

Biodegradable Poly(L-lactic acid)/Poly(butylene succinate-co-adipate) Blends: Miscibility, Morphology, and Thermal Behavior

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ABSTRACT: Blends of two biodegradable and semicrystalline polymers, poly(L-lactic acid) (PLLA) and poly(butylene succinate-co-adipate) (PBSA), were prepared by solvent casting in different compositions. The miscibility, morphology, and thermal behavior of the blends were investigated using differential scanning calorimetry and optical microscopy. PLLA was found to be immiscible with PBSA as evidenced by two independent glass transitions and biphasic melt. Nonisothermal crystallization measurements showed that fractionated crystallization behavior occurred when PBSA was dispersed as droplets, evidenced by multiple crystallization peaks at different supercooling levels. Crystallization

and morphology of the blends were also investigated through two-step isothermal crystallization. For blends where PLLA was the major component, different content of PBSA did not make a significant difference in the crystallization mechanism and rate of PLLA. For blends where PBSA was the major component, the crystallization rate of PBSA decreased with increasing PLLA content, while the crystallization mechanism did not change. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 3204–3210, 2007

Key words: biodegradable; polyesters; blends; miscibility; thermal properties

INTRODUCTION

Poly(L-lactic acid) (PLLA) is a biodegradable and biocompatible semicrystalline polyester, widely used in biomedical and environmental applications.^{1–3} Practical applications of this material are often limited by its brittleness and narrow processing window. Moreover, PLLA is expensive compared with the majority of commodity polymers. Blending of PLLA with other polymers has been reported in terms of improving processibility and flexibility, lowering the cost, and controlling the biodegradation rate. A few counterparts have been reported to give miscible blends: poly(DL-lactic acid),^{4,5} poly(D-lactic acid),⁶ poly(3-hydroxybutyrate),^{7,8} poly(ethylene oxide),⁷ poly(methyl methacrylate),⁹ poly(vinyl acetate),¹⁰ poly(ethylene glycol),¹¹ and poly(vinyl phenol).¹² Besides, immiscibility has been found in blends of PLLA with poly(ϵ -caprolactone),^{13,14} poly(vinyl alcohol),¹⁵ poly(vinyl acetate-co-vinyl alcohol),¹⁰ poly(3-hydroxybutyrate-co-3-hydroxyvalerate),¹⁶ and starch.¹⁷

Poly(butylene succinate) (PBS) is also among the most important biodegradable polyesters.² The blends of PLLA with PBS have been investigated by Park and Im¹⁸ concerning their phase behavior and morphology. Poly(butylene succinate-co-butylene adipate) (PBSA) is one of the important copolymers of PBS, with a lower glass transition and melting temperature and being more readily biodegraded than PBS.^{19–22} It has been reported that a PLLA/PBSA blend is used for the biodegradable sealing envelope, covering the foamed receptacles containing fried noodles such as Ramyun.²³ However, little attention has been now paid to the miscibility and thermal behavior of the PLLA/PBSA blends. Besides, PLLA and PBSA are both crystallizable. Blends in which both components are semicrystalline polymers, are more complex and thus open up new ways of studying the crystallization behavior and morphology in polymer blends.¹¹ Since the investigation on crystalline/crystalline blends is quite limited, PLLA/PBSA blends appear to be an interesting system for such a study.

In this work, the miscibility, morphology, and crystallization behavior of the PLLA/PBSA blends were investigated using differential scanning calorimetry and optical microscopy. It will be seen that PLLA and PBSA are immiscible. Besides, 'fractionated crystallization' phenomenon,^{24–27} which typically occurs when the semicrystalline polymer is dispersed into confin-

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ing droplets in immiscible amorphous polymer matrices, has been observed when PBSA is the dispersed phase in semicrystalline PLLA matrices.

EXPERIMENTAL

PLLA was provided by Boehringer Ingelheim, Germany. The number-average molecular weight (M_n) and polydispersity (M_w/M_n) of the material were evaluated from gel permeation chromatography (Shimadzu, LC 10A, Japan) using polystyrene as standard and chloroform as solvent. The values of M_n and M_w/M_n were 1.8×10^5 and 1.22, respectively. PBSA with the trade name Bionolle 3001 was provided by Showa Highpolymer, Japan. The molar ratio of the succinate unit to the adipate unit was $\sim 4 : 1$, and the content of the coupling agent (hexamethylene diisocyanate) unit was ~ 0.5 mol %. The values of M_n and M_w/M_n of the material were 4.6×10^4 and 1.97, respectively.²⁸ PLLA/PBSA blends, with various compositions ranging from 80/20 to 20/80 in weight ratio, were prepared by solvent casting using chloroform. The solution of the blends (0.02 g/mL) was cast on a petri dish at room temperature, followed by evaporating in a controlled air stream for 1 day, and further dried in vacuum at 50°C for 2 days.

Thermal analysis was performed using a Perkin-Elmer DSC 7 coupled with an intracooler system and under a nitrogen flow of 20 cm³ min⁻¹. The weight of sample was about 6 mg. Each sample was tested only once. Three groups of experiments were carried out. For the first group, the samples were melted at 200°C (or 120°C for pure PBSA) for 5 min and quenched to -60°C, then, the differential scanning calorimetry (DSC) traces were recorded during a subsequent heating process at 20°C min⁻¹. Calibrations for baseline and for temperature and energy were made at the same heating rate using a pure indium standard. For the second group, the DSC traces were recorded at cooling rate of 5°C min⁻¹, after melting the samples at 200°C (or 120°C for pure PBSA) for 5 min. The 4-Cyano-4'-octyloxy-biphenyl (M24), which was kindly supplied by Prof. Schick (University of Rostock, Germany), was used for the temperature calibration on cooling, and the procedure followed that suggested in the literature.²⁹ For the third group, the samples were heated to 200°C (or 120°C for pure PBSA) at 200°C min⁻¹, held for 5 min, then, quenched to 120°C and held the required time to complete the crystallization of PLLA followed by that at 65°C for PBSA. Crystallization temperatures were calibrated by extrapolating the melting temperatures of indium to zero heating rate, before isothermal treatments. Separate calibrations for baseline were made for all the processes.

The morphology was observed using an Olympus BH polarizing microscope, equipped with a digital camera system and a Mettler hot-stage (FP80).

RESULTS AND DISCUSSION

Miscibility

The miscibility of the melt-quenched PLLA/PBSA blends was evaluated by DSC from the glassy state at a heating rate of 20°C min⁻¹ (Fig. 1). Pure PBSA exhibits a glass transition T_g (taken as the middle point of the transition) at around -42°C, a premelting peak at 64°C and a main melting peak (T_m) at 90°C. Pure PLLA shows a T_g at around 62°C, a cold crystallization peak at 126°C, and a T_m at 178°C. In the blends, a T_g at around -42°C, which is close to that of pure PBSA, can be observed for 20/80 blend, and it decreases with increasing PLLA content. This may reflect that, for the quenched blends, the degree of crystallinity of PBSA decreases with increasing PLLA content. On the other hand, a T_g at around 62°C, which is close to that of pure PLLA, can be found for 80/20 and 60/40 blends, while it is masked by the premelting peak of PBSA for 40/60 and 20/80 blends. A cold crystallization peak of PBSA appears at around -11°C for 80/20, 60/40, and 40/60 blends, while this is not evident for 20/80 blend and pure PBSA. However, a cold crystallization exothermic peak is found at 126°C for pure PLLA, and shifts to 101°C upon blending with 20% of PBSA, while a further increase in PBSA composition has no effect on the position of the exotherm. Furthermore, the T_m s of PBSA and PLLA remain almost the same as those for the pure polymers. From the above results, it can be concluded that PLLA shows no miscibility with PBSA in the amorphous state.

Figure 2 shows the optical micrographs of the PLLA/PBSA blends in the molten state. For all of the compositions probed, clearly defined biphasic separa-

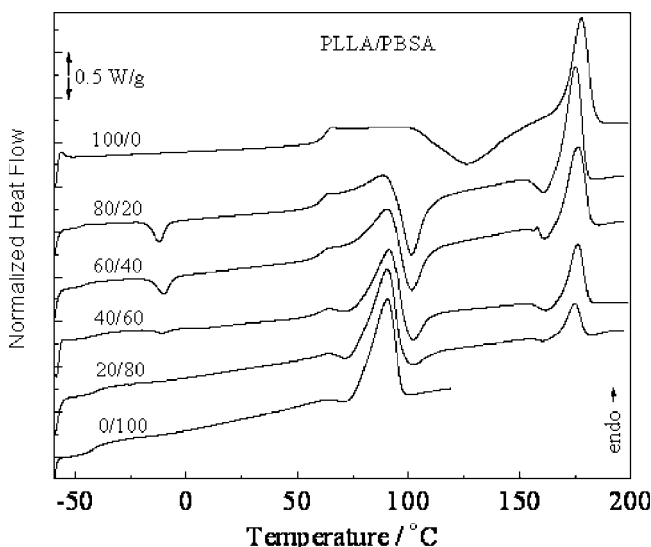


Figure 1 DSC traces of the PLLA/PBSA blends after melt quenching at a heating rate of 20°C min⁻¹.

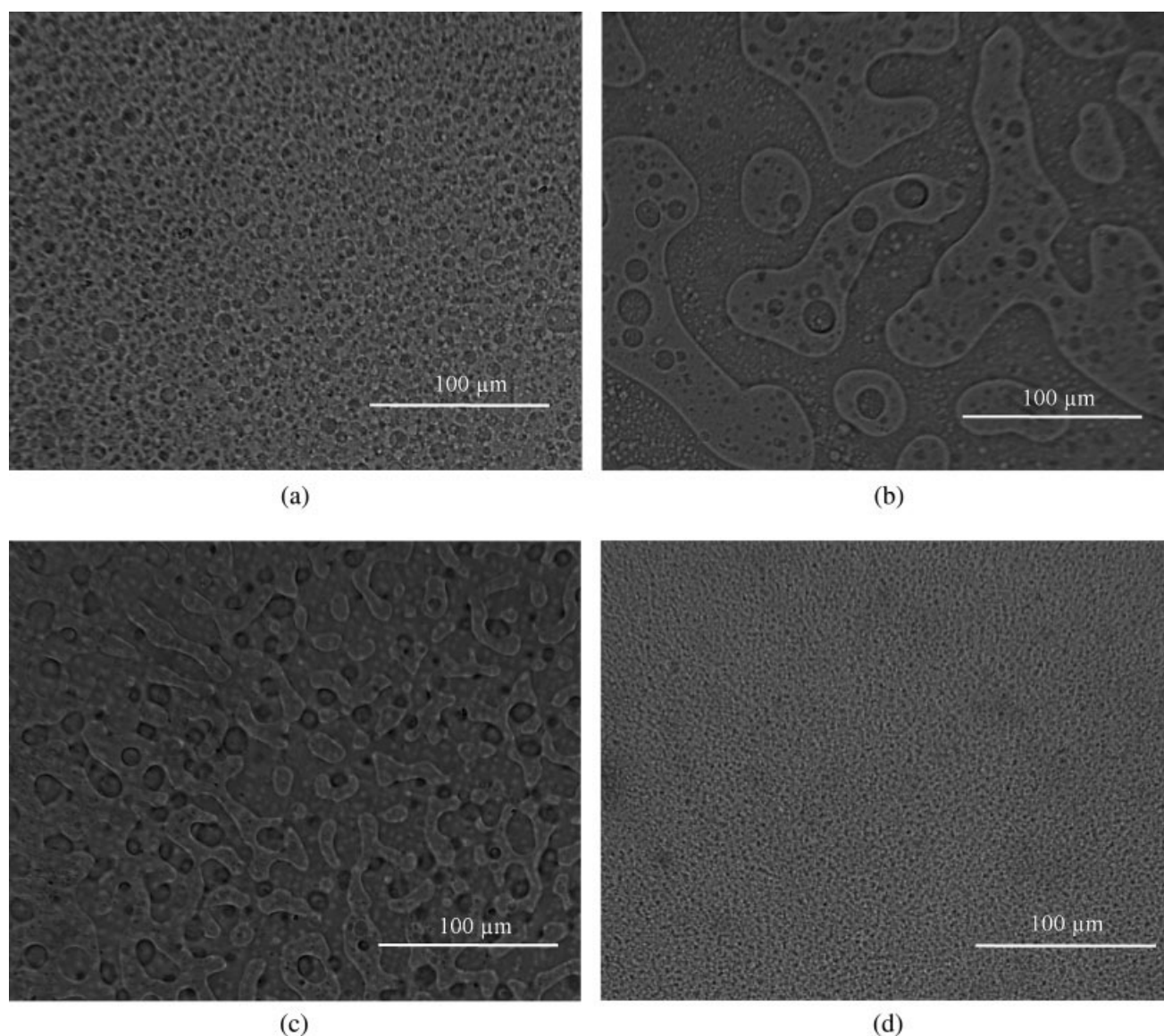


Figure 2 Optical micrographs of the PLLA/PBSA blends after melting at 200°C for 5 min: (a) 20/80, (b) 40/60, (c) 60/40, and (d) 80/20.

tion is observed, indicating that PLLA is immiscible with PBSA in the melt. Droplets of PLLA are distributed uniformly throughout a continuous PBSA matrix for 20/80 blend, while PBSA becomes dispersed phase with PLLA being the continuous phase for 80/20 blend. Instead, a more complicated phase structure can be observed in the cases of 40/60 and 60/40 blends. The blends exhibit a continuous morphology, and each continuous phase contains dispersed phase from another composition.

Note that for the blends of PLLA/PBS, the miscibility between these two components were not quite clear from literature.¹⁸ According to the Flory-Huggins theory, Park and Im¹⁸ calculated the depression of the equilibrium melting point of PLLA component in the blend with PBS, and suggested that PLLA/PBS blends were thermodynamically miscible. However, if we

look at Figure 1 in the literature,¹⁸ the depression of T_g of the blends was not significant with increasing the content of PBS component, which might suggest that PLLA/PBS blends were immiscible. On the other hand, because of the presence of the crystalline fraction of PBS in the blends, the T_g of PBS phase was not apparent, which might be responsible for the observation in the literature¹⁸ that a single glass transition, close to the T_g of PLLA, was detected in the PLLA/PBS blends over the entire composition range.

Nonisothermal crystallization

The nonisothermal crystallization behavior of the PLLA/PBSA blends from the melt is presented in Figure 3. The crystallization peak temperature (T_c) of pure PLLA appears at 105°C, and it does not suffer

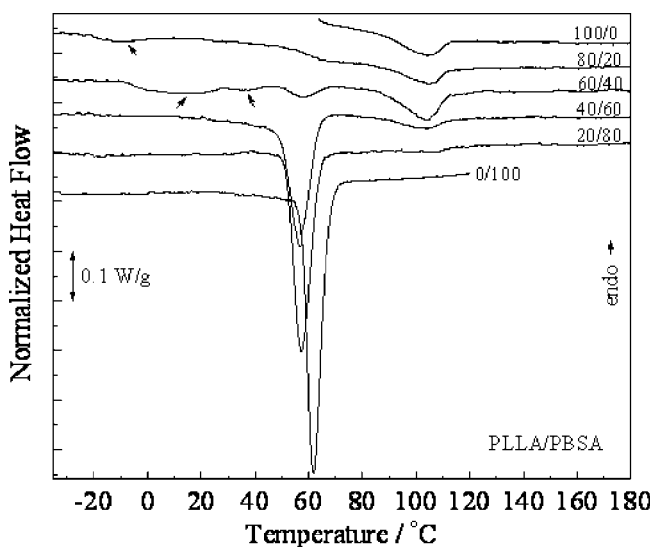


Figure 3 Nonisothermal crystallization of the PLLA/PBSA blends from the melt at cooling rate of $5^{\circ}\text{C min}^{-1}$. The arrows are indicative of the fractionated crystallization of PBSA.

significant variation for the 80/20, 60/40, and 40/60 blends. For the 20/80 blend, the crystallization of PLLA is not apparent, due to both the intrinsic low crystallization rate of PLLA^{30,31} and the low PLLA content in the blend. On the other hand, the crystallization of PBSA in the blends turns out to be strongly dependent on the blend composition. The T_c of pure PBSA exhibits at 62°C , and it shifts to around 57°C for both 20/80, and 40/60 blends. It is noteworthy that the crystallization exotherm of PBSA for the 60/40 blend splits into three peaks at 58, 36, and around 12°C . For the 80/20 blend, only a weak crystallization peak appears at around -11°C . These multiple crystallization peaks are similar to those found for several immiscible polymer blends where the dispersed component was crystallizable.^{24–27,32} It has been well established that semicrystalline polymers in the bulk usually crystallize through heterogeneous nucleation. However, if the semicrystalline polymer is dispersed into confining droplets, effects on the crystallization behavior may occur. In the case that the number of droplets is much greater than the number of active heterogeneities at low supercoolings, the efficiency of heterogeneous nucleation inside these droplets is less than that in the bulk polymer. As a result, nucleation has to occur at much higher supercooling, which is necessary for those heterogeneities to become active. This phenomenon has been mostly referred as ‘fractionated crystallization.’^{24–27}

In the cases of both 20/80 and 40/60 blends, where the crystallization occurs in only one exotherm located at high temperature range, we could consider that the polymer contain heterogeneities with similar feature as in the bulk. This is generally consistent with the

morphology that PBSA constitutes the matrix in the melt as shown in Figure 2. In the case of 60/40 blend where multiple crystallization peaks appear at different degrees of supercooling, we could consider that fractionated crystallization occurs. This finding is in agreement with the blend morphology seen by optical microscopy, where PBSA is dispersed as droplets inside the matrix (Fig. 2). A possible explanation is that, in the 60/40 blend, only a certain number of PBSA droplets contain heterogeneities as active as in the bulk polymer, while others contain two types of less active heterogeneities. Those droplets that contain less efficient heterogeneities will nucleate at higher supercooling. Finally, for 80/20 blend, the dispersion of PBSA into droplets in the blend is so fine (Fig. 2)

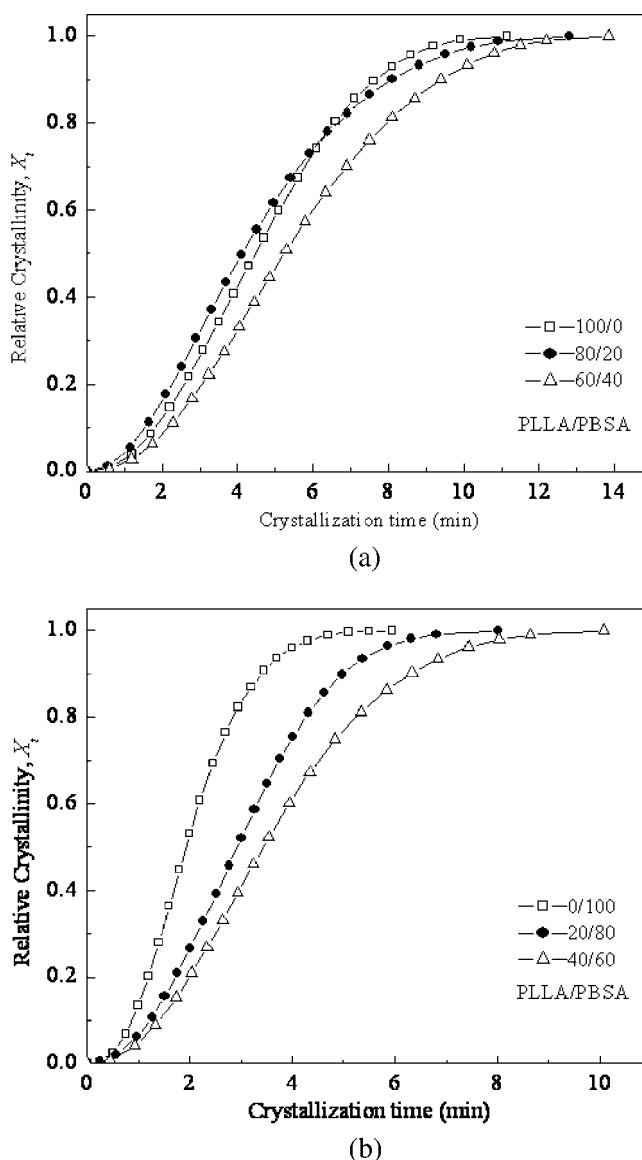


Figure 4 The plots of relative crystallinity X_t vs. crystallization time t of the PLLA/PBSA blends: (a) crystallization of PLLA at 120°C ; and (b) subsequent crystallization of PBSA at 65°C .

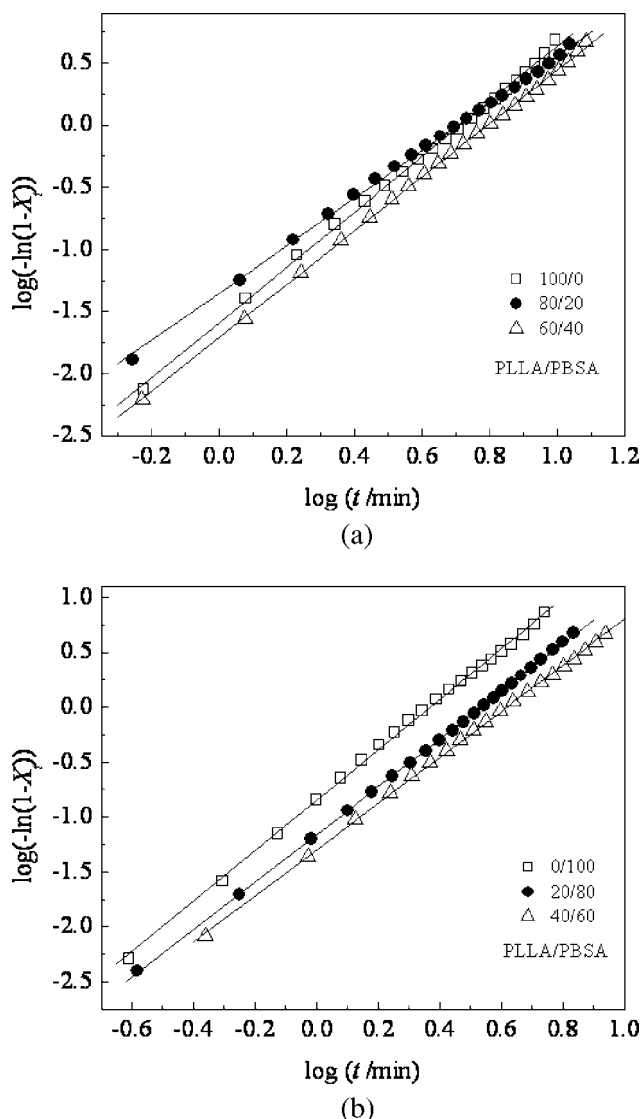


Figure 5 Avrami plots of the PLLA/PBSA blends: (a) crystallization of PLLA at 120°C; and (b) subsequent crystallization of PBSA at 65°C.

that those droplets might contain very low efficient heterogeneous nuclei, and hence nucleate at very high supercoolings.

Isothermal crystallization

The isothermal crystallization of PLLA/PBSA blends was also studied by DSC. The blends were isothermally crystallized at 120°C for PLLA, followed by that at 65°C for PBSA. By this procedure, it is possible to further explore the effect of liquid PBSA phase on the crystallization of PLLA, and that of PLLA crystals on the crystallization of PBSA.

The exothermic curves of heat flow as a function of time were recorded and investigated. The relative crystallinity X_t is a function of crystallization time and calculated by

TABLE I
Crystallization Kinetics Parameters of PLLA in PLLA/PBSA Blends at 120°C

PLLA/PBSA	n	k (min^{-n})	$t_{0.5}$ (min)
100/0	2.2	2.58×10^{-2}	4.40
80/20	1.9	4.49×10^{-2}	4.19
60/40	2.2	1.96×10^{-2}	5.26

$$X_t = \int_{t_0}^t \left(\frac{dH_c}{dt} \right) dt / \int_{t_0}^{t_\infty} \left(\frac{dH_c}{dt} \right) dt \quad (1)$$

where dH_c/dt is the rate of heat evolution, and t_0 and t_∞ represent the crystallization onset and end time, respectively. The plots of relative crystallinity X_t vs. the crystallization time t are shown in Figure 4 for the isothermal crystallization of PLLA component at 120°C and PBSA component at 65°C, respectively. Note that the isothermal crystallization peaks of PLLA in both 20/80 and 40/60 blends are not evident because of the dilution of this component as well as the intrinsic low crystallization rate of PLLA. In the same way, the isothermal crystallization peak for PBSA in 60/40 and 80/20 blends are not evident due to the dilution of this component.

The kinetics of isothermal crystallization was analyzed in terms of the Avrami equation³³ using the double logarithmic form:

$$\log(-\ln(1 - X_t)) = \log k + n \log t \quad (2)$$

where n is the Avrami exponent related to the geometry of the spherulitic growth and the mechanism of nucleation, and k is the overall kinetic rate constant. As shown in Figures 5(a) and 5(b), plots of $\log(-\ln(1 - X_t))$ vs. $\log t$ are linear with slope n at 120 and 65°C, respectively. The half-life crystallization time $t_{0.5}$, the time required to achieve 50% of the final crystallinity of the samples, is described as

$$t_{0.5} = (\ln 2/k)^{1/n} \quad (3)$$

In Tables I and II are listed the kinetic parameters for the crystallization process at 120 and 65°C, respectively. As shown in Table I, the value of n for pure PLLA is close to two and nearly does not change with the addition of PBSA, indicating that the presence of liquid PBSA phase does not apparently affect the crys-

TABLE II
Crystallization Kinetics Parameters of PBSA in PLLA/PBSA Blends at 65°C

PLLA/PBSA	n	k (min^{-n})	$t_{0.5}$ (min)
0/100	2.3	1.42×10^{-1}	1.99
20/80	2.2	6.94×10^{-2}	2.89
40/60	2.1	5.05×10^{-2}	3.48

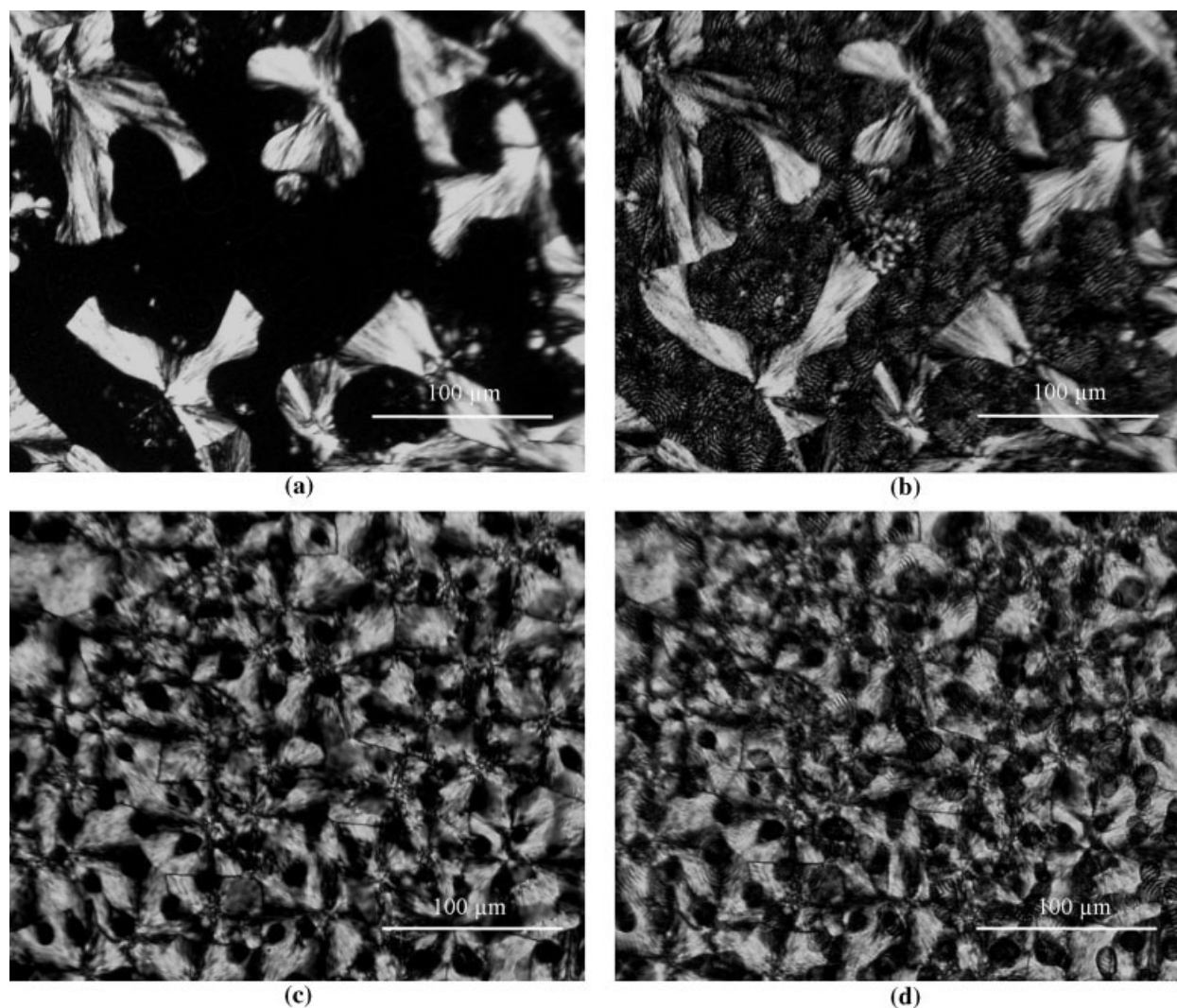


Figure 6 Polarized optical micrographs of the PLLA/PBSA system after melting at 200°C for 5 min, then quenched to indicated temperature and finished isothermal crystallization: (a) 40/60 blend, spherulites of PLLA grown at 120°C; (b) same sample as (a), after quenched to 65°C and complete crystallization of PBSA; (c) 60/40 blend, spherulites of PLLA grown at 120°C; (d) same sample as (c), after quenched to 65°C and complete crystallization of PBSA.

tallization mechanism of PLLA. The values of k and of $t_{0.5}$ are almost the same for pure and blended PLLA, indicating that the addition of PBSA does not exert a significant influence on the crystallization rate of PLLA. As shown in Table II, the value of n for PBSA is around two and does not change with the addition of PLLA, indicating that the presence of PLLA does not affect the crystallization mechanism of PBSA. However, it is found that k and $t_{0.5}$ for PBSA decrease with increasing PLLA content. The reduction in the crystallization rate of PBSA may be related to a physical restriction to the growth of PBSA spherulites by the PLLA domains, as the volume of PBSA domains resulting from the phase separation with PLLA are not sufficiently large.³⁴

Such two-step crystallization of PLLA/PBSA blends was also studied by polarized optical microscopy. As an example, Figure 6 presents the phase separation of

PLLA and PBSA for both 40/60 and 60/40 blends observed by polarized optical microscopy. Figures 6(a) and 6(c) show the spherulites of PLLA, which were crystallized at 120°C from the crystal-free melt with the dark PBSA melt dispersed in. On cooling the sample down to 65°C, PBSA could also crystallize and coexist with the PLLA crystals. Figures 6(b) and 6(d) show the banded spherulites of PBSA, which were crystallized at 65°C in the presence of the PLLA spherulites formed at 120°C.

CONCLUSIONS

PLLA is found to be immiscible with PBSA as evidenced by two separate glass transitions and the biphasic melt. Upon cooling from the melt, fractionated crystallization behavior occurs in case of PBSA is dispersed as droplets in PLLA matrix, characterized

by several crystallization events at different lower crystallization temperatures. Investigation through two-step isothermal crystallization shows that, for blends where PLLA is the major component, different content of PBSA does not make a significant difference in the crystallization mechanism and rate of PLLA. On the other hand, for blends where PBSA is the major component, the crystallization rate of PBSA decreases with increasing PLLA content, while the crystallization mechanism does not change.

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