

## ORIGINAL ARTICLE

# Miscibility and morphology of binary crystalline blends of poly(L-lactide) and poly(butylene adipate)

Lifen Zhao, Xinyu Peng, Xin Liu, Yanmin Wang, Shengxue Qin and Jun Zhang

Poly(L-lactide)/poly(butylene adipate) (PLLA/PBA) crystalline/crystalline blends with different weight ratios (from 90/10 to 20/80) were prepared using a solution blend method. According to the differential scanning calorimetry (DSC) results and the optical microscopy (OM) images, PLLA was partially miscible with PBA. The crystallization morphologies of the PLLA/PBA blends formed in a high-temperature region and in a low-temperature region were studied separately. In the high-temperature region, Maltese-cross spherulites, banded spherulites and branched structures were observed by changing the weight ratio and the thickness of the specimen. The distribution of PLLA and PBA in these morphologies was determined using polarized OM, which utilized a hot stage. Additionally, the thickness of the PLLA lamella, which was determined from the DSC results, decreased slightly with increasing PBA concentration. In the low-temperature region, the effect of PLLA on the morphologies of PBA was studied. In PBA-rich blends, the morphology of the PBA crystal was not significantly affected by PLLA. However, in PLLA-rich blends, PBA formed fragments because solid PLLA restricted the growth of the PBA crystal. The thickness of the PBA lamella, which was determined from the DSC results, decreased with increasing PLLA concentration.

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**Keywords:** binary crystalline blends; miscibility; morphology; poly(butylene adipate); poly(L-lactide)

## INTRODUCTION

Polymer blending, a useful and economical way to modify the properties of materials, provides many interesting systems for studying polymer structures. A polymer blend is generally classified according to the crystalline ability of its components as an amorphous/amorphous, amorphous/crystalline or crystalline/crystalline system. Crystalline/crystalline systems have generated a lot of attention in recent years because their complicated crystallization environments provide new insights into crystallization theory. The morphologies of binary crystalline systems become complicated due to changes in the crystallization environments. Many works have been published on the morphologies of binary crystalline blends, such as poly(butylene succinate)/poly(ethylene oxide),<sup>1,2</sup> poly(ethylene succinate)/poly(ethylene oxide),<sup>3,4</sup> poly(butylene adipate-co-butylene succinate)/poly(ethylene oxide),<sup>5</sup> poly(butylene adipate-co-butylene succinate)/poly(vinylidene fluoride)<sup>6</sup> and poly(butylene succinate)/poly(butylene adipate).<sup>7</sup> Interlock spherulites, interfibrillar spherulites and some strange morphologies were observed in these works. The appearance of a complicated morphology is related to the miscibility, crystallization condition, heat treatment, composition and other properties of the crystalline polymers.<sup>8</sup>

It should be noted that the understanding of binary crystalline polymer morphologies is not yet complete and requires more experimental results. Therefore, a crystalline polyester composed of

poly(L-lactide) (PLLA) and poly(butylene adipate) (PBA) was chosen to investigate its morphology in this study. PLLA is a very important type of biodegradable polyester, which can be derived from renewable resources. However, a disadvantage of PLLA is its inherent brittleness, despite having high tensile modulus and strength. Blending PLLA with biocompatible and biodegradable polymers is an effective way to improve the properties of PLLA while maintaining its biodegradability. Many investigations on the structures and properties of PLLA blends, including poly(butylene succinate)/poly(L-lactide),<sup>9</sup> poly(ethylene succinate)/poly(L-lactide)<sup>10</sup> and poly(3-hydroxybutyrate)/poly(L-lactic acid),<sup>11,12</sup> have been reported. PBA is also a type of biodegradable polyester and is used as a blend to improve the toughness of PLLA.<sup>13,14</sup> There are no reports on the crystallization structures of this type of blend to the best of our knowledge. PBA is a type of polymer with abundant crystallization phenomena, such as polymorphism,<sup>15</sup> a complex crystalline morphology<sup>16</sup> and multiple melting behaviors.<sup>17</sup> Thus, the crystalline behavior of PLLA and PBA blends is worth studying from both an academic and an industrial point of view.

PLLA/PBA blends have two typical features. One feature is the large difference between their melting points (the melting temperature of PLLA is ~160 °C and that of PBA is below 75 °C). Therefore, separate crystallization processes of the polymers can be achieved by controlling the temperature. The other feature is the glass transition

temperature of PLLA ( $\sim 59^\circ\text{C}$ ), which is close to the melting temperatures of PBA and means that the crystallization process of PBA can be studied while PLLA is in a glass state. Thus, PLLA and PBA blends can provide complicated crystalline environments, and their crystalline morphologies may be interesting. In the present study, the morphologies of PLLA/PBA blends formed in a high-temperature region and in a low-temperature region were studied using polarized optical microscopy (POM), which utilized a hot stage. Additionally, it is well known that the morphology of blends is influenced by the miscibility of the polymers. The miscibility was also studied using differential scanning calorimetry (DSC) and optical microscopy (OM) results. The obtained results could be helpful for future investigations of blends and be beneficial for studying the crystallization morphology of other polymer blends.

## EXPERIMENTAL PROCEDURE

### Materials

PLLA, with  $M_w = 250\,000$ , was produced by NatureWorks (Blair, NE, USA). PBA, with  $M_w = 10\,000$ , was purchased from Sigma-Aldrich (Milwaukee, WI, USA). Both of these materials were purified using solution deposition. PLLA or PBA was first dissolved in chloroform, then precipitated with methanol and finally dried under vacuum before being studied.

### Preparation of blends

Blends of PLLA/PBA were prepared using the mutual solvent chloroform. A total of 0.1 g of the polymers (PLLA and PBA) in 10 ml of the solvent was dissolved in a flask and well stirred. The blend solutions, with various weight ratios ranging from 100/0 to 0/100 and the first number referring to PLLA, were prepared. The blend solution was cast onto a Petri dish at room temperature. After evaporating the solvent under a controlled air stream for 2 days, the solution was further dried in vacuum at  $40\text{--}45^\circ\text{C}$  for 72 h to remove any residual solvent. Cast films of the PLLA/PBA blends, with various weight ratios ranging from 100/0 to 0/100, were also prepared.

### Differential Scanning Calorimetry

The glass temperatures of the blends were determined using DSC (Mettler-Toledo, TGA/DSC1/1600LF, Zurich, Switzerland) under nitrogen at a flow rate of  $20\text{ ml min}^{-1}$ . The temperature and the heat flow for different instrument heating rates were carefully calibrated using standard materials before measuring the blends. Polymer sample sizes of 3–5 mg were encapsulated in DSC sample holders. The blend samples were first heated to  $200^\circ\text{C}$  for 3 min and then quenched at a rate of  $80^\circ\text{C min}^{-1}$  to  $-80^\circ\text{C}$ . After 3 min, the blend samples were heated directly from  $-80^\circ\text{C}$  to the melt state at a rate of  $20^\circ\text{C min}^{-1}$ . Neat PLLA was only heated to  $200^\circ\text{C}$  for 3 min and then quenched to  $25^\circ\text{C}$  at a rate of  $80^\circ\text{C min}^{-1}$ .

DSC was also used to study the crystallization temperatures of the blends. The samples were first melted at  $200^\circ\text{C}$  ( $75^\circ\text{C}$  for neat PBA) for 3 min and then cooled from the melt to  $25^\circ\text{C}$  at a rate of  $5^\circ\text{C min}^{-1}$ . After holding the samples at  $25^\circ\text{C}$  for 1 min, they were heated to  $200^\circ\text{C}$  ( $75^\circ\text{C}$  for neat PBA) at a rate of  $20^\circ\text{C min}^{-1}$ .

The melting behavior of the blends after isothermal crystallization at  $40^\circ\text{C}$  was also studied using DSC. The blend samples were first heated to  $200^\circ\text{C}$ , held there for 3 min to melt them and then quenched to  $40^\circ\text{C}$  at a rate of  $80^\circ\text{C min}^{-1}$  to induce isothermal crystallization. After enough time had passed, the samples were directly heated from  $40^\circ\text{C}$  to the melt state at a rate of  $10^\circ\text{C min}^{-1}$ .

### Polarized Optical Microscopy

The crystallization morphologies of the samples were observed using POM (Nikon Optiphot-2, POM, Nikon, Tokyo, Japan), which utilized a charge-coupled device digital camera and a hot stage.

The samples for investigating the morphologies formed in the high-temperature region were prepared by casting the blend solution onto a cover glass ( $20 \times 20\text{ mm}^2$  in size). After the solvent was volatilized, the samples were melted on a hot stage at  $200^\circ\text{C}$  for 3 min and then transferred onto a  $110^\circ\text{C}$

hot stage for isothermal crystallization. After the samples were held at room temperature for 1 h, POM images of the samples were taken.

To obtain a thin film to observe the fine morphology of the blend samples, the films prepared by the above methods were covered by a piece of cover glass and gently pressed with tweezers.

The samples for studying the crystallization morphologies formed in the low-temperature region were prepared by pressing a small piece of cast film of solid blend into a thin film between two covered glasses. These films were also melted on a hot stage at  $200^\circ\text{C}$  for 3 min, then transferred onto a  $40^\circ\text{C}$  hot stage and held at this temperature for 6 h.

The different preparation methods were used for different investigation objectives. In the high-temperature region, blends with PLLA-rich components (including PLLA/PBA 90/10, 80/20, 60/40, 50/50, 40/60 and 20/80) were prepared mostly to study the morphology of PLLA. As the viscosity of PLLA is high, it is difficult to press cast films with PLLA-rich components into films that are thin enough to observe the blend morphologies, especially PLLA/PBA 90/10 and 80/20. Therefore, the samples used for the high-temperature region study were prepared by casting blend solutions onto cover glass. In the low-temperature region, the morphology of PBA was investigated. The study of the morphologies of blends with PBA-rich components, such as PLLA/PBA 40/60 and 20/80, is very important to avoid the high amount of PBA with low viscosity that leads to the separation of the blend solution and to a non-uniform film during casting onto the cover glass. Therefore, the samples used in the low-temperature region study were obtained by pressing solid cast films into thin films between two cover glasses.

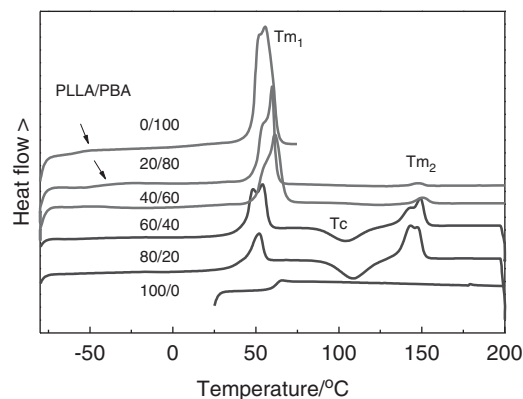
### Optical microscopy

The blend samples after crystallization, as prepared in section 2.4, were heated to  $200^\circ\text{C}$  on a hot stage to obtain a melt. The melt phase structures were observed using an optical microscope (Nikon Optiphot-2) equipped with a hot stage using the polarized mode or parallel mode. The images were recorded by a charge-coupled device digital camera.

## RESULTS AND DISCUSSION

### Miscibility of PLA/PBA

The miscibility of PLA/PBA was first studied by DSC. Figure 1 shows the DSC heating curves of blends for a heating rate of  $20^\circ\text{C min}^{-1}$  from the amorphous state. Neat PLLA exhibits a  $T_g$  at  $\sim 59^\circ\text{C}$ , and pure PBA exhibits a  $T_g$  at approximately  $-57^\circ\text{C}$ . However, there is only one obvious  $T_g$  at  $-40^\circ\text{C}$  for PLLA/PBA 80/20, because the  $T_g$  of PLLA is very close to the melting peak of PBA. Consequently, we cannot determine if the  $T_g$  at  $-40^\circ\text{C}$  corresponded to that of PBA in partially miscible blends or to a new  $T_g$  of completely miscible blends. With decreasing PBA content, the glass transition became unclear in the low-temperature region of PLLA/PBA 60/40, 40/60 and 20/80.



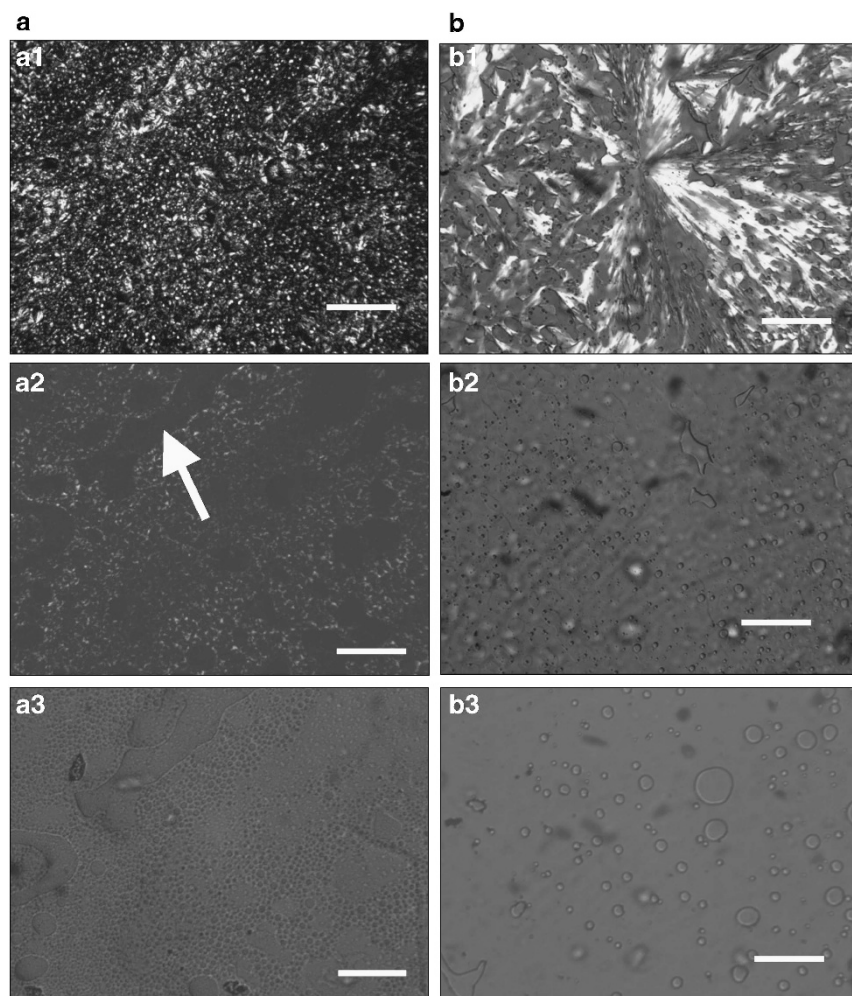
**Figure 1** Differential scanning calorimetry (DSC) traces of the Poly(L-lactide)/poly(butylene adipate) (PLLA/PBA) blends with a heating rate of  $20^\circ\text{C min}^{-1}$  after quenching from the melt at a rate of  $80^\circ\text{C min}^{-1}$ . A full color version of this figure is available at *Polymer Journal* online.

Therefore, it is difficult to analyze the miscibility of PLA/PBA blends using just the  $T_g$  data.

However, other thermal characteristics can be used to determine the miscibility of these blends. The DSC trace of neat PLLA exhibits only an apparent glass transition temperature, while the cold-crystallization peak and the melting peak are absent due to the slow crystallization rate of PLLA. However, the cold-crystallization peak ( $T_c$ ) corresponding to PLLA appears when PLLA is blended with PBA (PLLA/PBA 80/20 and 60/40). With increasing PBA content, the PLLA/PBA blends 40/60 and 20/80 do not exhibit apparent exothermic peaks, but the melting peaks ( $T_m$ ) of PLLA can still be observed at  $\sim 150^\circ\text{C}$ . These phenomena indicate that the crystallization rate of PLLA is improved owing to the addition of PBA. Although the cold-crystallization peak of PBA cannot be observed in the DSC traces because of its fast crystallization rate, the melting peak ( $T_m$ ) obviously decreased in the PLLA/PBA blends 80/20 and 60/40, indicating that the existence of PLLA also has significant effects on the crystallization behavior of PBA. Therefore, there are significant interactions between PLLA and PBA that influence their crystallization behaviors.

The phase structures were studied using OM characterization of the blend melts, which were crystallized from the melt and then heated

from room temperature to above the melt temperature on a microscope heating stage (temperature programmed). For brevity, Figure 2 just shows typical OM images during heating of the sample from room temperature to the melt at  $2^\circ\text{C min}^{-1}$  for PLLA/PBA 40/60, which was crystallized in both high- or low-temperature regions (as prepared in section 2.4). Figure 2(a) shows images from heating PLLA/PBA 40/60 that was crystallized at  $110^\circ\text{C}$ , and Figures 2(a1–a3) were obtained separately at room temperature,  $75^\circ\text{C}$  and  $200^\circ\text{C}$ . Comparing Figures 2(a1–a2), we can observe some melt regions (labeled by arrows) at  $75^\circ\text{C}$ , but the rest of the regions are still in the crystallization state. When the temperature was increased to  $200^\circ\text{C}$  (Figure 2(a3)), all of the crystals disappear and small, separate liquid drops appear in the field of view. Figure 2(b) shows images that were taken during the heating of the PLLA/PBA 40/60 sample that was crystallized at  $40^\circ\text{C}$ . Figures 2(b1–b3) were obtained separately at room temperature,  $75^\circ\text{C}$  and  $200^\circ\text{C}$ . As opposed to Figure 2(a), all of the crystals disappeared completely at  $75^\circ\text{C}$  (as shown in Figure 2(a2)). When the sample was heated to  $200^\circ\text{C}$ , round liquid drops formed, which were distributed over a large smooth region (as shown in Figure 2(b3)). The differences in Figures 2(a) and (b) are owing to their different original crystallization structures. The sample used in

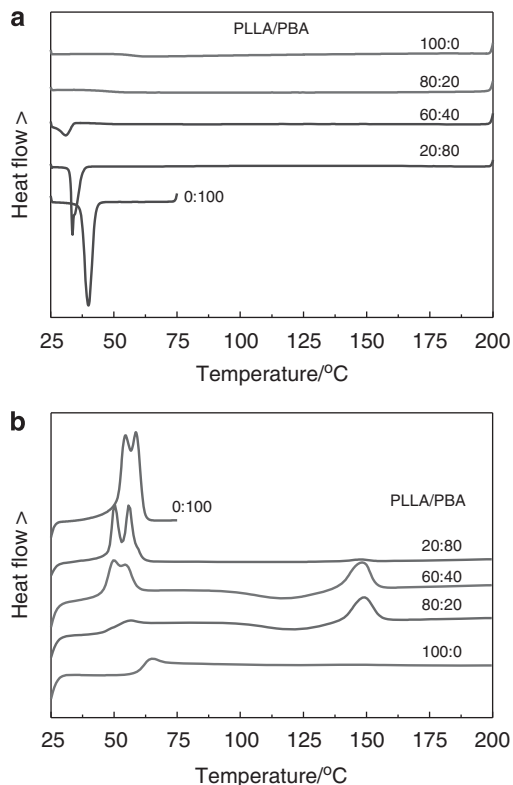


**Figure 2** Optical micrographs of Poly(L-lactide)/poly(butylene adipate) (PLLA/PBA) 40/60 taken at different temperatures. (a) The sample was first isothermally crystallized at  $110^\circ\text{C}$  for 6 h, and images were taken at (a<sub>1</sub>) room temperature, (a<sub>2</sub>)  $75^\circ\text{C}$  and (a<sub>3</sub>)  $200^\circ\text{C}$ . (b) The sample was first isothermally crystallized at  $40^\circ\text{C}$  for 6 h, and images were taken at (b<sub>1</sub>) room temperature, (b<sub>2</sub>)  $75^\circ\text{C}$  and (b<sub>3</sub>)  $200^\circ\text{C}$ . The scale bar is  $10\ \mu\text{m}$ . (a<sub>1</sub>), (a<sub>2</sub>), (b<sub>1</sub>) and (b<sub>2</sub>) were taken using the polarized mode. (a<sub>3</sub>, b<sub>3</sub>) were taken using the parallel mode.



Figure 2(a) consists of crystallized PLLA and PBA, but the sample in Figure 2(b) consists of crystallized PBA and amorphous PLLA. Therefore, when the samples were heated to 75 °C, a PBA melt and a PLLA crystal were obtained in the former and a PBA melt and PLLA in a rubbery state were obtained in the latter. However, by continuing to heat the samples to 200 °C, both PBA and PLLA formed melts, and both of the samples exhibited heterogeneity and obviously separate domains in the field of view.

Therefore, the obvious phase separation shown in Figure 2 indicates that the  $T_g$  of PLLA/PBA 80/20 (shown in Figure 1) in the low-temperature region is not a new  $T_g$  of completely miscible blends but a  $T_g$  of partially miscible blends. Combining the results of



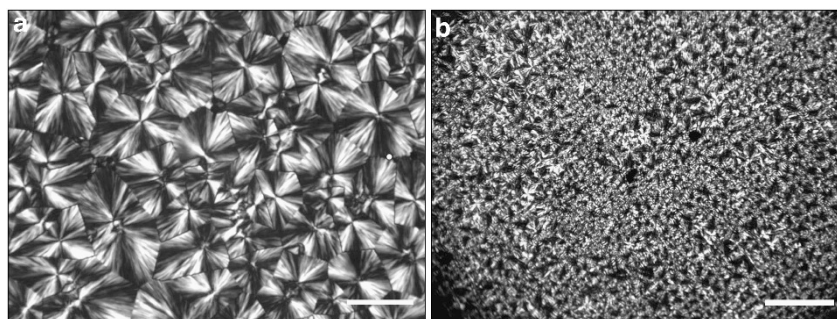
**Figure 3** Differential scanning calorimetry (DSC) curves for the Poly(L-lactide)/poly(butylene adipate) (PLLA/PBA) blends. (a) Cooling traces from 200 to 25 °C at a rate of 5 °C/min. (b) Heating traces from 25 to 200 °C at a rate of 20 °C min<sup>-1</sup>. A full color version of this figure is available at *Polymer Journal* online.

Figures 1 and 2, the PLLA/PBA blends can be determined to be a partially miscible system.

#### Crystalline morphologies of PLLA/PBA blends formed in the high-temperature region

As PLLA/PBA blends are binary crystalline systems and as the two components have a large difference in their melting points, by controlling the crystallization temperature, we can obtain the crystal of one component. Therefore, the effects of the different components on the crystallization morphologies can be investigated in different temperature regions. To determine the proper crystallization temperature regions, DSC was used to determine the crystallization temperature regions of the blends. Figure 3(a) shows the DSC cooling traces from the melts to room temperature at a rate of 5 °C min<sup>-1</sup>, and Figure 3(b) shows the subsequent heating traces at a rate of 20 °C min<sup>-1</sup>. From Figure 3(a), it can be observed that there are no exothermic peaks exhibited during the whole cooling scan for neat PLLA and PLLA/PBA 80/20. However, there are exothermic peaks at low temperatures (below 50 °C) for PLLA/PBA 60/40, 20/80 and neat PBA. From Figure 3(b), it can be observed that there is only one glass transition for neat PLLA, while there are cold-crystallization peaks in the temperature region of 100–135 °C and melting peaks at ~150 °C for PLLA/PBA 80/20 and 60/40. For PLLA/PBA 20/80 and neat PBA, there are only melting peaks below 75 °C. These results indicate that the crystallization rate of neat PLLA is very slow, resulting in no crystallization phenomena during the cooling and heating processes used in this procedure. However, the existence of PBA can improve the crystallization rates of the blends, leading to the cold-crystallization of PLLA in the high-temperature region for PLLA/PBA 80/20 and 60/40. Additionally, the crystallization process of PBA in the low-temperature region can be easily achieved when the PBA content is 40% or higher.

Therefore, to determine the crystallization morphologies of blends formed in the high-temperature region and to study the effect of PBA on the crystallization morphology of PLLA, 110 °C, which is close to the peak temperature of PLLA cold-crystallization, was chosen as the isothermal crystallization temperature in the high-temperature region, and 6 h, which is above ten times of  $t_p$  (see Supplementary Figure S1) for most PLLA/PBA blends as isothermal crystallization time. Specimens were first quenched from the melt to 110 °C and held there for 6 h to enable PLLA to crystallize and then held at room temperature to enable PBA to crystallize. Figure 3 shows the POM images of the neat PLLA and PBA morphologies formed during this process. PLLA spherulites ~10 μm in diameter can be observed, and the boundaries of the spherulites are black and very straight (Figure 4a). This result



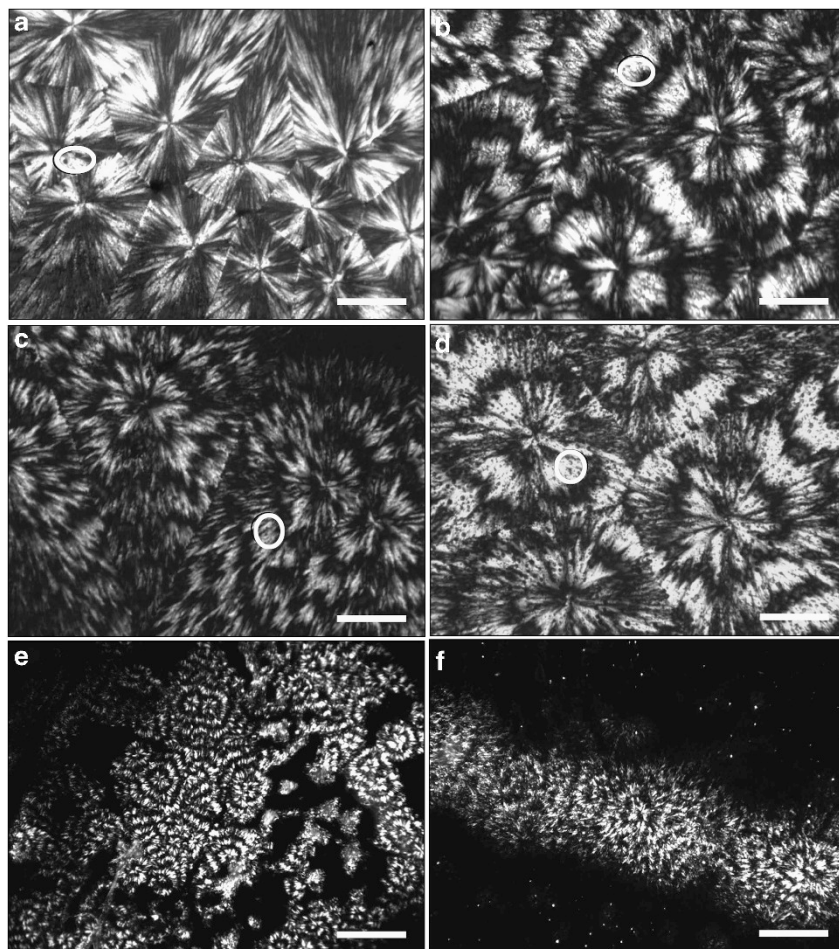
**Figure 4** Polarized optical micrographs of the neat Poly(L-lactide) (PLLA) and poly(butylene adipate) (PBA) morphologies formed after isothermal crystallization at 110 °C for 6 h and then holding the samples at room temperatures (~25 °C) for 1 h. (a) Neat PLLA and (b) neat PBA. The scale bar is 10 μm.

indicates that during this experimental procedure, neat PLLA spherulites have sufficient time to grow until they impact with each other. Figure 4(b) shows that the morphology of PBA consists of very small banded spherulites that pack together. As the melting point of PBA is below 75 °C, this type of PBA morphology is not formed at 110 °C, but forms during the non-isothermal crystallization process of cooling from 110 °C and holding at room temperature.

Figure 5 shows the POM images of the PLLA/PBA blends after they were held at 110 °C for 6 h and then held at room temperature for 1 h. As previously discussed, PLLA first crystallizes at 110 °C and PBA will crystallize during the following process if it can. As the crystallization of PLLA occurs first in this process, mostly PLLA-rich blends were prepared, including PLLA/PBA 90/10, 80/20, 60/40, 50/50, 40/60 and 20/80. Similar to neat PLLA, the morphology of PLLA/PBA 90/10 consists of spherulites ~15 μm in diameter (Figure 5(a)). The spherulites of the blends are larger than those of neat PLLA for two reasons: first, PBA has diluting effects on PLLA, resulting in a decrease in the nuclei density of PLLA. Second, the molecular weight of PBA is 10 000, while that of PLLA is 250 000. Thus, the viscosity of PBA is much smaller than that of PLLA. The addition of low viscosity PBA will promote the mobility of the PLLA chain and improve the growth rate after the nucleation process. Therefore, the blends have larger spherulites and faster crystallization rates, as shown in Figure 3(b). However, the boundary of the spherulites becomes bright and very

small spherulites are distributed in these regions. Comparing the blends with neat PLLA, it can be deduced that the boundary spherulites are PBA that formed after PLLA crystallization. This result indicates that during the PLLA crystallization process, the PBA melt will separate into the interspherulite boundaries. Additionally, the spherulites of the blends are not smooth and are distributed with small black dots (as illustrated in Figure 5(a)). According to the principles of POM, a black region has no birefringence and can be determined to be an amorphous region. As previously discussed and shown in Figure 4, neat PLLA can sufficiently crystallize during this experimental procedure. Therefore, these small black dots can be determined to be amorphous PBA that cannot crystallize because of the limits of the solid environment formed by the high PLLA content.

In the POM images of PLLA/PBA 80/20, 60/40 and 50/50 (Figures 5(b–d)), the spherulite boundaries are not as bright as in PLLA/PBA 90/10, and the number of small black dots in the spherulites increases. This result indicates that PBA may tend to distribute not at the boundaries, but instead in the interior of the spherulites with increasing PBA content. The black color indicates that these PBA still cannot crystallize. Additionally, banded spherulites with irregular ring edges appear in these blends. Although there are large areas without birefringence, banded spherulites can still be observed in some of the regions in the PBA-rich blends (Figures 5(e–f)). It should be noted that a high amount of PBA with low viscosity leads to



**Figure 5** Polarized optical micrographs of the Poly(L-lactide)/poly(butylene adipate) (PLLA/PBA) blend morphologies formed after isothermal crystallization at 110 °C for 6 h and then holding the samples at room temperature (~25 °C) for 1 h. (a) PLLA/PBA 90/10, (b) PLLA/PBA 80/20, (c) PLLA/PBA 60/40, (d) PLLA/PBA 50/50, (e) PLLA/PBA 40/60 and (f) PLLA/PBA 20/80. The scale bar is 10 μm. The outlines indicate areas where black dots can be observed.



non-uniform blend solutions during casting onto the cover glass (as discussed in section 2.4). Thus, the weight ratios of the blends shown in Figures 5(e–f) are not exact, and the reason a large black region exists is ignored. Interestingly, the existence of PBA leads to a banded spherulite morphology in the PLLA/PBA blends. Generally, it is difficult for neat PLLA to form banded spherulites, but banded spherulites can be formed when PLLA is blended with miscible amorphous components.<sup>18–21</sup> In the present study, PBA is partially miscible with PLLA and is a melt at 110 °C. Thus, the appearance of this type of banded spherulite is related to PBA. The amorphous components of PBA might change the environment of the growth front end, leading to changes in the growth mode of the PLLA spherulites. The specific reasons for these changes need to be investigated further.

In the present work, POM with a hot stage was used to obtain images of the banded spherulites during PLLA/PBA melting to study the banded spherulites. POM images of PLLA/PBA 50/50 at room temperature and at 75 °C were taken (Figures 6(a, b)). Comparing these two pictures, it can be observed that the intensity of the birefringence changed significantly. This result indicates that some crystallized regions melted. Considering that the melting temperature of PLLA is ~160 °C, the melting region must be PBA, which can be sufficiently melted at 75 °C. Therefore, when the composition of PBA is high enough, PBA can also crystallize and distribute in the spherulites of PLLA. However, because the morphology of the banded features does not change, the exact locations of PBA in the spherulites cannot be determined.

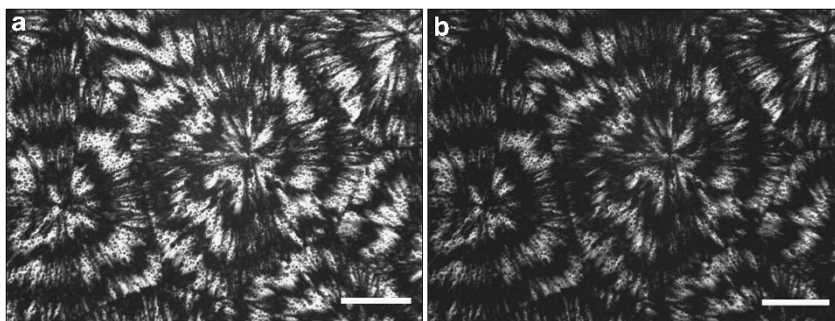
The thin film, as prepared in section 2.4, was used to investigate the distribution of PBA. The PLLA/PBA blend 50/50 was held at 110 °C for 6 h and then held at room temperature for 1 h. Figure 7 shows the POM images of the sample at room temperatures (Figure 7(a)) and at

75 °C (Figure 7(b)). From Figure 7(a), it can be observed that the morphology of the blend exhibits branched structures. Similar to Figure 6, the birefringence of Figure 7(b) is weaker than that of Figure 7(a). Additionally, some regions between the branches, labeled by arrows, melt at 75 °C. Thus, the PBA crystal can be determined to be distributed in the interlamellar regions of PLLA.

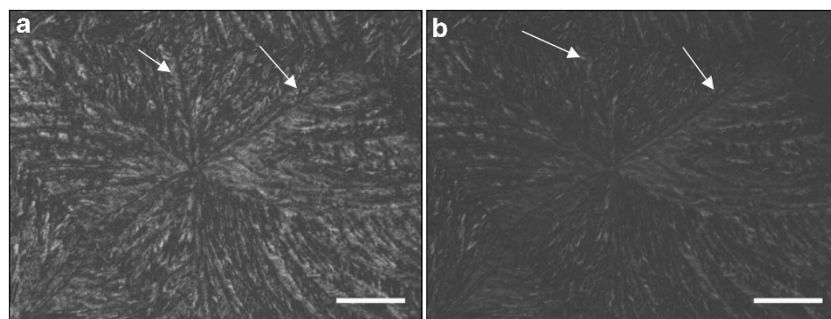
From the above investigation of the PLLA/PBA morphologies, it was determined that PBA can form a crystal or an amorphous state in the internal or external regions of the PLLA crystal with changing composition. Therefore, the existence of PBA may change the lamellae thickness of PLLA, and this type of change cannot be observed using POM. However, according to the classical concept of a chain-folded lamellar crystal, the melting point is related to the thickness of the lamella. Therefore, DSC was used to study the melting behavior of PLLA. Figure 8 shows the heating curves of PLLA after isothermal crystallization at 110 °C for 100 min with a heating rate of 10 °C min<sup>-1</sup>. The melting peak of neat PLLA is ~148.5 °C, and those of the blends move to slightly lower temperatures, ~147.8 °C for PLLA/PBA 80/20 and 60/40 and 146.4 °C for PLLA/PBA 40/60. These results suggest that the existence of PBA decreased the lamellae thickness of PLLA, but the influence of PBA is not strong. The decrease in the lamellae thickness is caused by the exclusion of the PBA components during the PLLA crystallization process. However, this type of effect is not significant because of the low viscosity of PBA and the partial miscibility between PLLA and PBA.

#### Crystalline morphologies of PLLA/PBA blends formed in the low-temperature region

According to the DSC results shown in Figure 3(a), 40 °C, which is close to the peak temperature of non-isothermal crystallization, was chosen as the isothermal crystallization temperature in the

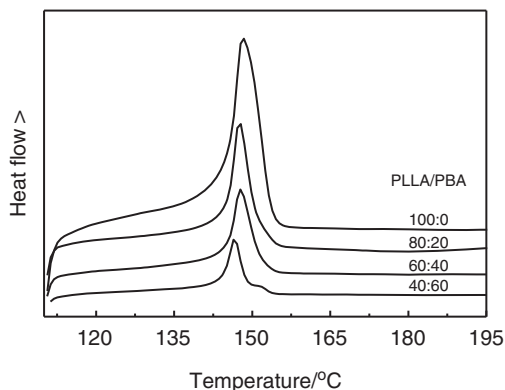


**Figure 6** Polarized optical micrographs of the Poly(L-lactide)/poly(butylene adipate) (PLLA/PBA) blend 50/50. Images were taken at (a) room temperature and at (b) 75 °C. The scale bar is 10 μm.



**Figure 7** Polarized optical micrographs of the Poly(L-lactide)/poly(butylene adipate) (PLLA/PBA) 50/50 thin film. Images were taken at (a) room temperature and at (b) 75 °C. Arrows label the regions that show significant differences. The scale bar is 10 μm.

low-temperature region. PLLA/PBA blends with different weight ratios were quenched to 40 °C to enable PBA to crystallize, and the morphologies formed in the low-temperature region were investigated. Figure 9 shows the morphologies of PLLA/PBA blends that were formed after isothermal crystallization at 40 °C for 6 h. The

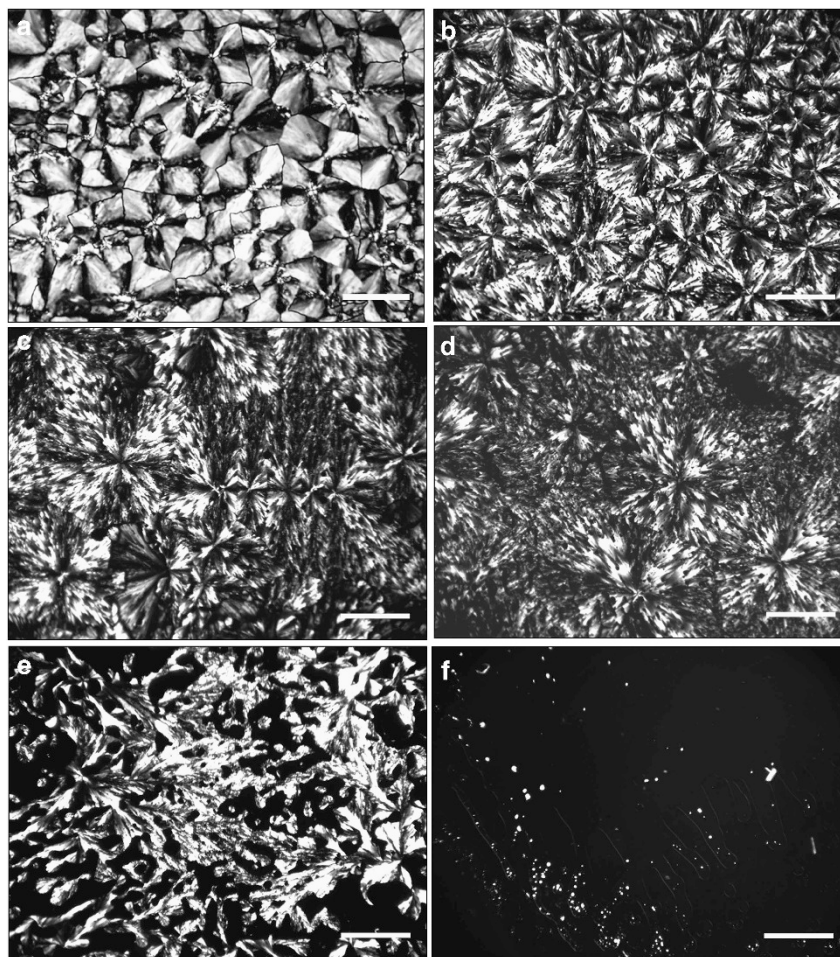


**Figure 8** Differential scanning calorimetry (DSC) melting curves for the Poly(L-lactide)/poly(butylene adipate) (PLLA/PBA) blends after isothermal crystallization at 110 °C for 100 min. The heating rate is 10 °C min<sup>-1</sup>.

morphology of neat PBA formed at 40 °C consists of Maltese-cross spherulites (Figure 9(a)). Although Maltese-cross spherulites can also be observed in PBA-rich blends (PLLA/PBA 20/80, 40/60 and 50/50), these spherulites are distributed with many small black dots that do not exhibit birefringence. Considering that PLLA cannot crystallize during this procedure, it can be determined that the small black dots consist of PLLA. Thus, the PLLA component in PBA-rich blends is in an amorphous state and does not alter the features of the Maltese-cross spherulites of PBA in the low-temperature region.

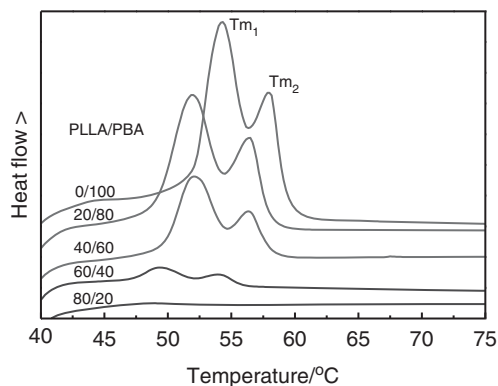
However, the morphology of a PLLA-rich blend (PLLA/PBA 60/40) is very different to those of PBA-rich blends, as shown in Figure 9(e). In this image, PBA crystals are separated into fragments by amorphous PLLA. As the amount of amorphous PLLA is so high, the PBA components cannot separate from PLLA and form a complete spherulite. In PLLA/PBA 80/20, only a small amount of PBA crystal can be observed because the crystallization of PBA was limited by the solid PLLA (Figure 9(f)).

From the POM images, it can be determined that the morphology features of the PBA spherulites are not influenced by PLLA in PBA-rich blends and that PBA cannot form complete spherulites in PLLA-rich blends. Does solid PLLA really not affect the PBA spherulites in PBA-rich blends? The melting behavior of the blends after isothermal crystallization at 40 °C was investigated to study the effects of PLLA.



**Figure 9** Polarized optical micrographs of the Poly(L-lactide)/poly(butylene adipate) (PLLA/PBA) blend morphologies formed after isothermal crystallization at 40 °C for 6 h. (a) PLLA/PBA 0/100, (b) PLLA/PBA 20/80, (c) PLLA/PBA 40/60, (d) PLLA/PBA 50/50, (e) PLLA/PBA 60/40 and (f) PLLA/PBA 80/20. The scale bar is 10 μm.





**Figure 10** Differential scanning calorimetry (DSC) melting curves for the Poly(L-lactide)/poly(butylene adipate) (PLLA/PBA) blends after isothermal crystallization at 40 °C for 40 min. The heating rate is 10 °C min<sup>-1</sup>. A full color version of this figure is available at *Polymer Journal* online.

Figure 10 shows the DSC melting curves of PLLA/PBA blends after isothermal crystallization at 40 °C for 40 min with a heating rate of 10 °C min<sup>-1</sup>. The same results as those from POM are observed, there is no obvious melting peak in PLLA/PBA 80/20. However, some blends (PLLA/PBA 20/80, 40/60 and 60/40) and neat PBA exhibited double melting peaks. As determined in Gan's work,  $T_{m1}$  is the original melting peak of the PBA  $\alpha$  crystal and  $T_{m2}$  is the recrystallization of the  $\alpha$  crystal.<sup>17</sup> The melting peaks of the blends decreased to lower temperatures with increasing PLLA content. As the melting point is related to the thickness of the lamella, the decrease in the melting peak temperatures indicates that the PBA lamella thicknesses in the blends decrease with the addition of PLLA.

As discussed in section 3.1, PLLA/PBA blends are a partially miscible system, and the glass transition temperature of PLLA moves to lower temperatures while that of PBA shifts to higher temperatures in the blends. If the glass transition temperature of PLLA moved to a low enough temperature (below 40 °C), PLLA will gradually co-crystallize with the PBA segments at 40 °C. However, because the crystallization rate of PLLA is very slow at such a low temperature, PLLA may form an amorphous solid. Therefore, there are two possible reasons for the decrease in the lamella thickness: One reason is that the PLLA gradually co-crystallized at 40 °C with the PBA segments, and such an impurity insertion into the PBA crystals decreased the lamella thickness. The other reason is that amorphous PLLA restricted the growth of the PBA lamella, leading to the lamella thickness decreasing. According to Figure 2(b), there are large regions that do not exhibit birefringence and no obvious crystals can be observed when the sample was heated to 75 °C. This result indicates that the structure formed at 40 °C mainly consists of crystalline PBA and amorphous PLLA. As a result, although the existence of PLLA does not change the morphology features of PBA in PBA-rich blends, the amorphous PLLA restricted the growth of the PBA lamella, leading to a decrease in the lamella thickness of the PBA crystal.

## CONCLUSIONS

The miscibility and crystallization morphologies of PLLA/PBA blends were investigated in this work. According to the changes in the glass transition temperature, the cold-crystallization peak ( $T_c$ ) and the heterogeneity of the OM images, PLLA was determined to be partially miscible with PBA. The morphologies of the PLLA/

PBA blends in the high-temperature region (above the melting temperature of PBA) and in the low-temperature region (below the glass transition temperature of PLLA) were studied. In the high-temperature region, the morphology features of PLLA were significantly affected by PBA. When the PBA content was 10 wt%, PLLA formed spherulites with amorphous PBA on the surfaces and with crystalline PBA, which formed when the sample was subsequently held at room temperature, distributed in the boundaries. When the content of PBA was 20 wt% or higher, the blends formed banded spherulites. The melting images of the banded spherulites indicated that the PBA crystals were distributed in the internal parts of the spherulites. However, from the DSC results, it was determined that the lamellae thickness of PLLA is only weakly influenced by PBA. From studying a thin film of PLLA/PBA, it was determined that these PBA crystals were distributed in interlamellar region of the PLLA crystal, leading to a morphology that exhibited branched structures. In the low-temperature region, both neat PBA and PBA-rich blends exhibited Maltese-cross spherulites. The morphology of the PBA crystal was not significantly affected by PLLA, but the thickness of the PBA lamella, which was determined from the DSC results, decreased with increasing PLLA content. PBA formed fragments in PLA-rich blends because solid PLLA restricted the growth of the PBA crystal.

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