

MISCIBILITY, CRYSTALLIZATION AND MECHANICAL PROPERTIES OF PPC/PBS BLENDS*

Hui-liang Zhang, Xiao-hong Sun, Qing-yong Chen, Min-qiao Ren, Zhi-hao Zhang,
Hong-fang Zhang and Zhi-shen Mo**

State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Graduate School of
Chinese Academy of Science, Changchun 130022, China

Abstract In this paper, melt blends of poly(propylene carbonate) (PPC) with poly(butylene succinate) (PBS) were characterized by dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), tensile testing, wide-angle X-ray diffraction (WAXD), polarized optical microscopy and thermogravimetric analysis (TGA). The results indicated that the glass transition temperature of PPC in the 90/10 PPC/PBS blend was decreased by about 11 K comparing with that of pure PPC. The presence of 10% PBS was partially miscible with PPC. The 90/10 PPC/PBS blend had better impact and tensile strength than those of the other PPC/PBS blends. The glass transition temperature of PPC in the 80/20, 70/30, and 60/40 PPC/PBS blends was improved by about 4.9 K, 4.2 K, and 13 K comparing with that of pure PPC, respectively; which indicated the immiscibility between PPC and PBS. The DSC results indicated that the crystallization of PBS became more difficult when the PPC content increased. The matrix of PPC hindered the crystallization process of PBS. While the content of PBS was above 20%, significant crystallization-induced phase separation was observed by polarized optical microscopy. It was found from the WAXD analysis that the crystal structure of PBS did not change, and the degree of crystallinity increased with increasing PBS content in the PPC/PBS blends.

Keywords: Poly(propylene carbonate); Poly(butylene succinate); Miscibility; Crystallization; Mechanical properties.

INTRODUCTION

Poly(propylene carbonate) (PPC), synthesized by Inoue *et al.* first^[1], is a copolyesters of carbon dioxide and propylene epoxide. Due to the fixation of carbon dioxide and the biodegradability PPC is becoming important^[2–5]. PPC can be used to produce one-off packaging materials, one-off dishware, and board materials, biodegradable materials, controlled drug-releasing agents, processing aids, coating materials, surfactants, *etc.* Compared with commercial plastics, PPC has some blemishes such as lower glass transition temperature, non-crystalline and poorer mechanical properties. In order to improve the glass transition temperature, many studies have been done^[6–10].

Poly(butylene succinate) (PBS) is the most economically competitive polymer among the biodegradable polymers^[11, 12]. PBS can be degraded by bacteria in soil, and it is a so-called environmentally friendly polymer. PBS is a semi-crystalline polymer with high crystalline content and clear melting behavior ($T_m = 114^\circ\text{C}$) as well as glass transition ($T_g = -34^\circ\text{C}$)^[13]. Blending PPC with PBS is expected to improve the tensile strength, and the creep resistance, on the one hand, and to ameliorate the degree of crystallinity and the mechanical properties for PPC, on the other hand, so that a biodegradable material can be prepared. The properties of PPC/PBS blends have not been studied up to date. In the present article, PBS is used as an additive for improving the mechanical properties and glass transition temperature of PPC. The crystallization, thermal and mechanical properties of

* This work was supported by the National Natural Science Foundation of China (Nos. 270274049 and 220374051).

** Corresponding author: Zhi-shen Mo (莫志深), E-mail: mozs@ciac.jl.cn

Received October 17, 2006; Revised November 27, 2006; Accepted December 4, 2006

PPC/PBS were studied by alternating the amount of PBS. From the analysis of X-ray diffraction of PPC/PBS blends and the tensile testing we found that the 90/10 PPC/PBS blend had better impact and tensile strength than the pure PPC. In particular, this study was focused on the morphology of PPC/PBS blends for obtaining a better understanding of their crystallization and mechanical properties.

EXPERIMENTAL

Material and Blend Preparation

The PPC samples used were supplied by the Laboratory of Polymer Engineering, Changchun Institute of Applied Chemistry (China) with viscosity-average molecular weights of approximately 8.00×10^4 . PBS (Bionolle No. 1003) in dry-pellet form was supplied by the Showa High Polymer Company, Ltd, (Osaka, Japan) with weight-average molecular weights of approximately 7.36×10^4 . PPC and PBS were dried in vacuo for 3 days and then mixed with a Brabender instrument operating at 140°C at a rotation speed of 40 r/min for 5 min. The PBS weight contents were from 10% to 40% in the PPC/PBS blends. After blending, all the samples were cooled to room temperature under air atmosphere.

Methods of Characterization

Dynamic mechanical analysis was performed on a NETZSCH DMA 242C that provided the plots of the loss tangent ($\tan\delta$) and the storage module (E') against temperature. The scans from -100°C to 140°C were carried out in tension mode at a constant heating rate of 3 K/min and a frequency of 3.33 Hz.

Thermal analysis was carried out with a Perkin-Elmer DSC-7 differential scanning calorimeter calibrated with indium. The heating and cooling rates were 10 K/min with nitrogen purge, and the sample weights were between 4.5 mg and 5.5 mg. The DSC analysis was carried out by first heating the sample from the room temperature to 150°C and then cooled it down to 0°C (at a rate of 10 K/min). Moreover, to verify the changes in crystallinity the sample was reheated from 0°C to 150°C . The melting temperature (T_m) of PBS was obtained from heating curves. The degree of crystallinity was calculated with the assumption that the value of heat of fusion is 110.3 J/g for 100% crystalline PBS^[14].

The crystallite morphology of PPC/PBS blends was observed with a Leica DMLP polarized microscope equipped with a Linkam TM600 hot stage and a computer-controlled charged-coupled-device camera. A small amount of samples with the thickness of approximately 0.05 mm was sandwiched between two microscopic cover glasses and then placed on the hot stage. The samples were heated from room temperature to 140°C at a rate of 80 K/min, held there for 5 min to eliminate any thermal and mechanical history, and then cooled to the designed temperature at a rate of 100 K/min. The morphology changes were recorded during the crystallization process.

Wide-angle X-ray diffraction patterns were performed using a Rigaku D/max 2500PC type X-ray diffractometer with a 18 kW rotating-anode generated at 40 kV and 200 mA and $\text{CuK}\alpha_1$ radiation filtered by a curved graphite crystal monochromator. Prior to measurements, the samples were melted and crystallized isothermally at 70°C for 1 h.

Notched Izod impact tests were performed at $(23 \pm 2)^\circ\text{C}$ according to ASTM D256 on an XJU-22 apparatus. The samples with dimensions 63.5 mm \times 12.7 mm \times 6.35 mm were obtained from injection molded specimens. The notch was milled with a depth of 2.54 mm, an angle of 45° and a notch radius of 0.25 mm. The uniaxial tensile tests were carried out on an INSTRON-1121 tensile tester at $(23 \pm 2)^\circ\text{C}$ and a cross-head speed of 50 mm/min according to GB/T 1040-92. The average values were obtained from the tests of more than three specimens.

Thermogravimetric (TGA) measurements were performed by using a Perkin-Elmer TGA 7 (N_2 , scan rate, 20 K/min).

RESULTS AND DISCUSSION

Miscibility

DMA is one of the most sensitive techniques available for characterizing and interpreting the mechanical behavior of materials. The concept of DMA is based on observing the viscoelastic response of materials subjected to a small oscillatory strain. Figures 1 and 2 show the dependence of loss factor ($\tan\delta$) and storage modulus (E') against the temperature of PPC modified with different contents of PBS, respectively. The major $\tan\delta$ peak corresponding to the glass transition temperature of pure PPC occurred around 38°C , while that of pure PBS occurred at approximately -34°C . The motion of the polymer chain corresponding to the glass transition temperature was generally known to be the micro-Brownian motion of chain segments^[15]. For the 90/10 PPC/PBS blend the peak temperature of the α -relaxation of PPC decreased by about 11 K, it indicated that the 90/10 PPC/PBS blend was partially miscible. But in the 80/20, 70/30, and 60/40 PPC/PBS blends, the peak temperature of the α -relaxation of PPC increased about 4.9 K, 4.2 K, and 13 K (Table 1), respectively; which indicated that these samples were immiscible. It could be explained that the PPC/PBS blends took place phase separation during the cooling process from the melting state. The height of $\tan\delta$ peak was generally a measurement of the damping nature of the compound. With the increase of the content of PBS the height of the loss factor ($\tan\delta$) peak of amorphous PPC decreased. This indicated that the PPC/PBS blends had lower damping and improved strength with the increase of the content of PBS. Compared with the curve of pure PPC, the loss factor ($\tan\delta$) peak on the curves of the 90/10, 80/20, 70/30, and 60/40 PPC/PBS blends became broader, which might indicate the compositional heterogeneity. From the curves of Fig. 2 it can be seen that the E' increases with increasing the PBS percentage in the blends. The E' s of the PPC/PBS blends became higher than that of the pure PPC. The increase of the storage modulus with increasing the PBS content was due to the reinforcing effect of PBS.

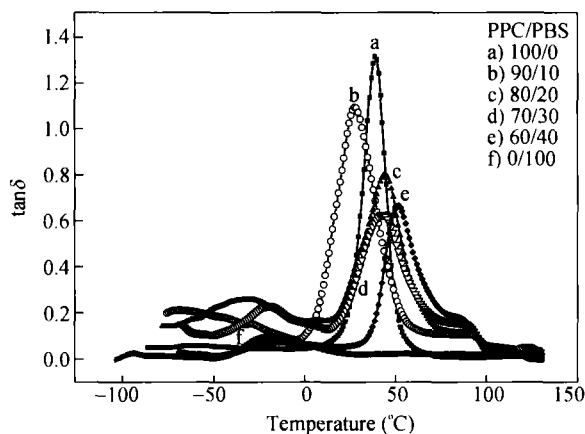


Fig. 1 DMA plots of $\tan\delta$ versus temperature for PPC/PBS blends

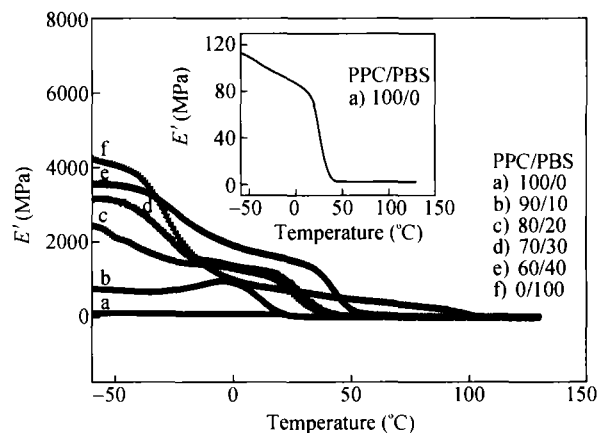


Fig. 2 DMA plots of storage modulus (E') versus temperature for PPC/PBS blends

Table 1. The various crystallization parameters of the samples (PPC/PBS)

PPC/PBS	T_g ($^\circ\text{C}$)	T_c ($^\circ\text{C}$)	T_{onset} ($^\circ\text{C}$)	T_m ($^\circ\text{C}$)	ΔH_f (J/g)	$W_{c,h}$ (%)	$W_{c,x}$ (%)
100/0	38.3				0	0	
90/10	27.2	34.8	60.6	109.1	6.56	5.9	6.9
80/20	43.2	66.9	74.1	109.7	10.94	9.9	12.7
70/30	42.5	70.3	77.4	112.4	17.10	15.5	19.4
60/40	51.3	72.5	78.3	112.4	25.85	23.4	27.7
0/100	-34.0	76.1	81.3	113.6	57.49	52.1	67.0

Thermal Properties

The DSC analysis was carried out by first heating the sample to 150°C and then cooled it down to 0°C. Moreover, in order to verify the changes in crystallinity, the sample was reheated from 0°C to 150°C (Fig. 3a). Figure 3(b) depicts the DSC crystallization traces of samples recorded during cooling from the isotropic melt at a cooling rate of 10 K/min. All data obtained included crystallization temperature (T_c), onset-of-crystallization temperature (T_{onset}), melting temperature (T_m), heat of fusion (ΔH_f) of PBS, as well as the degree of crystallinity ($W_{c,h}$) calculated from the heat of fusion for all the samples are listed in Table 1. The position of the melting peak of the PPC/PBS blends shifted to higher temperatures when the content of PBS increased. The results showed that the onset-of-crystallization temperatures [T_{onset} (°C)] of 60/40, 70/30, 80/20, and 90/10 PPC/PBS blends decreased by 3.0, 3.9, 7.2, and 20.7 K, respectively comparing with that of pure PBS. These results indicated that the crystallization of PBS became more difficult, and the potential energy required for crystallization increased when the PPC content was increased. Therefore, the matrix of PPC hindered the crystallization process of PBS.

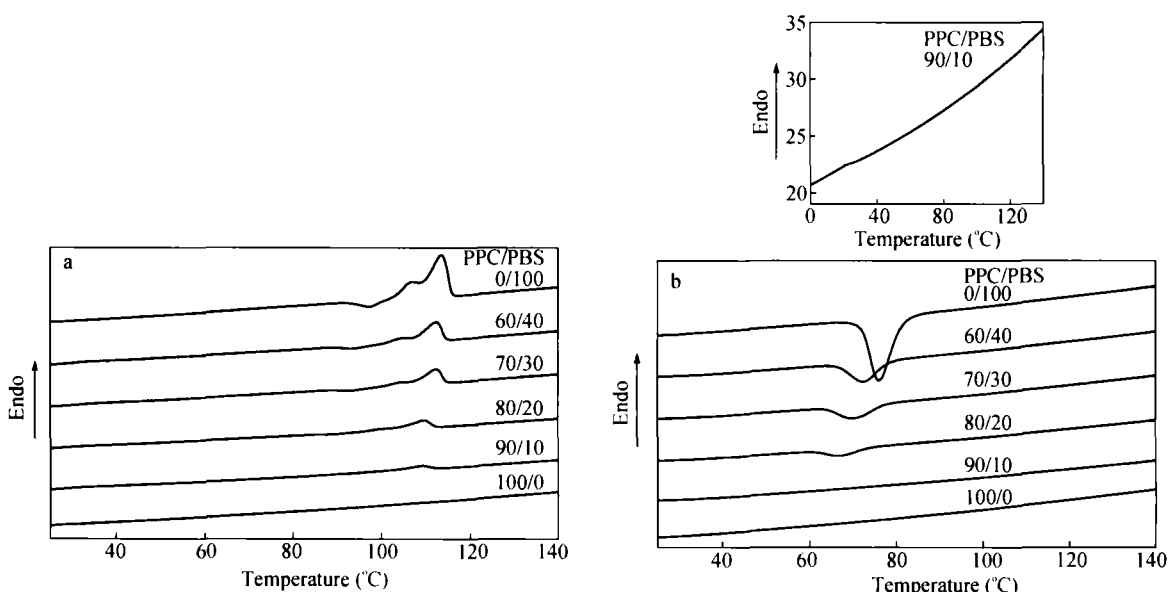


Fig. 3 DSC plots for PPC/PBS blends: (a) reheated from 0°C to 150°C and (b) cooled from 150°C to 0°C

It is clear that the value of $T_{onset} - T_c$ of the pure PBS was lower than that of the blends, and this further indicated that the pure PBS exhibited higher crystallization rate. According to the polymer crystallization theory, the smaller $T_{onset} - T_c$ is, the greater the rate of crystallization is. With the increasing of the PPC content, the values of $T_{onset} - T_c$ increase. It is concluded that PPC reduced the crystallization rate of PBS. Moreover, the PPC/PBS blends show a double melting behavior, this may be due to the recrystallization process during heating^[16].

Spherulitic Morphologies

Figure 4 shows the polarized optical micrographs of the PPC/PBS blends at various blend compositions. For the 90/10 PPC/PBS blend (Fig. 4a), a few small spherulites were dispersed in the PPC matrix. The numbers of small spherulites were increased while the crystallization temperature decreased from 70°C to 30°C (Fig. 4b). At this composition, largely as a result of the low content of PBS, the average radius of the spherulites was about 1 μm, significant crystallization-induced phase separation did not take place, the PBS crystals could not grow larger. While the PBS content was 20% (Fig. 4c), the average radius of the spherulites was about 10 μm. The large spherulites of PBS were shown, and their shapes were less regular than those of pure PBS (Fig. 4g). The average

radius of the spherulites did not change when the crystallization temperature decreased from 70°C to 30°C (Fig. 4d). With the increase of the PBS content in the PPC/PBS blends (Figs. 4e, 4f), spherulites of PBS became larger and denser, and the Maltese cross became clearer. In particular, for 60/40 blend (Fig. 4f), large spherulites of PBS were observed in a partially continuous phase. The pure PBS showed well-grown spherulites (Fig. 4g), which were very tightly stacked, and the average radius of the spherulites was about 20 μm . Some small-sized spherulites appeared between the large spherulites, this phenomenon usually was called the weak spots^[17-19]. The cavities were produced when the crystallization of pure PBS was accompanied by the buildup of negative pressure. The weak spots caused by the cavities were the major reason for the decrease of mechanical properties in polymer materials^[20-22].

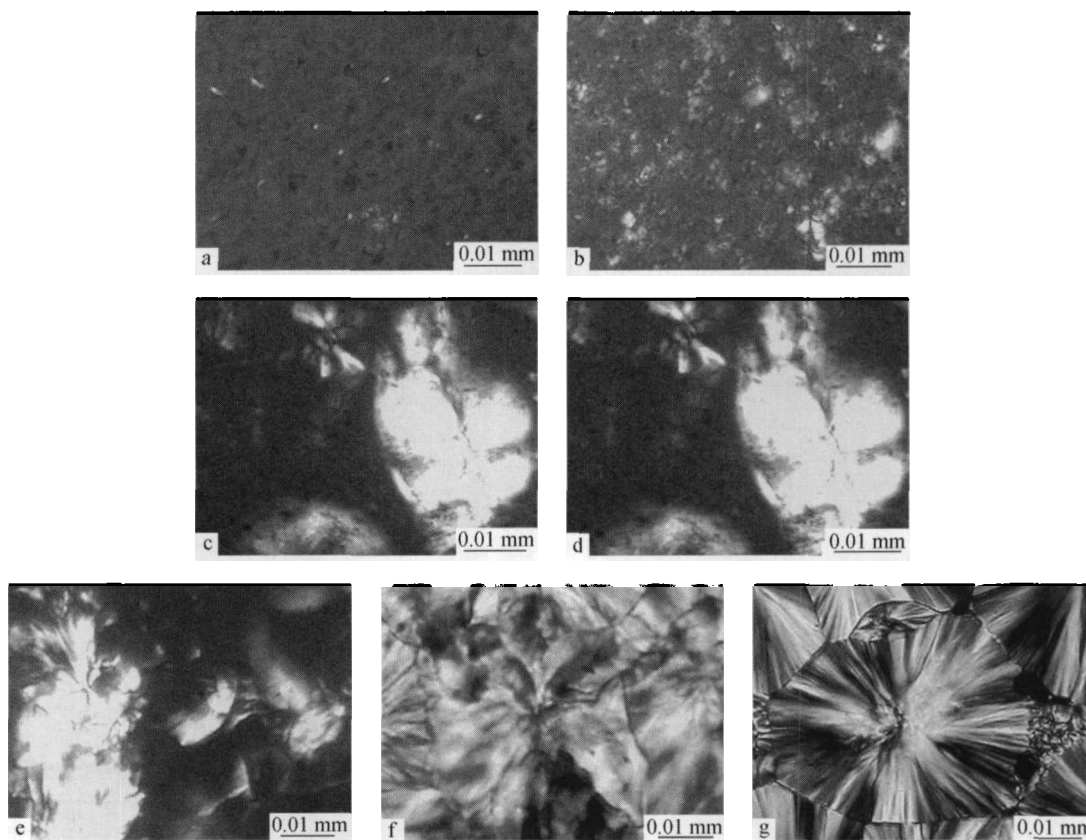


Fig. 4 Representative POM micrographs of PPC/PBS blends and pure PBS crystallized for 10 min
 a) 90/10 at 70°C; b) 90/10 at 30°C; c) 80/20 at 70°C; d) 80/20 at 30°C; e) 70/30 at 70°C;
 f) 60/40 at 70°C; g) Pure PBS at 70°C

Analysis by WAXD

Figure 5 shows the WAXD patterns for PPC/PBS blends. The pattern of the pure PBS showed a strong peak of (110) at 23.1° and weak peaks of (020), (021), ($1\bar{2}\bar{1}$), (111), ($1\bar{2}1$), ($\bar{1}3\bar{3}$) and (024) at 20.0°, 22.4°, 26.4°, 29.3°, 34.1°, 39.0° and 45.2°, respectively. The position of the non-crystalline peak was at about 21.26°^[23]. By means of the graphic multippeak resolution method^[24-27] the WAXD curve of the pure PBS was resolved into crystalline and amorphous portions (Fig. 6). The degrees of crystallinity of PBS and PPC/PBS blends determined by WAXD were calculated as follows^[28, 29].

$$W_{c,x} = \frac{\sum_i C_{i,hkl}(\theta) I_{i,hkl}(\theta)}{\sum_i C_{i,hkl}(\theta) I_{i,hkl}(\theta) + k_i C_a(\theta) I_a(\theta)} \times 100\% \tag{1}$$

where $I_{i,hkl}(\theta)$ and $I_a(\theta)$ were relative intensity of the crystalline peaks and amorphous peak, respectively; $C_{i,hkl}(\theta)$ and $C_a(\theta)$ were correction factors of crystalline peaks and amorphous peak, respectively, the total correction factor $K = C_a(\theta) \cdot k_i$, and k_i was the relative scattering coefficient, which was the ratio of calculated diffraction intensity ($\sum I_{i,cal}$) to total scattering intensity ($\sum I_{i,total}$) for unit weight of crystalline polymer, $k_i = \sum I_{i,cal} / \sum I_{i,total}$ ($k_i \leq 1$). Here, $C_{i,hkl}(\theta)$ or $C_a(\theta)$ could be calculated by the following equation:

$$C_{i,hkl}^{-1} \text{ or } C_a^{-1}(\theta) = f^2 \cdot \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cdot \cos \theta} \cdot e^{-2B(\sin \theta / \lambda)^2}$$

$$= \sum_i N_i f_i^2 \cdot \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cdot \cos \theta} \cdot e^{-2B(\sin \theta / \lambda)^2} \tag{2}$$

where f was the atomic scattering factor for one crystallographical structural repeating unit; f_i was the scattering factors of the i -th atom, N_i was the number of i -th atom in a repeating unit; 2θ was the Bragg angle; the angle factor $LP = (1 + \cos^2 2\theta) / \sin^2 \theta \cos \theta$; the temperature factor $T = e^{-2B(\sin \theta / \lambda)^2}$; and $2B = 10$.

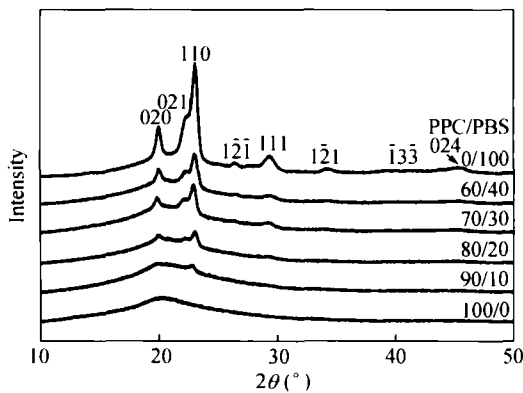


Fig. 5 WAXD patterns of PPC/PBS melt-crystallized at different compositions

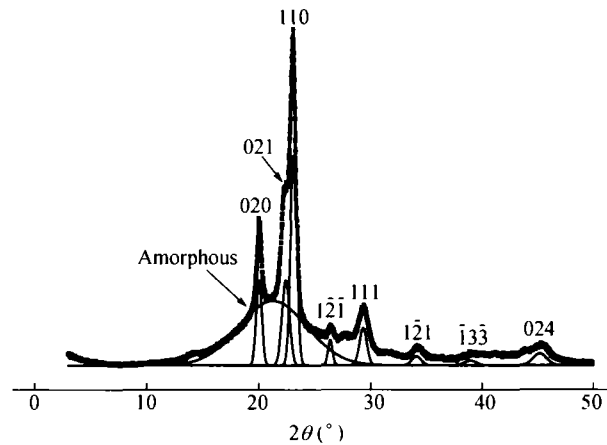


Fig. 6 Resolution of the WAXD curve of PBS into crystalline and amorphous portion

The atomic scattering factor f_i could be expressed approximately by:

$$f_i(\sin \theta / \lambda) = \sum_{i=1}^4 a_i \cdot e^{-b_i (\sin \theta / \lambda)^2} + C \tag{3}$$

where the values of a, b and C were given in Ref. [30].

Using Eqs. (1), (2), and (3), X-ray diffraction data of PPC/PBS blends are listed in Table 2. $I = C_{i,hkl}(\theta) \cdot I_{i,hkl}(\theta)$ or $C_a(\theta) \cdot I_a(\theta)$, is the integrating intensity scattered over a suitable angular interval by the crystalline and the amorphous phases, respectively. There are eight atoms of carbon, twelve atoms of hydrogen and four atoms of oxygen in a repeating unit of PBS, the total atomic scattering factor is

$f_{hkl}^2 = 8f_C^2 + 12f_H^2 + 4f_O^2$, $k_i = 0.9$, $C_a(\theta) = 1.2$, $K = k_i \cdot C_a(\theta) = 1.08$. Using the data of Table 2, Eq. (1) can be reduced to give Eq. (4).

$$W_{c,x} = \frac{I_{020} + 1.40I_{021} + 1.55I_{110} + 2.40I_{121} + 3.5I_{111} + 6.35I_{121} + 11.3I_{133} + 22.94I_{024}}{I_{020} + 1.40I_{021} + 1.55I_{110} + 2.40I_{121} + 3.5I_{111} + 6.35I_{121} + 11.3I_{133} + 22.94I_{024} + 1.20I_a} \quad (4)$$

Table 2. X-ray diffraction data of PPC/PBS blends

hkl	A	020	021	110	$1\bar{2}\bar{1}$	111	$1\bar{2}1$	$\bar{1}3\bar{3}$	024
2θ	21.26	20.01	22.39	23.10	26.38	29.33	34.12	38.97	45.16
<i>I</i>	128894	14241	18977	38880	3395	8103	2531	1740	4731
<i>T</i>	0.87	0.88	0.85	0.84	0.80	0.76	0.70	0.63	0.54
$f^2 = 12f_H^2 + 8f_C^2 + 4f_O^2$	385	399	371	362	324	292	246	206	164
<i>LP</i>	55.9	63.3	50.2	47.0	35.6	28.4	20.5	15.3	11.0
$C(\theta)$	1.20	1	1.40	1.55	2.40	3.51	6.35	11.31	22.94
<i>K</i>	1.08								

A: amorphous peak

Using the above Eq. (4), the degrees of crystallinity ($W_{c,x}$) of PBS and PPC/PBS blends are determined by WAXD in Table 1. With the increase of PBS content in PPC/PBS blends, the degree of crystallinity of PBS in PPC/PBS blends increases. The crystallinity values in Table 1 exhibit the order $W_{c,x} > W_{c,h}$. The crystallinity determined from X-ray diffraction ($W_{c,x}$) was equal to the sum of the crystalline and interphase contents, while the measurement of fusion enthalpy by calorimetry ($W_{c,h}$) yields values which are equal to the crystalline content. Imperfections of crystals are not easily distinguished from the amorphous phase. Therefore, some disagreements among the quantitative results of crystallinity by different measurement methods are frequently encountered. Comparing the pattern of the pure PBS with those of the blends, we can see that the *d*-spacing values are constant for the (110), (021), (020), and (111) crystallographic planes, which indicates that the crystal structure of PBS is not affected by the PPC matrix in the blends.

Mechanical Properties

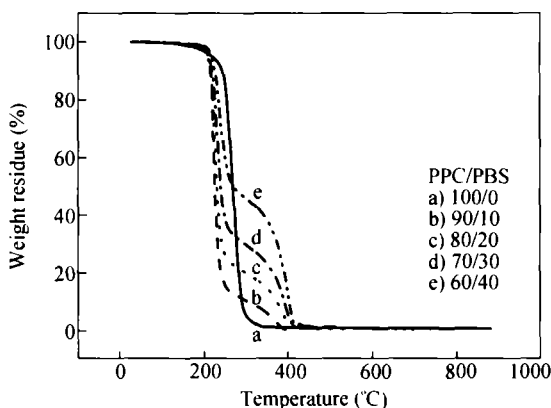
The ultimate goal of the studies lies in the improvement of mechanical properties of the PPC/PBS blends, especially the impact and tension strength. The degree of crystallinity, dynamic mechanical properties, and morphology of the blends discussed in the previous section were closely related to the tensile properties of samples. Notched Izod impact strengths and tensile properties of the PPC/PBS blends are listed in Table 3. The mechanical properties of PPC/PBS blends are improved by adding 10% PBS. The Izod impact strength of PPC/PBS 90/10 is 35.3 J/m, which is higher than that of pure PPC (31.7 J/m). However, with further increasing the PBS content to 40% continually, the impact strength slightly decreases to 27.6 J/m. The tensile strength and energies absorbed at break of the blends show the same trend. The elongation at break gradually decreases with the increasing of the PBS weight percent. It is obvious that 10% is an optimum content of PBS for improving the mechanical properties of PPC/PBS blends in this work. From the analysis of DMA, the 90/10 PPC/PBS blend is partially miscible. But the 80/20, 70/30, and 60/40 PPC/PBS blends are immiscible. These mechanical results were in agreement with the analysis of DMA. In the PPC/PBS blends, PPC has good ductile property and PBS has some extents of the rigidity. The POM micrograph (Fig. 4b) shows that PBS disperses uniformly in the PPC matrix in the 90/10 PPC/PBS blend, so the rigidity of PBS might improve the tension strength of PPC. However, in the 90/10 PPC/PBS blend the spherulite size decreases and the degree of crystallinity is depressed. During fracture, the dispersed PBS spherulites may act as energy absorbers in the continuous phase of PPC. This indicates that the PPC/PBS blend with 10% of PBS is likely to absorb greater energies. The measurement of mechanical properties also shows that the 90/10 PPC/PBS exhibits higher tensile strength. The degree of crystallinity is closely related to the impact strength, elongation at break, and energy absorbed at break for the PPC/PBS blends. In order to improve the impact strength, the optimal composition is 90/10 for the PPC/PBS blends in this work.

Table 3. Mechanical properties of PPC/PBS blends

PPC/PBS	Impact strength (J/m)	Tensile strength (MPa)	Elongation at break (%)	Energies absorbed (mJ)
100/0	31.7	8.0	1196	4856
90/10	35.3	12.8	907	6480
80/20	34.5	5.6	687	2146
70/30	29.6	11.5	5.35	32
60/40	27.6	7.2	2.71	9

Thermal Stability

Thermal stability of the PPC/PBS blends investigated in this work is evaluated by TGA. Figure 7 reports the thermal decomposition behaviors of PPC/PBS blends with changing compositions, the thermal decomposition temperature (T_d) of PBS was much higher than that of PPC. The 90/10, 80/20, 70/30, and 60/40 PPC/PBS blends showed a two-step degradation; PPC degrades in the region from 200°C to 250°C while PBS degraded between 250°C and 410°C. Moreover, the weight losses at 250°C of the 90/10, 80/20, 70/30, and 60/40 PPC/PBS blends are about 84, 74, 64, and 54 wt%, respectively. It indicates that the addition of PBS doesn't affect the degradation of PPC.

**Fig. 7** Thermal stability of PPC/PBS blends measured by TGA

CONCLUSIONS

The properties of PPC/PBS blends can be affected by changing the PBS content. The glass transition temperature of PPC/PBS blends can be improved by about 13 K by adding 40% PBS. In mechanical properties, the PPC/PBS blends show improved tensile strengths (30%) and impact strength (11%) when the PBS content is 10%. Based on the present study it is concluded that PBS can be effectively used as fillers in PPC, the obtained PPC/PBS blends are new biodegradable materials.

The crystallization behaviors of PPC/PBS blends had also been studied by using DSC, and WAXD methods. When the content of PBS in PPC/PBS blends increases, the degree of crystallinity of PBS in PPC/PBS blends also increases, but the crystal structure is not changed in the blends. The morphologies of PPC/PBS blends are observed by using POM, for the 90/10 PPC/PBS blend, a large number of small spherulites are dispersed in the PPC matrix; however, for the 80/20, 70/30, and 60/40 PPC/PBS blends, significant crystallization-induced phase separation was observed.

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