Available online at www.sciencedirect.com

ScienceDirect

Polymer 48 (2007) 4196–4204

polymer

www.elsevier.com/locate/polymer

Fully biodegradable blends of poly(L-lactide) and poly(ethylene succinate): Miscibility, crystallization, and mechanical properties

Jiaoming Lu [a], Zhaobin Qiu [a,b,*], Wantai Yang [a]

[a] State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China
[b] The Key Laboratory of Beijing City on Preparation and Processing of Novel Polymer Materials,
Beijing University of Chemical Technology, Beijing 100029, China

Received 14 January 2007; received in revised form 19 March 2007; accepted 16 May 2007
Available online 21 May 2007

Abstract

Both poly(L-lactide) (PLLA) and poly(ethylene succinate) (PES) are biodegradable semicrystalline polyesters. The disadvantages of poor mechanical properties and slow crystallization rate of PLLA limit its wide application. Fully biodegradable polymer blends were prepared by blending PLLA with PES. Miscibility, crystallization behavior, and mechanical properties of PLLA/PES blends were investigated by differential scanning calorimetry (DSC), polarizing optical microscopy (POM), wide angle X-ray diffraction (WAXD), scanning electron microscopy (SEM), and tensile tests in this work. Experimental results indicated that PLLA was immiscible with PES. Crystallization of PLLA/PES blends was studied by DSC using two-step crystallization condition and analyzed by the Avrami equation. The crystallization rate of PLLA at 100 °C was accelerated with the increase of PES in the blends while the crystallization mechanism did not change. In the case of the isothermal crystallization of PES at 67.5 °C, the crystallization mechanism did not change, and the crystallization rate decreased with the increase of PLLA. The mechanical properties of PLLA/PES blends were examined by tensile testing. The elongation at break of PLLA was improved significantly in the blends, while its considerably high Young's modulus was still kept. SEM images of fracture surfaces indicated that the fracture behavior of PLLA/PES blends changed from brittle fracture to ductile fracture behavior in the blends.

Keywords: Biodegradable polymer; Crystalline/crystalline polymer blends; Miscibility

---

1. Introduction

Biodegradable polymers have recently received more and more attention from the viewpoint of environment protection and resource recycle. Based on the difference in the preparation method, biodegradable polymers can usually be classified into two types. One is the biosynthetic polymer, such as bacterial polyhydroxyalkanoates (PHAs). The other is the chemosynthetic polymer, such as the aliphatic polyesters. PLLA and PES are just two of the aliphatic biodegradable polyesters. The chemical structures of PLLA and PES are $-[CH(CH_3)\text{-}COO]_n-$ and $-[OCH_2CH_2O_2CCH_2CH_2CO]_n-$, respectively.

PLLA is a biodegradable crystalline polyester, which can be produced from renewable sources. The crystal structure and crystallization behavior of PLLA have been investigated extensively [1–3]. The hard and brittle mechanical properties of PLLA limit its development and practical application; therefore, several modifications have been proposed to improve processing and mechanical properties, such as copolymerization, plasticization, and polymer blending. Among the several modifications, polymer blending is regarded as a useful and economical way to produce new materials with a variety of properties. PLLA was found to be miscible with natural poly(3-hydroxybutyrate) (PHB) [4], synthetic atactic poly(3-hydroxybutyrate) (a-PHB) [5], poly(methyl methacrylate) (PMMA) [6], poly(vinyl phenol) (PVPh) [7], and poly(vinyl

---

* Corresponding author. State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China. Tel./fax: +86 10 6441 3161.
E-mail address: qiuzb@mail.buct.edu.cn (Z. Qiu).

0032-3861/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2007.05.035

acetate) (PVAc) [8]. On the other hand, immiscibility has been found in blends of PLLA with some polymers, such as poly(butadiene-*co*-acrylonitrile) (NBR) [9], poly(*p*-dioxanone) [10], poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) [11], poly(vinyl alcohol) (PVA) [12], and poly(butylene adipate-*co*-terephthalate) (PBAT) [13].

PES is a chemosynthetic biodegradable polyester. The crystal structure, morphology and melting behavior of PES have been reported in literature [14–17]. In previous works we studied the nonisothermal melt and cold crystallization kinetics of PES and the subsequent melting behavior [18–20]. Blends of PES with other polymers have also been studied in order to modify the properties and extend its practical application. Till now, less work has been done on the blending PES with other polymers. PES was reported to be miscible with some polymers, including PHB, poly(ethylene oxide) (PEO), and PVPh [21–24].

The disadvantages of poor mechanical properties and slow crystallization rate of PLLA limit its wide application; however, PES is a biodegradable polyester with good mechanical properties, especially its elongation at break. As a result, it is expected that blending with PES may enhance the crystallization rate and improve the mechanical properties of PLLA. To the best of our knowledge, the study of PLLA/PES blends has not been reported in literature so far. The features of PLLA/PES blends can be summarized as follows. First, PLLA/PES blends are fully biodegradable polymer blends since both the components are biodegradable polyesters. Second, PLLA/PES blends are crystalline/crystalline polymer blends and thus can provide various phase behavior and crystalline morphology depending on blend composition and crystallization condition since both the components can crystallize in a wide crystallization temperature range. Third, the mechanical properties and crystallization rate of PLLA can be modulated in the blends by changing the blend composition and crystallization condition. Therefore, it is believed that the miscibility, crystallization behavior, and mechanical properties' study of this work will be helpful for a better understanding of the relationship between structure and properties of biodegradable polymer blends. It should be of great interest and importance to modify the properties and extend the practical application for biodegradable polymers from both academic and industrial viewpoints.

2. Experimental section

PLLA ($M_w = 177,000$) was produced by Unitika Co. Ltd., Japan, and PES ($M_w = 213,000$) was supplied by Shokubai Co. Ltd., Japan. Both PLLA and PES were used as received. PLLA/PES blends were prepared with mutual solvent chloroform. The solution of both polymers (0.02 g/ml) was cast on a Petri dish at room temperature and held for 1 day to evaporate the solvent in a controlled air stream. The resulting films were further dried in vacuum at 50 °C for 3 days to remove the solvent completely. Thus, PLLA/PES blends were prepared with various compositions ranging from 100/0 to 0/100 in weight ratio, the first number referring to PLLA.

Thermal analysis was performed using a TA Instruments differential scanning calorimetry (DSC) Q100 with a Universal Analysis 2000. The glass transition temperature (T_g) and the melting temperature (T_m) of the melt-quenched PLLA/PES blends were measured at a heating rate of 20 °C/min. The samples were first annealed at 190 °C for 3 min to erase any thermal history and subsequently quenched to −70 °C at a cooling rate of 100 °C/min. On the basis of the heat of fusion of 100% crystalline PLLA (93 J/g) [25] and PES (180 J/g) [26], the degree of crystallinity of PLLA and PES components was calculated from the melting endotherms of the sample and normalized with respect to the composition of each component in the blend. The crystallization peak temperature was obtained from the DSC cooling traces from the crystal-free melt at the cooling rate of 5 °C/min. The isothermal crystallization from the melt was also examined by DSC. The samples were cooled to 100 °C at a cooling rate of 40 °C/min to crystallize PLLA after being held at 190 °C for 3 min to destroy any thermal history. The samples were further cooled to 67.5 °C to crystallize PES after the crystallization of PLLA. The aforementioned isothermal crystallization conditions consist of the following two steps, namely, the isothermal crystallization of PLLA from the melt at 100 °C and the isothermal crystallization of the PES at 67.5 °C from the liquid phase in the presence of previously crystallized PLLA.

A polarizing optical microscope (Olympus BX51) equipped with a first order retardation plate and a temperature controller (Linkam THMS 600) was used to investigate the spherulitic morphology and growth of PLLA/PES blends.

Wide angle X-ray diffraction experiments were performed on a Rigaku D/Max 2500 VB2+/PC X-ray Diffractometer at 40 kV and 200 mA. The samples for WAXD experiments were prepared as follows. The samples were first pressed into films with thickness of around 1 mm on a hot stage at 190 °C, and then transferred into a vacuum oven at 70 °C for 3 days.

Tensile tests were carried out on an Instron 1185 tensile testing machine at a rate of 10 mm/min at room temperature. Three samples were used at least.

The fracture surfaces of PLLA/PES blends after tensile testing were observed using scanning electron microscopy (SEM) (Cambridge stereoscan 250 MK3). All specimens were coated with gold before examination.

3. Results and discussion

3.1. Miscibility and phase morphology of PLLA/PES blends

In this work miscibility of PLLA/PES blends was studied by DSC. As described in Section 2, the samples were first melted at 190 °C for 3 min to destroy any thermal history, and then quenched to −70 °C to reach the amorphous state at a cooling rate of 100 °C/min. Fig. 1 shows the DSC traces of PLLA/PES blends at a heating rate of 20 °C/min from the amorphous state. Neat PLLA showed a T_g at 54.6 °C, a cold crystallization peak temperature (T_{ch}) at 133.4 °C with the

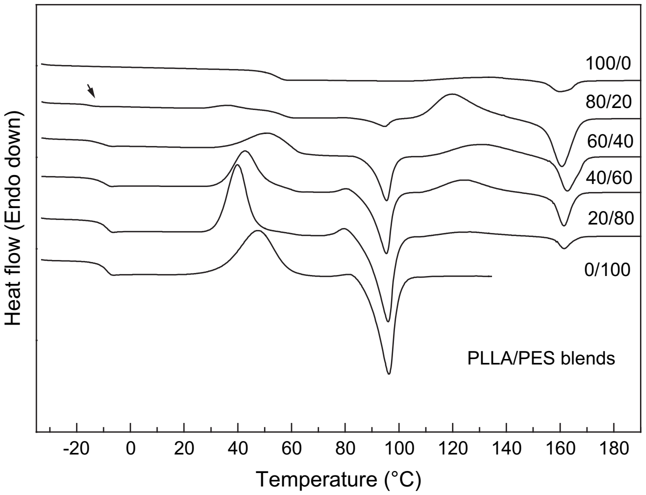

Fig. 1. DSC traces of PLLA/PES blends at 20 °C/min after quenching from the melt at 100 °C/min.

crystallization enthalpy of 4.2 J/g, and a T_m at 160 °C with the heat of fusion of 5.3 J/g. Neat PES showed a T_g at −8.5 °C, a T_{ch} at 47.4 °C with the crystallization enthalpy of 36.3 J/g, and a T_m at 96.2 °C with the heat of fusion of 39.4 J/g. However, only one T_g at around −9 °C was found in the blends despite the blend composition, which was attributed to T_g of PES. T_g of PLLA phase was not found because it was too close to T_{ch} of PES in the blends. Furthermore, two T_ms at around 95 and 161 °C were found in the PLLA/PES blends, corresponding to T_m of PES and that of PLLA, respectively, irrespective of blend composition. The aforementioned results indicated that PLLA was immiscible with PES in the blends. The immiscibility was also confirmed by the OM study, which will be described in the following section. On the basis of the values of melting enthalpies and blend composition, the crystallinity of neat PLLA was found to be only 5.7%, indicating that PLLA was difficult to crystallize at 20 °C/min from the amorphous state for the melt-quenched sample. However, the values of crystallinity of PLLA increased significantly to around 29.3% for PLLA/PES 80/20 blend sample, indicating that the crystallization of PLLA was enhanced significantly upon only blending 20% PES in the blends. With further increasing PES content, the values of the crystallinity of PLLA were around 24.2, 30.4, and 21.7% for PLLA/PES 60/40, 40/60, and 20/80 blend samples. The increased crystallinity of PLLA in the blends showed that the addition of PES played a positive and significant role in the crystallization of PLLA for the melt-quenched PLLA/PES blends from the amorphous state. However, in the case of PES, the crystallinity was found to be around 20.2% for neat PES, varied very slightly between 19.8 and 23.7% with increasing PLLA content from 20 to 60%, and decreased sharply to only 9.2% for PLLA/PES 80/20 blend sample, probably due to too low PES content in the blends. In conclusion, blending with PES could enhance the crystallinity of PLLA significantly, while the addition of PLLA to PES did not change the crystallinity of PES for almost all the blends except PLLA/PES 80/20 sample.

From the aforementioned results, it was found that the cold crystallization of PLLA occurred at low temperature range in the blends compared with that of neat PLLA, and the values of crystallization enthalpy and heat of fusion of PLLA in the blends were also greater than those of neat PLLA. The fact that blending with PES enhanced the crystallization and crystallinity might be attributed to the following reason. In the PLLA/PES blends, PES crystallized first in the temperature range of around 35–70 °C and then melted at around 80–110 °C on heating from the amorphous state. The residue of PES crystals in the blends might play a role of nucleation agent for the cold crystallization of PLLA on further heating. Therefore, the cold crystallization of PLLA was enhanced upon blending with PES.

For comparison, the melting behavior of PLLA/PES blends for the as cast samples was also studied by DSC. Fig. 2 shows the DSC traces of PLLA/PES blends at a heating rate of 20 °C/min with two melting peaks at around 162 and 95 °C, corresponding to T_ms of PLLA and PES, respectively. T_m of PLLA varied slightly between 161 and 162 °C for the as cast samples irrespective of blend composition. However, in the case of PES, T_m was around 96 °C for neat PES, 20/80, and 40/60 blend samples, which shifted to 93.6 and 89.9 °C with further increasing PLLA content for 60/40 and 80/20 blend samples. This indicated that crystallization of PES was restricted in PLLA-rich blends for the as cast samples. The decrease of T_m of PES in the PLLA-rich blends was probably due to morphological factors such as crystalline lamellar thickness. On the basis of the values of melting enthalpies and blend composition, the crystallinity of neat PLLA was found to be 37.4%, and decreased steadily to 25.5% for PLLA/PES 20/80 sample with increasing PES content in the blends. In the case of PES, the values of crystallinity decreased from 34.4% for neat PES to 21.5% for PLLA/PES 80/20 blend, indicating again that the crystallization of PES was suppressed. Thus, the mechanical properties and biodegradability of PLLA/PES blends may be adjusted by changing blend composition and crystallization conditions.

Spherulitic morphology and growth rates of neat PLLA and neat PES were studied by POM in this work. Figs. 3 and 4 show the spherulitic morphology of PLLA and PES,

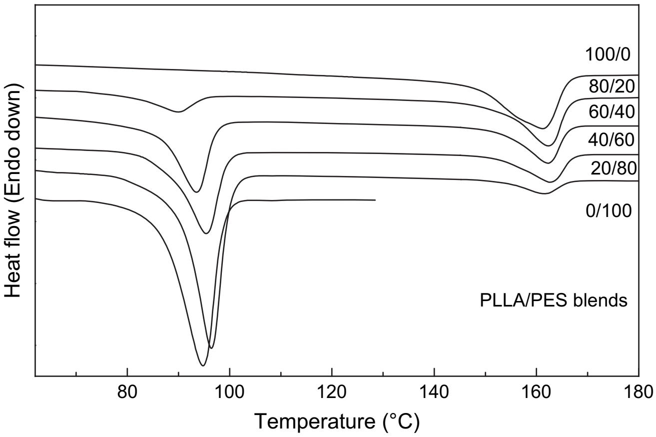

Fig. 2. Melting behavior of PLLA/PES blends at 20 °C/min for the as cast samples.

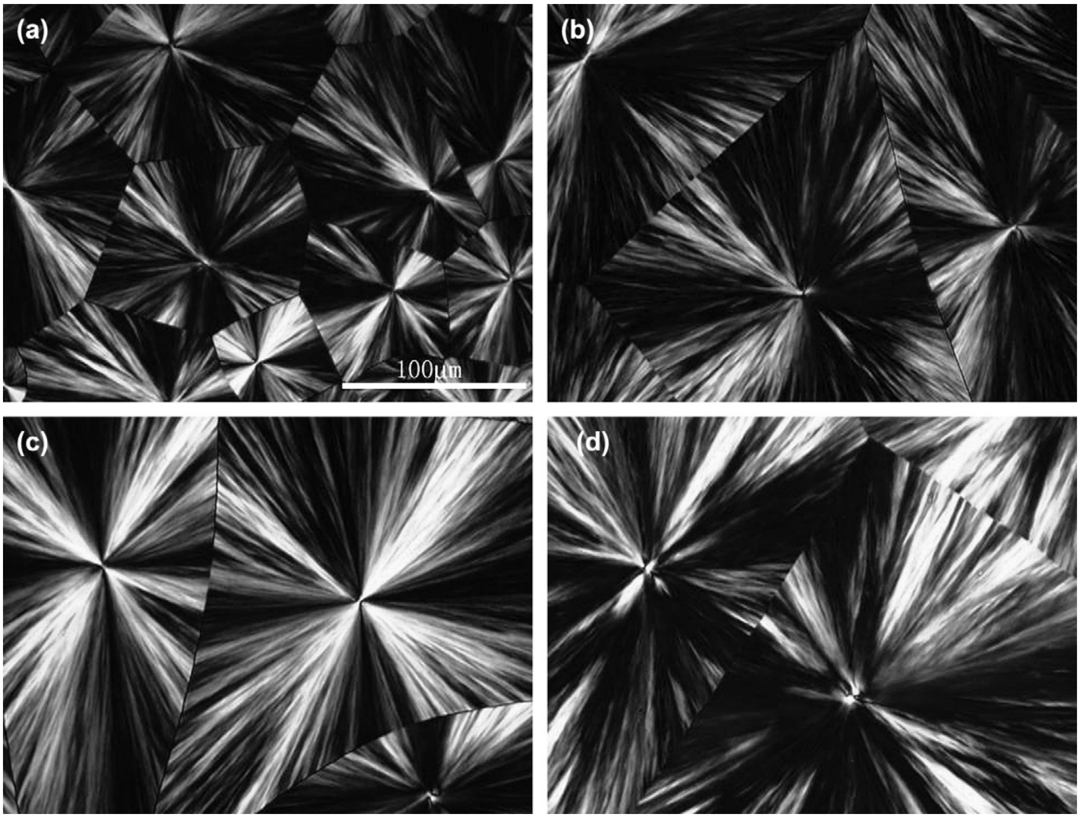

Fig. 3. Spherulitic morphology of neat PLLA (same magnification, bar = 100 μm) at different crystallization temperatures: (a) 110, (b) 115, (c) 120, and (d) 125 °C.

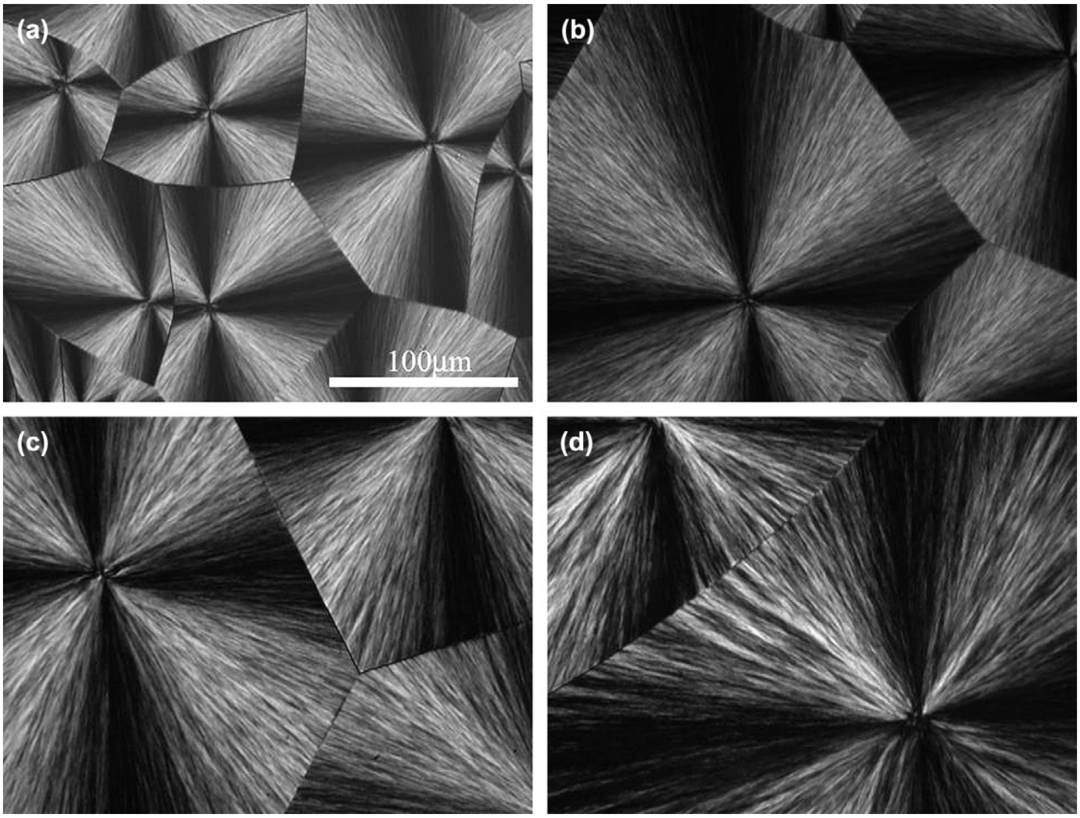

Fig. 4. Spherulitic morphology of neat PES (same magnification, bar = 100 μm) at different crystallization temperatures: (a) 55, (b) 60, (c) 65, and (d) 70 °C.

respectively. Fig. 3 shows that PLLA crystallized according to a spherulitic growth in the temperature range of 110–125 °C and it showed compact spherulites. The spherulites' size increased with the crystallization temperature, indicating that the nucleation density decreased with the increase of crystallization temperature. PES showed compact spherulites with clear Maltese cross in the crystallization temperature range of 40–70 °C. The size of the spherulites also became larger with increasing crystallization temperature, indicative of a decrease in the nucleation density.

The spherulitic growth rates of PLLA and PES were measured by following the development of radius with time. Both PLLA and PES spherulites showed a linear growth till the contact with other spherulites during the crystallization process. Fig. 5 shows the temperature dependence of the spherulitic growth rates of PLLA and PES. Both PLLA and PES exhibited a bell shape curve for the growth rates in the crystallization temperature range of 40–70 °C and 110–125 °C, respectively. From Fig. 5, it could be seen that PES showed a maximum value of 2.27 μm/min for the growth rate at 55 °C, while PLLA showed a maximum value of 0.973 μm/min at 115 °C.

The phase morphology of PLLA/PES blends was further studied by POM. It is possible to infer whether the melt is single-phased or biphasic if the refractive indices of PLLA and PES are not the same. Therefore, the single-phased melt should be observed if PLLA and PES are miscible. Otherwise, the biphasic melt should be observed if the two components are immiscible. In this work clearly biphasic separation was observed for all compositions of PLLA/PES blends, indicating that PLLA is not miscible with PES in the melt. POM results further confirmed the immiscibility of PLLA/PES blends. For the sake of briefness, the POM micrographs were not shown in this manuscript.

3.2. Crystallization of PLLA/PES blends

PLLA/PES blends are crystalline/crystalline polymer blends with PLLA being the high T_m component and PES being the low T_m component. In order to study the influence of the existence of the crystallinity of one component on the other, we studied the crystallization of PLLA/PES blends by DSC using two different crystallization conditions, namely, nonisothermal crystallization and isothermal crystallization.

The nonisothermal crystallization of PLLA/PES blends was studied by DSC at a cooling rate of 5 °C/min from the crystal-free melt as shown in Fig. 6. The crystallization peak temperature (T_c) of neat PLLA was around 99.8 °C. T_c of PLLA shifted to 94.2 °C for PLLA/PES 80/20 blend, and could not be found in the PLLA/PES blends with PES content greater than 40%. On the other hand, T_c of neat PES was around 62.9 °C. In the blends, T_c of PES shifted to around 57.5 °C and was almost unchanged with the increase of PLLA content to 40%. However, it was found that PES failed to crystallize in PLLA/PES 80/20 blend, probably due to its too small content. From the aforementioned experimental results, the following two conclusions could be drawn. First, the crystallization of PLLA was suppressed in the blends after blending with 20% PES, and lost the crystallizability with increasing PES content greater than 40%. Second, the crystallization of PES was also suppressed in the blends from 80/20 to 40/60 compared with that of neat PES; however, the blend composition of PLLA influenced T_c of PES very slightly. PES must crystallize in its own domain; therefore, the existence of phase separated PLLA crystal and/or melt did not influence the crystallization of PES significantly despite blend composition.

As described in Section 2, the process of the isothermal crystallization of PLLA/PES blends was investigated at two crystallization temperatures: 100 °C for PLLA and 67.5 °C for PES. The plots of relative crystallinity X_t versus the crystallization time t are shown in Fig. 7a for the isothermal crystallization at 100 °C of neat and blended PLLA with PES content up to 60%. It was found that the crystallization time for PLLA at 100 °C shortened in the blends compared with that of neat PLLA. The well-known Avrami equation is often used to analyze the isothermal crystallization kinetics; it assumes that the relative degree of crystallinity develops with crystallization time t as

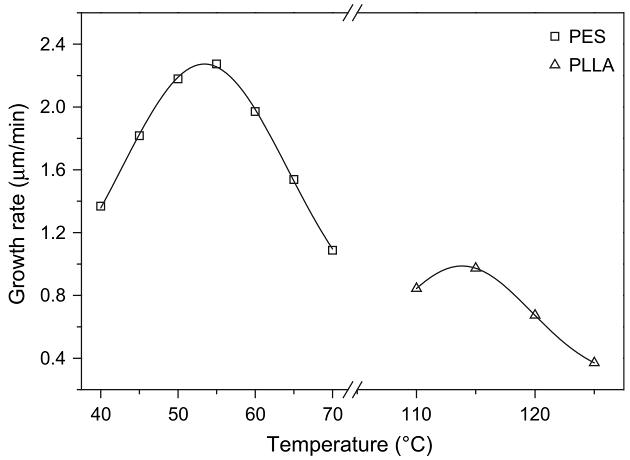

Fig. 5. Temperature dependence of spherulitic growth rates of neat PLLA and neat PES.

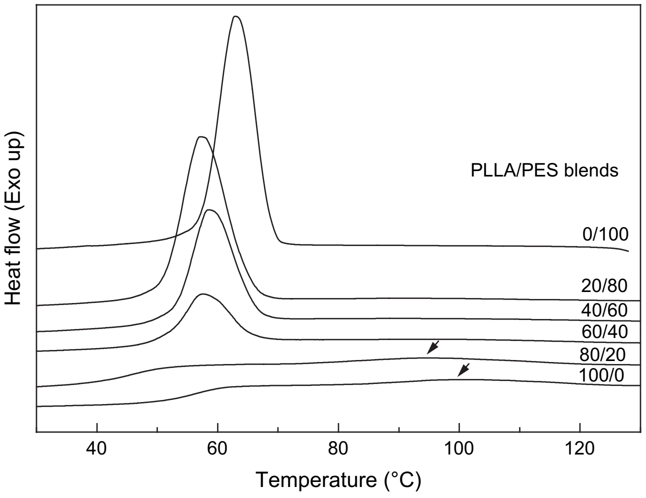

Fig. 6. DSC traces of PLLA/PES blends cooled from the melt at 5 °C/min.

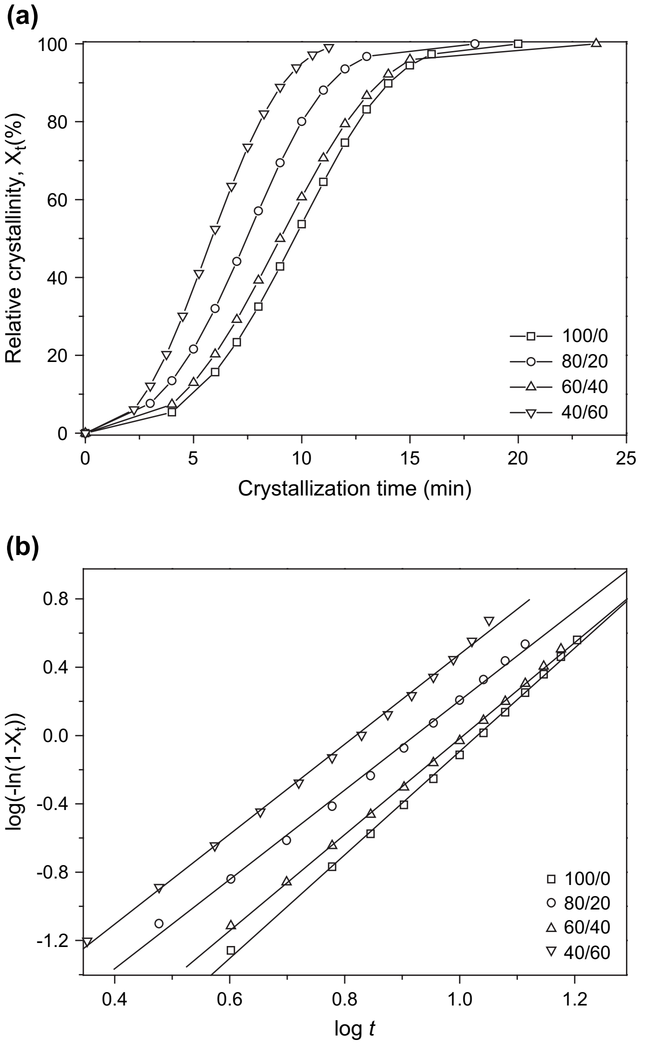

Fig. 7. (a) Plots of relative crystallinity of PLLA crystallized at 100 °C versus crystallization time for PLLA/PES blends and (b) the Avrami plots of PLLA/PES blends crystallized at 100 °C.

$$1 - X_t = \exp(-kt^n) \qquad (1)$$

where n is the Avrami exponent depending on the nature of nucleation and growth geometry of the crystals, and k is a composite rate constant involving both nucleation and growth rate parameters [27]. The Avrami parameters n and k were obtained from the plots of $\log(-\ln(1 - X_t))$ versus $\log t$ as shown in Fig. 7b. The Avrami exponents n and crystallization rate constants k of the neat and blended PLLA are shown in Table 1.

The values of n are close to 3 for the isothermal crystallization of both neat and blended PLLA, probably suggesting a spherulitic growth of PLLA with heterogeneous nucleation. The almost unchanged n with the addition of PES indicated that the crystallization mechanism of PLLA was not affected in the presence of PES melt in PLLA/PES blends. On the other hand, the values of k in the blends are higher than that of neat PLLA, indicating that blending with PES enhanced the crystallization rate of PLLA. The increase of crystallization rate of PLLA in the blends might be attributed to the increase of nucleation rate of PLLA in the blends. PLLA and PES are immiscible, and the interface of the phase separated domains may provide favorable nucleation sites for crystallization of PLLA. Therefore, the crystallization rate of PLLA was enhanced by lowering the nucleation barrier in the blends than that of pure PLLA. Similar results were also found in PLLA/PCL blends, and it was reported that the crystallization rate of PLLA increased also with increasing PCL content in the blends [28].

Table 1
Crystallization kinetic parameters of PLLA at 100 °C in PLLA/PES blends

PLLA/PES	n	k (min^{-n})
100/0	3.0	7.5×10^{-4}
80/20	2.6	3.9×10^{-3}
60/40	2.8	1.5×10^{-3}
40/60	2.6	6.9×10^{-3}

Similarly, the isothermal crystallization of low T_m component PES at 67.5 °C was also studied by DSC and analyzed by the Avrami equation in PLLA/PES blends after the samples finished the crystallization of PLLA at 100 °C in advance as described in Section 2. The crystallization kinetic parameters are listed in Table 2. The average Avrami exponent was around 2.2, and did not change with the addition of PLLA. On the other hand, it was found that the values of k decreased with the increase of PLLA in the blends except that the value of k in PLLA/PES 20/80 was close to that of PLLA/PES 40/60. It is apparent that the crystals of PLLA formed at 100 °C must play a significant role of the crystallization of PES in crystalline/crystalline polymer blends. The presence of high T_m component PLLA crystals should have two different influences on the crystallization of low T_m component PES. One is the possible positive effect on the nucleation of PES crystallization. The other is the possible negative effect on the crystal growth of PES spherulites since PES must crystallize in the phase separated domains with the presence of PLLA crystals in the blends. The slow-down of the crystallization rate of PES may be attributed to the competition between the two opposite effects. The negative effect of the presence of the PLLA crystals on the spherulitic growth of PES seems to play a dominant role during the crystallization of PES. The crystallization mechanism of PES did not change with the addition of PLLA in the blends; however, the crystallization rate of PES decreased with the increase of PLLA content.

In summary, the crystallization mechanisms of PLLA and PES did not change in the blends; however, the crystallization rate of PLLA was accelerated in the blends, while the crystallization rate of PES was reduced in the blends.

Table 2
Crystallization kinetic parameters of PES at 67.5 °C in PLLA/PES blends

PLLA/PES	n	k (min^{-n})
0/100	2.1	2.7×10^{-1}
20/80	2.2	1.1×10^{-1}
40/60	2.1	1.3×10^{-1}
60/40	2.3	7.8×10^{-2}

WAXD experiments were performed to study the crystal structure of PLLA/PES blends. Fig. 8 shows the WAXD patterns of PLLA/PES blends. Neat PLLA presented two strong diffraction peaks at around 16.31° and 18.55° corresponding to (200)/(110) and (203) planes, respectively [1]. Neat PES showed two strong diffraction peaks at around 20.08° and 23.23° corresponding to (120) and (200) planes, respectively [14]. For PLLA/PES blends, they involved all the diffraction peaks corresponding to neat PLLA and neat PES, and the intensity of the diffraction peaks of each component decreased with increasing the other component content in the blends. Such results indicated that PLLA and PES crystallized separately in the blends. Blending with other semicrystalline polymer did not modify the crystal structure in the blends but only reduced the intensity of diffraction peak.

3.3. Mechanical properties

The DSC and POM results mentioned above have confirmed the immiscibility between PLLA and PES, which may lead to a poor adhesion between phases and result in poor mechanical properties. However, one of the aims of the present work is focused on the improvement of the brittleness of PLLA without sacrificing modulus by blending some amount of PES. Tensile tests can provide an answer to this issue. Tensile test experiments were performed to investigate the effect of blending with PES on the mechanical properties of PLLA. Fig. 9 shows the tensile properties of PLLA/PES blends. The Young's modulus of neat PLLA was found to be around 1974 MPa, and decreased steadily to be around 1489 and 1392 MPa for PLLA-rich blends, namely, PLLA/PES 80/20 and 60/40. On the contrary, the Young's modulus of neat PES was around 287 MPa, and increased significantly to be around 566 and 1098 MPa for PES-rich blends, namely, PLLA/PES 20/80 and 40/60. Furthermore, it should be noted that the elongation at break of PLLA/PES blends increased significantly with respect to that of neat PLLA as shown in Fig. 9. The elongation at break was only around 5.3% for neat PLLA, increased significantly to around 15.2% for PLLA/PES 80/20, and further increased tremendously to around 143.7% for PLLA/PES 60/40. The elongation at break of PLLA increased by around 2 and 26 times in the PLLA-rich blends (PLLA/PES 80/20 and 60/40), while the Young's modulus of PLLA only decreased by 25 and 30%. Similar results were also found in PLLA/PBAT blends [13] and PLLA/poly(butylene succinate) (PBSU) blends [29]. Blending a small amount of PBAT or PBSU was able to improve significantly the elongation at break of PLLA without reducing the modulus apparently [13,29].

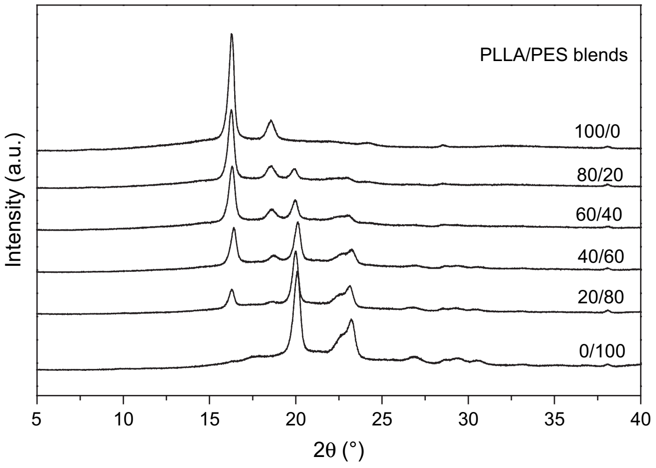

Fig. 8. WAXD patterns of PLLA/PES blends.

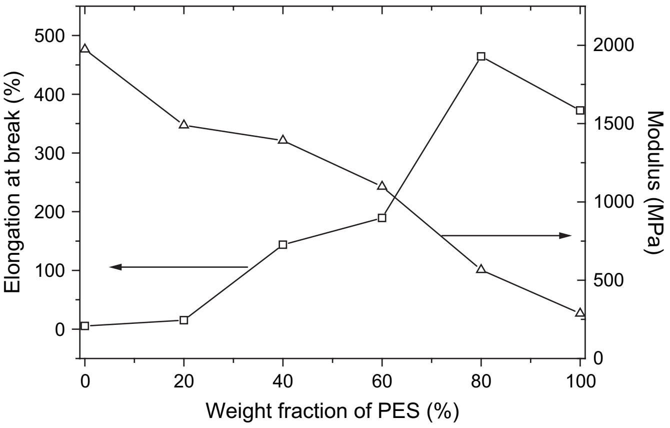

Fig. 9. Tensile testing results of PLLA/PES blends.

The fracture behavior of the specimen in the tensile tests was expected to change from brittle fracture of neat PLLA to ductile fracture of the PLLA/PES blends. SEM was employed to study the fracture surfaces of PLLA/PES blends of the tensile samples. Fig. 10 shows SEM micrographs of the fracture surfaces of PLLA/PES blends. The SEM images revealed that neat PLLA morphology was distinct from that of neat PES. PLLA showed a smooth surface, while PES presented a rough surface. The smooth fracture surface indicated the brittle fracture behavior of neat PLLA, while the rough surface implied the ductile fracture behavior of neat PES. For PLLA/PES blends, the surface changed from smooth to rough with increasing PES content, especially with PES content higher than 40%. It can be seen from Fig. 10b that the PLLA/PES 80/20 blend comprised an immiscible, two-phase system with PES evenly dispersed in the form of 1 μm domains within the PLLA matrix. With further increasing PES content up to 40%, PLLA and PES form two continuous phase. The SEM images showed consistence with tensile testing results. The results indicated that blending with PES improved the mechanical properties of PLLA. Thus, the mechanical properties of PLLA can be improved significantly by simple blending with PES while it still keeps biodegradability. The practical application of PLLA is expected to extend, especially in some cases where excellent mechanical properties are required.

4. Conclusions

The miscibility, phase morphology, crystallization kinetics, crystal structure, mechanical properties of PLLA/PES blends

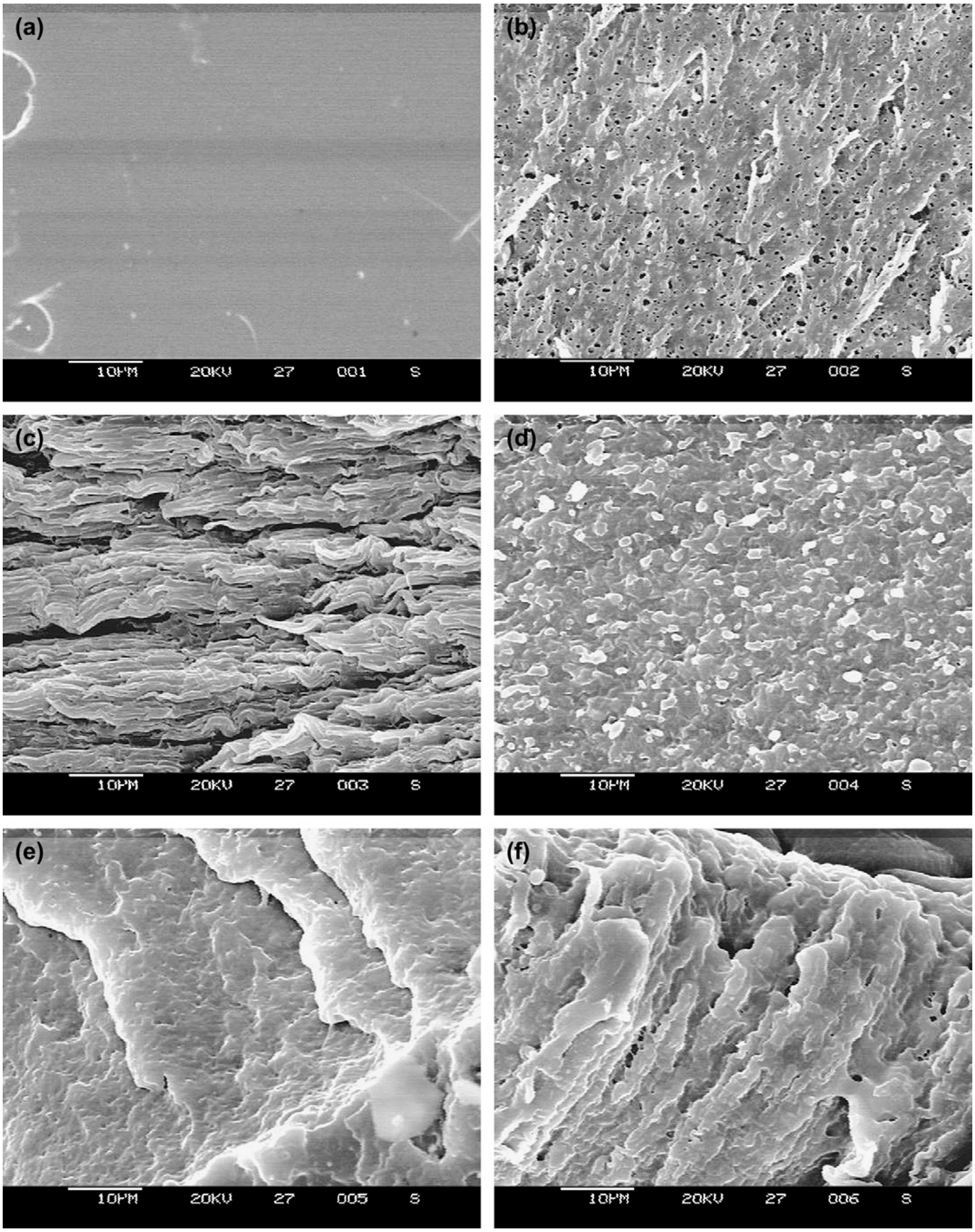

Fig. 10. SEM images of the fracture surfaces of PLLA/PES blends after tensile testing: (a) 100/0, (b) 80/20, (c) 60/40, (d) 40/60, (e) 20/80, and (f) 0/100.

were investigated by DSC, POM, WAXD, SEM, and tensile testing in detail. Blending a small amount of PES can improve the mechanical properties and accelerate the crystallization rate of PLLA. The following detailed conclusions were obtained.

(1) PLLA and PES were immiscible since PLLA/PES blends showed blend composition independent T_g of PES and T_ms of two components. POM experiments further confirmed phase separation of PLLA/PES blends.
(2) For the melt-quenched samples, blending with PES enhanced the crystallinity of PLLA significantly, indicating that the crystallization of PLLA was promoted by the presence of PES, while the addition of PLLA to PES did not change the crystallinity of PES for almost all the blends.
(3) Both neat PLLA and neat PES could crystallize according to spherulitic growth in a wide crystallization temperature range. PLLA showed a maximum value of 0.973 μm/min at 115 °C, while PES showed a maximum value of 2.27 μm/min for the growth rate at 55 °C.
(4) The crystallization mechanisms of both PLLA and PES did not change in the blends and remained the same as those of parent polymers. However, the crystallization

rate of PLLA was found to increase with increasing PES content, while on the contrary that of PES decreased with increasing PLLA content in the blends. The former was attributed to the fact that the interface of the immiscible blends provided favorable nucleation sites for crystallization of PLLA. The latter might arise from the fact that PES must nucleate and grow under a confined crystallization condition due to the presence of PLLA crystals.

(5) The mechanical properties of PLLA was improved apparently by blending with PES. The elongation at break of PLLA was improved significantly in the blends while still keeping considerably high Young's modulus. SEM images of fracture surfaces indicated that the fracture behavior of PLLA/PES blends changed from brittle fracture behavior for neat PLLA to ductile fracture behavior for blended PLLA in the blends.

Acknowledgements

Thanks are due to Prof. Masami Okamoto of Toyota Technological Institute for kindly providing PLLA samples. This work was supported by the National Natural Science Foundation, China (grant no. 20504004), Program for New Century Excellent Talents in University, and the projects of Polymer Chemistry and Physics, BMEC (XK100100433 and XK100100540).

References

[1] Zhang J, Duan Y, Sato H, Tsuji H, Noda I, Yan S, et al. Macromolecules 2005;38:8012.
[2] Gazzano M, Focarete ML, Riekel C, Scandola M. Biomacromolecules 2004;5:553.
[3] Hoogsteen W, Postema AR, Pennings AJ, ten Brinke G, Zugenmaier P. Macromolecules 1990;23:634.
[4] Blümm E, Owen AJ. Polymer 1995;36:4077.
[5] Focarete ML, Ceccorulli G, Scandola M, Kowalczuk M. Macromolecules 1998;31:8485.
[6] Shirahase T, Komatsu Y, Tominaga Y, Asai S, Sumita M. Polymer 2006;47:4839.
[7] Meaurio E, Zuza E, Sarasua JR. Macromolecules 2005;38:1207.
[8] Ogata N, Jimenez T. J Polym Sci Part B Polym Phys 1997;35:389.
[9] Park EU, Kim HK, Shim JH, Kim HS, Jang LW, Yoon JS. J Appl Polym Sci 2004;92:3508.
[10] Pezzin APT, Alberda van Ekenstein GOR, Zavaglia CAC, ten Brinke G, Duek EAR. J Appl Polym Sci 2003;88:2744.
[11] Ferreira BMP, Zavaglia CAC, Duek EAR. J Appl Polym Sci 2002;86:2898.
[12] Tsuji H, Muramatsu H. J Appl Polym Sci 2001;81:2151.
[13] Jiang L, Wolcott MP, Zhang J. Biomacromolecules 2006;7:199.
[14] Ueda AS, Chatani Y, Tadokoro H. Polym J 1971;2:387.
[15] Al-Raheil IA, Qudah AMA. Polym Int 1995;37:249.
[16] Ichikawa Y, Washiyama J, Moteki Y, Noguchi K, Okuyama K. Polym J 1995;27:1264.
[17] Iwata T, Doi Y, Isono K, Yoshida Y. Macromolecules 2001;34:7343.
[18] Qiu Z, Ikehara T, Nishi T. Polymer 2003;44:5429.
[19] Qiu Z, Fujinami S, Komura M, Nakajima K, Ikehara T, Nishi T. Polym J 2004;36:642.
[20] Qiu Z, Komura M, Ikehara T, Nishi T. Polymer 2003;44:7781.
[21] Al-Salah HA. Polym Bull 1998;41:593.
[22] Chen HL, Wang SF. Polymer 2000;41:5157.
[23] Qiu Z, Ikehara T, Nishi T. Macromolecules 2002;35:8251.
[24] Qiu Z, Fujinami S, Komura M, Nakajima K, Ikehara T, Nishi T. Polymer 2004;45:4515.
[25] Fisher EW, Sterzel HJ, Wegner G. Kolloid Z Z Polym 1973;251:980.
[26] Papageorgiou GZ, Bikiaris DN. Polymer 2005;46:12081.
[27] Avrami M. J Chem Phys 1939;7:1193.
[28] Dell'Erba R, Groeninckx G, Maglio G, Malinconico M, Migliozzi A. Polymer 2001;42:7831.
[29] Shibata M, Inoue Y, Miyoshi M. Polymer 2006;47:3557.