer acting as mass diffusion barrier for volatile combustible systems from the polymer degradation.[13] Talc cannot be exfoliated by using cationic surfactant due
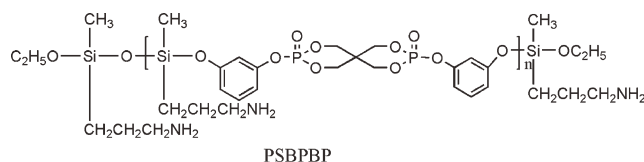
Scheme 1 The structure of FR PSBPBP.

to the absence of metallic cations between the layers which is different from montmorillonite, hectorite, or saponite; however, delamination can be achieved by mechanical treatments.[14,15] Laurent suggests that talc lamellar particles may have similar effects to those of clay layers in the material.[16]

A novel solid FR poly(3-aminopropyl methylsiloxane bis(3-hydroxyphenyl spirocyclic pentaerythritol bisphosphate) (PSBPBP) containing phosphorus, nitrogen, and silicon was synthesized successfully in the previous work.[17] In this study, novel FR PC composites had been prepared by blending PSBPBP and talc into PC resin to partly replace PSBPBP. Its thermal properties and flame retardancy were investigated by thermogravimetric analysis (TGA), LOI, and UL-94 tests. The structure and morphology of the intumescent char layer was analyzed by Raman spectra and SEM. Mechanical properties of FR PC/PSBPBP/talc systems were also measured.

EXPERIMENTAL

Materials

PC 201-15, general grade, medium viscosity (Dow Chemical Co., USA). Talc, average particle diameter, 7 μm (Shanghai Shuosi French White Co., French).

Preparation of FR PSBPBP

The synthesis of FR PSBPBP is according to the previous publications by our group.[17] First, bispirophosphorus chloride (SPDPC) was obtained after the reaction of pentaerythritol and phosphorus oxychloride with the ratio of 1 : 6 at 80°C for 12 h under nitrogen. Then, resorcinol was reacted with SPDPC in a ratio of 4 : 1 under nitrogen at 75°C for 12 h to obtain the intermediate bis(m-hydroxyphenyl spirocyclic pentaerythritol bisphosphate) (BPSPBP). Finally, the product PSBPBP (Scheme 1) was obtained by reacting BPSPBP and N-aminopropyl methyl diethoxy silane with the ratio of 3 : 5 at 75°C for 24 h.

Preparation of PC/PSBPBP/talc systems

Processing was done by mixing PC material with FR PSBPBP and different loading of talc in a Haake internal mixer at 220°C for 6 min. Then the samples were hot-pressed into sheets of suitable size for tests.

Measurements

TGA data were obtained at a heating rate of 10°C/min under nitrogen using a TA Q5000IR thermo gravimetric analyzer. In each case, a 10-mg sample was examined under a nitrogen flow rate of 40 mL/min at temperatures ranging from room temperature to 700°C.

Limiting oxygen index (LOI) was measured on sheets $100 \times 6.5 \times 3$ mm^3 according to the standard oxygen index test ASTM D 2863-77 as descried below:

$$LOI = \frac{[O_2]}{[O_2] + [N_2]} \times 100\%$$

$[O_2]$ and $[N_2]$ are the concentration of oxygen and nitrogen in a mixture of the two gases, respectively. UL-94 test was measured on sheets $127 \times 127 \times 1.6$ mm^3 according to ASTM D 635-77. The Raman spectra are performed at 633-nm line of an argon laser with a Thermo Fisher Scientific DXR laser Raman spectrometer at room temperature. The laser power was 4 mW and the spectral resolution of the apparatus was 2 cm^{-1}. Typical data acquisition times were in the range of 64 s. The morphology of char residue after LOI test was studied by scanning electron microscope (JHHT, SEM, and Hitachi S-520). The char residue was previously coated with a conductive gold layer. The tensile behavior of all samples was determined by an Instron tensile tester (Instron 4465) at room temperature. Izod impact strength was obtained through Ray–Ran test equipment.

RESULTS AND DISCUSSION

Thermal analysis

TGA is widely used to characterize the thermal stability of polymer materials. In this work, pure PC, PC/PSBPBP, and PC/PSBPBP/talc systems were studied by TGA. The TGA and DTG curves are presented in Figure 1. The data are visible in Table I.

For pure PC, the thermal degradation occurs around 450–550°C under nitrogen with a T_{onset} of 474°C and a T_{max} of 525°C. It was proposed that the main degradation pathway of PC follows chain scission of isopropylidene linkages and hydrolysis/alcoholysis of carbonate linkages. Carbonate linkages undergo rearrangement to form ether linkage or react with alcohol end groups to form char.[18] The char yield of pure PC was 21% at 700°C.

For PC/PSBPBP system, the T_{onset} decreased dramatically to 385°C. However, T_{max} increased to 537°C and the char yields slightly increased from 21 wt % to 23 wt % at 700°C compared with that of pure PC. It is assumed that the aromatic spriopolyphosphates in the FR PSBPBP decomposed in the earlier stage to
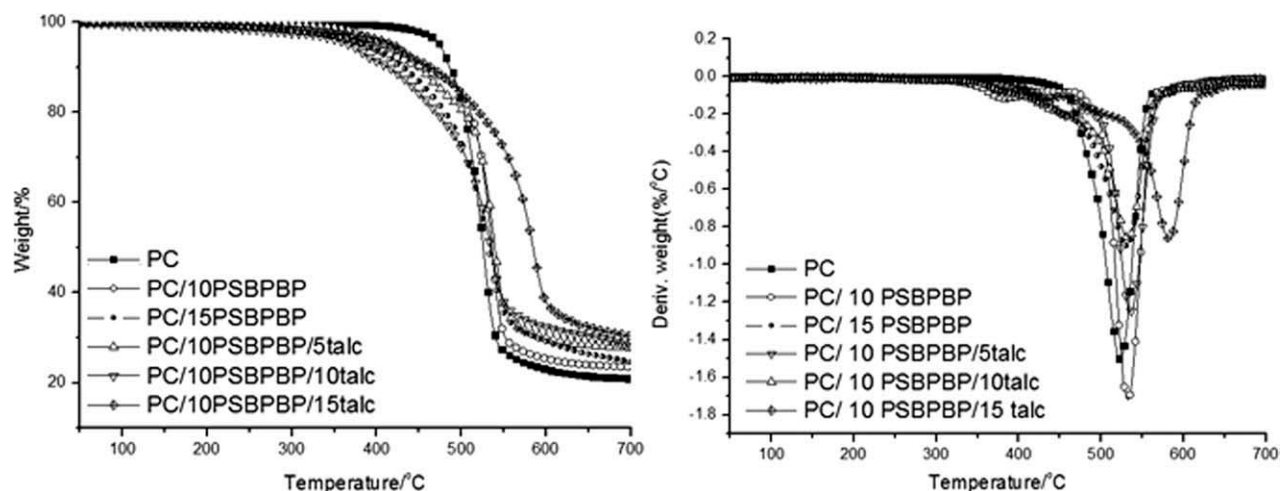
Figure 1 TGA and DTG curves of pure PC and PC composites.

form volatile substances such as water and PO. In the gas phase, the free radical, PO·could dilute the combustible gas and capture active free radicals to interrupt the flame.[19,20] The thermal stability of the PC/PSBPBP system were improved by the formation of phosphoric acid esters and phosphoric acid during the decomposition of PC/PSBPBP system at higher temperature, which could accelerate the char forming process by affecting the cross-linking reaction of PC.

When adding talc into the PC/PSBPBP system, the T_{onset} shifted up to higher temperature and the char yield of the composites increased with talc loading. From Table I, the char residue at 700°C increased to 27 and 28.2% after the combination with 5 and 10 wt % of talc, respectively. It showed that the thermal stability of PC/PSBPBP/talc system was better than PC/PSBPBP systems.

Fire performance

LOI and UL-94 ratings tests were employed to investigate the fire performance of pure PC, PC/PSBPBP, and PC/PSBPBP/talc systems. The results are listed in Figure 2 and Table II.

TABLE I
TGA Data of Pure PC and PC Composites

Samples	T_{onset}^{a} (°C)	T_{max}^{b} (°C)	Char yield (700°C, wt %)
PC	474	525	21.0
PC/10% PSBPBP	385	537	23.0
PC/15% PSBPBP	385	535	24.7
PC/10% PSBPBP/5% talc	403	536	27.0
PC/10% PSBPBP/10% talc	411	540	28.2
PC/10% PSBPBP/15% talc	415	582	30

[a] T_{onset} is the decomposition temperature at 5% weight loss.
[b] T_{max} is the temperature at maximum rates of weight loss.

Pure PC showed a LOI value of 25% and passed V2 rating with dripping in the UL-94 test. When 10 wt % PSBPBP was added, the LOI value increased to 30% and V1 rating was achieved with fragile char in the UL-94 test, indicating that the flame retardancy was improved by the addition of PSBPBP.

From Figure 2, it can be seen that the LOI values of PC/PSBPBP/talc composites increased with talc loading, and the highest LOI value is 34, obtained at 10 wt % talc (Fig. 2). In addition, PC/PSBPBP with 10% talc passed V0 rating with more stable intumescent char and nondripping in UL-94 test. The results of LOI and UL-94 tests imply the synergetic effect between PSBPBP and talc.

Raman spectrum

Since the laser was used as a Raman source, laser Raman spectroscopy (LRS) has become an effective technique for the characterization of carbon
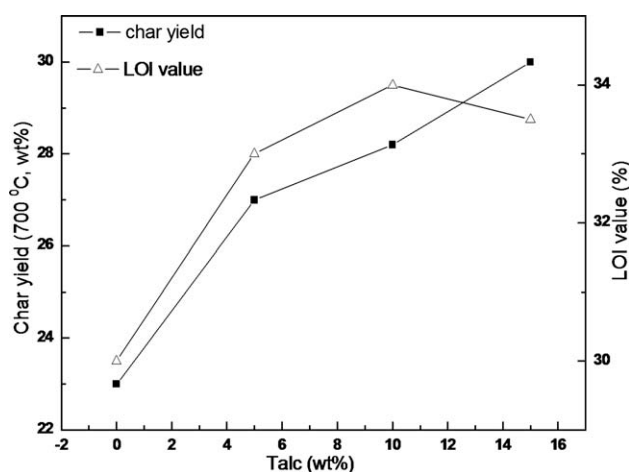

Figure 2 The char yield and LOI values with different talc loadings.

TABLE II
The LOI Values and UL-94 Test Results of Pure PC and PC Composites

Sample	LOI	UL-94
PC	25	V2
PC/10% PSBPBP	30	V1
PC/15% PSBPBP	31	V0
PC/10% PSBPBP/5% talc	33	V1
PC/10% PSBPBP/10% talc	34	V0
PC/10% PSBPBP/15% talc	33.5	V0

materials.[21–26] Generally, the Raman spectra of char layer exhibit two broad characteristic bands around 1360 and 1580 cm^{-1}, called D and G bands, which are usually assigned to zone center phonons of E_{2g} symmetry and K-point phonons of A_{1g} symmetry, respectively. D band only corresponds to amorphous char and G band is related to the structural organization of char layer.[27] The intensity ratio value of I_D/I_G is called R, which is related to the microcrystal size of the char layer.[18,28,29] Knight has reported that the R is proportional to $1/L_a$, where L_a is the crystallite size, for 2.5 nm $< L_a <$ 300 nm.[30] G linewidth means the half width of the line at half of 1580 cm^{-1} peak intensity. The G linewidth is determined by cluster size, the cluster size distribution, and stress in the carbon films. The upward shift of the G linewidth indicates the improved hardness of carbon material, which is a reflection of the stiffening of the host matrix.[31] Therefore, the barrier property of carbon materials can be estimated by taking both the G linewidth and R value into consideration. The larger G linewidth and R value indicate the smaller size of crystalline region, which is proportional to the pore diameter of the intumescent char layer.[25,32–35] The barrier property to the gas and heat rises with decreasing pore diameter of the char residue.
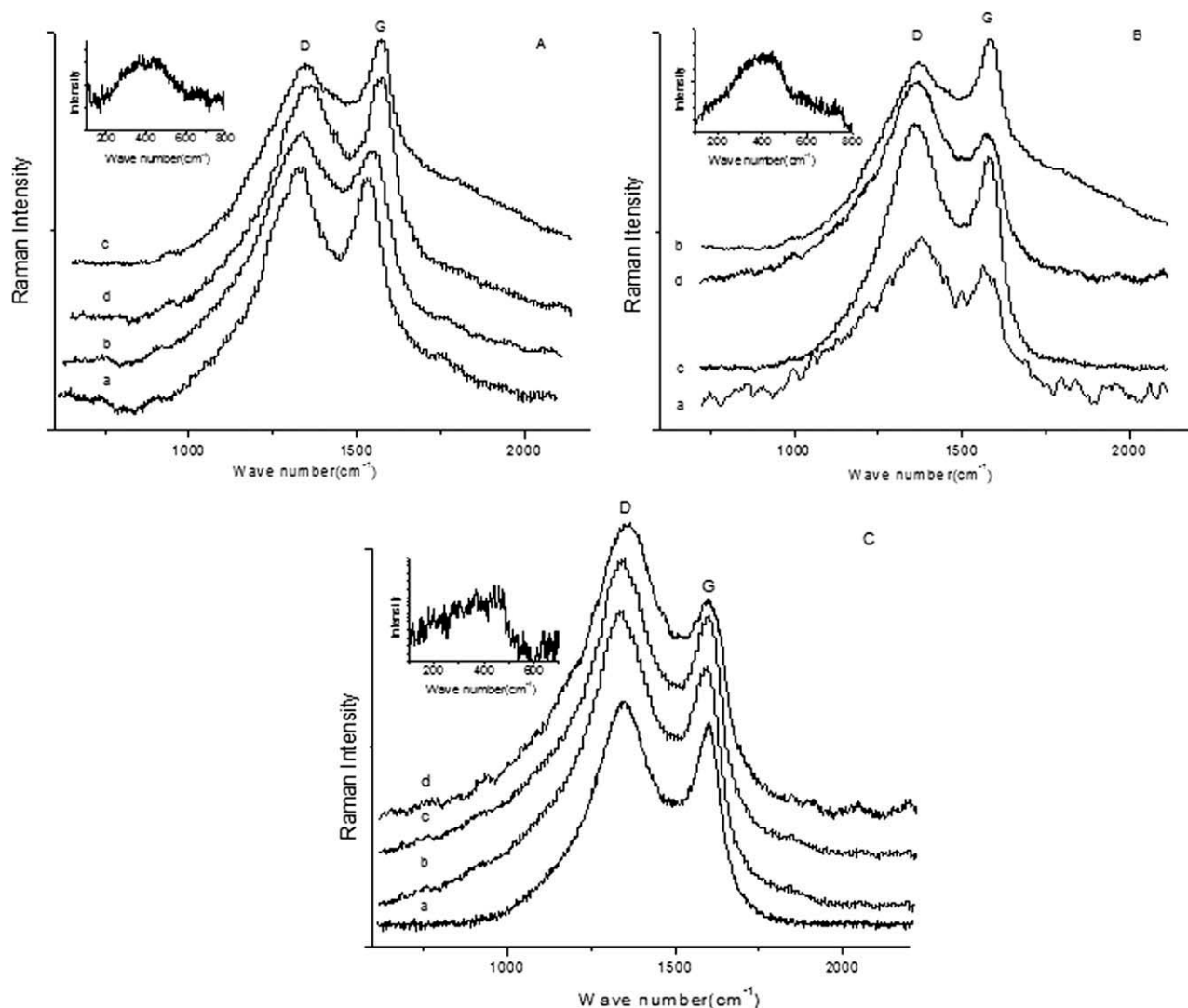
Figure 3 Raman spectra of the char residue of pure PC and PC composites: (a) after 30 min heating, (b) after 90 min heating, and (c) after LOI test; the inset shows a expanded view of 200-800 cm^{-1} region of PC/PSBPBP/talc composites.

TABLE III
R Values and G Linewidths of the Char Residue of Pure PC and PC Composites

Sample	30 min		90 min		After LOI test	
	R	G linewidth (cm^{-1})	R	G linewidth (cm^{-1})	R	G linewidth (cm^{-1})
PC	1.05	79	1.12	66	1.12	43
PC/10% PSBPBP	0.89	74	0.93	60	1.15	53
PC/10% PSBPBP/5% talc	1.08	85	1.16	76	1.25	60
PC/10% PSBPBP/10% talc	1.03	89	1.39	78	1.41	65

Figure 3 presents the Raman spectra of heat-treated pure PC, PC/PSBPBP, and PC/PSBPBP/talc systems in a muffle furnace at 400°C for 30 and 90 min respectively, as well as after LOI test. The corresponding R values and G linewidth of all systems are listed in Table III. The assignment of Raman bands for the char residue of pure PC and PC composites are showed in Table IV.[36–45]

From Table III, PC/10% PSBPBP system showed lower R values and G linewidth than that of pure PC after 30 and 90 min heating, showing that the char formed in this stage has larger microcrystals than that of pure PC possibly as the result of the crosslinking of phosphoric acid esters.

The R values and G linewidth of PC/PSBPBP with talc systems were higher than those of PC/PSBPBP systems. For example, the R value and G linewidth of PC/PSBPBP with 10 wt % talc composite increased to 1.41 and 65 cm^{-1} from 1.12 and 43 cm^{-1} of pure PC, respectively. The results imply that talc could decrease the pore diameter of the char residue with the rising talc loadings.

Moreover, G linewidth is a good measure to evaluate the hardness and density of char, which correlate with the fraction of quaternary carbon. The density and hardness of the char increase with rising G linewidth.[26] In Table III, G linewidth increased

to 65 cm^{-1} from 43 cm^{-1} of PC composite with 10 wt % talc loading compared to pure PC after LOI test. The increasing G linewidth with higher talc loading suggests that the density and hardness of the char residue were improved in the PC/PSBPBP/talc systems.

Mapelli[46] and Beeman[47] have reported that smaller aromatic clusters has higher D band; however, the amorphous carbon has lower D band. Ferrari[48] has considered that the higher G band implied the existence of nanocrystalline structure and the lower G band implied the existence of amorphous carbon material.

From Table IV, it is seen that D bands ranged from 1380 to 1330 cm^{-1}, G bands from 1590 to 1575 cm^{-1}, respectively for all the PC composites after LOI test in this work. When heating 30 min, pure PC and PC/PSBPBP composite showed higher D bands, 1380 and 1372 cm^{-1}, than those of PC/PSBPBP/talc composites. It suggests that the char formed in the early heating stage had smaller clusters for pure PC and PC/PSBPBP composite. With the increasing heating time, the D band shifted downwards 1350 and 1340 cm^{-1}, which indicates that the amorphous char was formed after LOI test. Furthermore, C—N stretching vibration peak (1330–1345 cm^{-1}) appeared after the addition of PSBPBP and talc. The shift of D band to

TABLE IV
Assignments of the Raman Bands for the Char Residue of Pure PC and PC Composites

	30 min		90 min		After LOI test		
	W.N. (cm^{-1})	Assign.	W.N. (cm^{-1})	Assign.	W.N. (cm^{-1})	Assign.	References
D							
Pure PC	1380	ν(C—C) stretch. inter-ring	1354	$A_{1g}\nu$(C—C) stretch	1350	$A_{1g}\nu$(C—C) stretch	36–45
PC/10% PSBPBP	1372	ν(C—C) stretch. (Q*) ν(C—H) bending (B*)	1350	$A_{1g}\nu$(C—C) stretch	1340	ν(C—N) stretch	36–45
PC/10% PSBPBP/5% talc	1350	$A_{1g}\nu$(C—C) stretch	1335	ν(C—N) stretch	1330	ν(C—N) stretch	36–45
PC/10% PSBPBP/10% talc	1345	ν(C—N) stretch	1342	ν(C—N) stretch	1330	ν(C—N) stretch	36–45
G							
Pure PC	1590	ν(C—C) stretch (B)	1565	ν (C—C) stretch (B)	1590	ν(C—C) stretch (B)	42–45
PC/10% PSBPBP	1590	ν(C—C) stretch (B)	1590	ν(C—C) stretch (B)	1580	ν(C=C) stretch (Q)	42–45
PC/10% PSBPBP/5% talc	1590	ν(C—C) stretch (B)	1580	ν(C=C) stretch (Q)	1580	ν(C=C) stretch (Q)	42–45
PC/10% PSBPBP/10% talc	1590	ν(C—C) stretch (B)	1577	ν(C=C) stretch (Q)	1575	ν(C=C) stretch (Q)	42–44

B*, benzoid ring; Q*, quinoid ring; W.N., wave numbers; Assign., assignment.
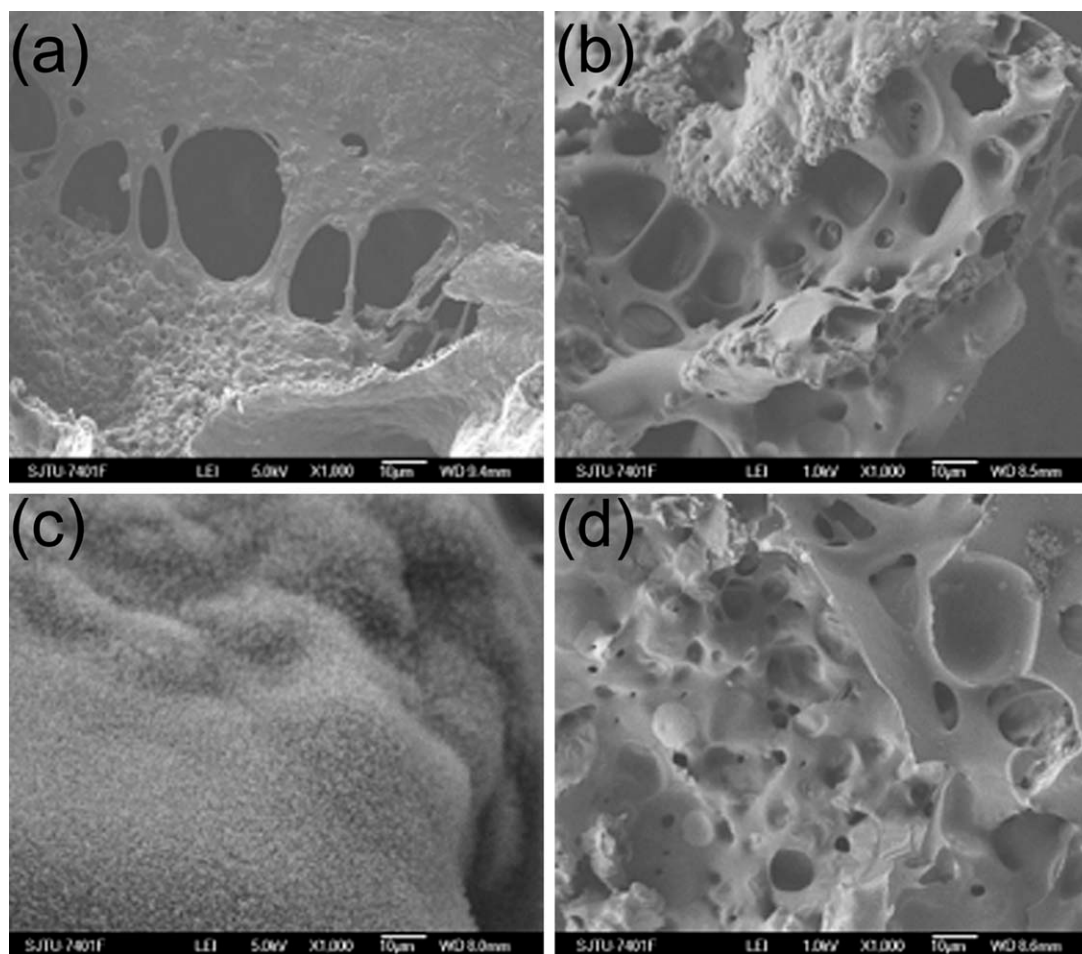
Figure 4 SEM morphology of the char samples: (a) outer surface, the pure PC; (b) inner surface, the pure PC; (c) outer surface, the PC/10% PSBPBP/10% talc; and (d) inner surface, the PC/10% PSBPBP/10% talc.

C—N stretching vibration peak results from that nitrogen could involve in the formation of thermal stable aromatic structure, to form more thermal stable char.

In the contrast, D band of PC/PSBPBP/talc composites had lower position since 30 min heating, and shifted downwards to 1330 cm^{-1} after LOI test compared to pure PC and PC/PSBPBP/talc composites. Moreover, D band was always lower than the no talc systems with all the heating time, suggesting the earlier appearance of C—N stretching vibration peak after the addition of talc. This implies that the addition of talc could accelerate the forming process of thermal stable char layer containing nitrogen.

Pure PC and PC composites showed G bands around 1590 cm^{-1} (assigned to the stretching vibration of C—C of benzoid ring)[49] due to the remained origin structure when heating 30 min. After LOI test, G band of pure PC was still around 1590 cm^{-1}, indicating that the benzoid ring structure was kept at high temperature. While PC/PSBPBP composite still kept around 1590 cm^{-1} at 90 min, downshifting to 1580 cm^{-1} until after LOI test, which was assigned to the stretching vibration of C=C quinoid ring

structure. Compared with PC/PSBPBP, quinoid ring structure of the PC/PSBPBP/5% talc and PC/PSBPBP/10% talc composites appeared earlier around 1580 and 1575 cm^{-1}, respectively, when heating 90 min.

Above the analysis of LOI, UL-94, and Raman spectra, it can be indicated that talc has well synergetic effect with FR PSBPBP, which could improve the char thermal stability. In Figure 3, the inset of PC/PSBPBP/talc composites showed features evident in the range 320–490 cm^{-1}, confirming the presence of P in the char.[50,51] Therefore, the possibly mechanism is that the interaction between talc and FR PSBPBP could form the species maybe like "magnesium-silico-phosphocarbonaceous" during the decomposition process, which could stabilize the residue structure in situ in conditions of fire.[34,35]

Morphology

As shown in Figure 4, SEM was employed to investigate the surface morphology of the char residue of pure PC and PC/10% PSBPBP/10% talc compounds

TABLE V
Mechanical Properties of Pure PC and PC Composites

Sample	Tensile strength (MPa)	Elongation at break (%)	Impact strength (V-notch) (J/m)	Impact strength (no notch)
PC	59.6	84.8	907	Unbroken
PC/10% PSBPBP	61.7	82.3	859	Unbroken
PC/10% PSBPBP/5% talc	67.7	78.9	866	Unbroken
PC/10% PSBPBP/10% talc	67.9	80.7	869	Unbroken

after UL-94 test. The outer surface of char layer for pure PC had obviously cracked and the inner surface had big pores from Figure 4. Moreover, the outer surface of the char residue of PC/10% PSBPBP/10% talc compound was very condense and the inner surface had more pores with smaller diameter. Obviously, the latter provides a better mass-transfer and heat-transfer barrier than the pure PC's char layer.

Mechanical properties

Table V summarizes the tensile strength and impact strength of pure PC, PC/PSBPBP, and PC/PSBPBP/talc systems. The tensile strength and elongation of PC/PSBPBP systems at break were similar to pure PC; however, the impact strength had slightly decreased.

When adding talc to the PC/PSBPBP system, the tensile strength did not get affected, because lamellar structure of talc could orientate in the process. On the contrary, the impact strength slightly increased, which is related to the good compatibility and dispersion between PC and talc. The hydrophobic nature of talc allows it to be more compatible with PC resin.[33] In a word, the addition of talc has no remarkable influence on the mechanical properties of PC composites.

CONCLUSION

In this study, talc could replace partial PSBPBP and endow the PC composites (PC/PSBPBP) with better flame retardancy. A synergetic effect of flame retardancy between PSBPBP and talc has been indicated through UL-94 and LOI tests. The LOI value of PC/10% PSBPBP/10% talc system increased to 34% and V0 rating was arrived in UL-94 vertical test. The R values and G linewidth of PC/PSBPBP with talc systems were higher than PC/PSBPBP systems in the Raman measure. The R value increased to 1.41 with 10 wt % talc loading from 1.21 of pure PC after LOI test. The thermal stability of the PC/PSBPBP/Talc was remarkably improved in TGA analysis. Furthermore, the addition of talc has no remarkable influence on the mechanical properties of PC. PC/PSBPBP/talc composites may form the species like magnesium-silico-phosphocarbonaceous during the

decomposition process, which could stabilize the residue structure.

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