

Miscibility and Isothermal Crystallization of Poly(L-lactide) and Poly(trimethylene carbonate) Blends^{*}

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Abstract Miscibility, isothermal crystallization kinetics, and morphology of poly(L-lactide)/poly(trimethylene carbonate) (PLLA/PTMC) crystalline/amorphous blends were studied by differential scanning calorimetry (DSC) and optical microscopy (OM). The heterogeneity of OM images and an unchanged glass transition temperature showed that PLLA was immiscible with PTMC. During isothermal crystallization, the crystallization rate of PLLA improved when the PTMC content was low ($\leq 20\%$). However, when the PTMC content was high ($\geq 30\%$), the crystallization rate decreased significantly. The reason of these nonlinear changes in crystal kinetics was analyzed according to the nucleation and growth process by virtue of a microscope heating stage. The isothermal crystallization morphologies of the blends were also studied by polarized optical microscopy and the results confirmed the conclusions obtained from crystallization kinetics.

Keywords: Poly(L-lactide); Poly(trimethylene carbonate); Miscibility; Crystal kinetics.

INTRODUCTION

Biodegradable polymers have received increased attention in recent years owing to their potential environmental and medicinal applications. Poly(L-lactide) (PLLA) is a particularly important biopolymer because of its renewable raw materials' source, biodegradability, biocompatibility and good processing ability^[1]. However, two inherent shortcomings limit the applications of PLLA in soft tissues. First, its mechanical properties show hardness and brittleness^[2, 3]. Second, its biodegradable by-products such as lactic acid can lead to local infections^[4].

Many studies have focused on modifying PLLA to improve its mechanical and biodegradable properties by copolymerization, blending and loading of nanomaterials^[5–7]. Blending is an effective and convenient modification method. Many biodegradable polymers such as poly(butylene succinate), poly(ϵ -caprolactone), and poly(3-hydroxybutyrate)^[8–10] have been blended with PLLA to improve their elongation, flexibility and biodegradability. Poly(trimethylene carbonate) (PTMC) is a biodegradable polymer with good elastic properties at ambient temperatures^[11–14]. By blending PLLA with PTMC, the brittleness of PLLA can be improved dramatically^[6]. An interesting property of PTMC blending is that it can prevent the decrease in pH associated with the biodegradation of PLLA^[15]. Therefore, by blending with PTMC, the elasticity and biodegradable properties of PLLA could be improved.

However, PLLA is a crystalline polymer and its crystallization can be altered by blending, which will cause

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the changes of mechanical and processing properties of the materials. On the basis of the crystallization ability of the second component of the blends, PLLA blends can be divided into crystalline/crystalline and crystalline/amorphous blends. In crystalline/crystalline blends of PLLA, it was found that the morphologies, crystallization kinetics and melting behavior were influenced by the second component^[8–10, 16, 17]. Our previous study on PLLA/PBA crystalline/crystalline blends showed that they had significantly improved crystallization rates and that banded spherulites formed easily in the blends^[16, 17]. Other studies have reported that in the crystalline/amorphous blends of PLLA, the crystallization behavior of the crystalline component can be influenced by the amorphous component. For example, Wu *et al.* reported that the crystallization rate of PLLA/acrylic rubber (ACR) could be improved with 1 wt% ACR^[18]. Therefore, irrespective of the blend type, the crystallization behavior of blended PLLA is usually influenced by factors such as miscibility, component contents and molecular weight^[19, 20].

PLLA/PTMC blends are crystalline/amorphous systems and a few studies have focused on the miscibility of the two polymers. Moon *et al.* studied the miscibility behavior of PTMC and PLLA blends in LB monolayers^[21]. They found that the miscibility of PTMC and PLLA at the air/water interface was dependent on the pH of the subphase. Under neutral conditions (pH 7.4), PTMC and PLLA were miscible, whereas they were immiscible under basic conditions (pH 10.7). In a study on PLA/PTMC/talc composites, Qin *et al.* also discussed the miscibility of PLLA/PTMC^[6]. However, to our knowledge, there are still no reports on the crystallization behavior of PLLA/PTMC.

Therefore, the aim of this study is to clarify the crystallization behavior of PLLA in PLLA/PTMC blends. Because miscibility has a great effect on crystallization behavior, the miscibility of the blends was first investigated by using differential scanning calorimetry (DSC) and polarized optical microscopy (POM). The isothermal crystallization kinetics and melting behavior of the PLLA/PTMC blends were studied using DSC. Additionally, the morphology of the blends with different components was studied by POM. The information obtained from this study could be helpful in controlling the structures of PLLA/PTMC blends and beneficial for studying the crystallization of other crystalline/amorphous polymer blends.

EXPERIMENTAL

Materials

PLLA ($M_w = 250000$) was purchased from Nature-works and PTMC ($M_w = 83000$) was purchased from Jinan Daigang Biomaterial Co., Ltd. Both polymers were purified by dissolution and precipitation. First, PLLA or PTMC was dissolved in chloroform, and then reprecipitated from methanol and dried in a fume cupboard for 72 h. The polymers were then dried further under vacuum before experimentation.

Preparation of Blends

Chloroform was chosen as the mutual solvent to prepare the PLLA/PTMC blends. PLLA and PTMC polymers (0.1 g) were dissolved in the solvent (10 mL) and solutions with various PLLA/PTMC polymer weight ratios (100/0–50/50) were prepared. The blend solutions were then cast into a Petri dish at room temperature. The solvent was evaporated under a controlled air stream for 72 h and the samples were then dried under vacuum at 40 °C for one week (to evaporate any residual solvent). The PLLA/PTMC blend films with weight ratios ranging from 100/0 to 50/50 were prepared.

Differential Scanning Calorimetry

The glass transition temperatures (T_g) of the blends were tested on a Mettler-Toledo differential scanning calorimeter (DSC) (TGA/DSC1/1600LF) and operated under nitrogen at a flow rate of 20 mL/min. The temperature and heat flow at different heating rates were carefully calibrated using standard materials before the measurements. The polymer samples (3–5 mg) were encapsulated in the DSC sample holder and then heated to 190 °C for 3 min followed by quenching at a rate of 80 K/min to –30 °C. The neat PLLA samples were also heated to 190 °C for 3 min; however, they were quenched to 25 °C at a rate of 80 K/min. After 3 min, the samples were heated directly from –30 °C or 25 °C to their melting state at a rate of 10 K/min.

The isothermal crystallization of the blends was also investigated with DSC. Because the crystallization rate of PLLA during isothermal crystallization is very low, isothermal cold crystallization procedures were used. The samples were first melted at 190 °C for 3 min and then cooled from the melt to 25 °C at a rate of 80 K/min. After holding at 25 °C for 1 min, the samples were then heated to the isothermal crystallization temperature to process cold crystallization.

Polarized Optical Microscopy

The crystal morphology of the samples were observed with a POM (Nikon Optiphot-2) equipped with a charge-coupled device (CCD) digital camera and hot stage. To obtain a thin film suitable for POM, the samples were prepared by casting the blend solutions with a concentration of 0.01 g/mL on a covered glass slide (20 mm × 20 mm). After the solvent was volatilized, the samples were melted on a hot stage at 190 °C for 3 min and then transferred onto another hot stage at 120 °C for isothermal crystallization. After 24 h, the POM images were taken at room temperature.

Optical Microscopy

To observe the phase structures of the blend during melting, the samples after melting crystallization were heated to 190 °C on a hot stage. An optical microscope (Nikon Optiphot-2) equipped with a hot stage under a parallel polarizer was used to observe the melts, and the images were recorded with a CCD digital camera.

RESULTS AND DISCUSSION

Miscibility of PLLA/PTMC

Optical microscopy images give a visual representation of the phase structures of the samples. Figure 1 shows the typical OM images of PLLA/PTMC 60/40 before and after melting. Figures 1(a) and 1(b) are the images of PLLA/PTMC 60/40 taken at room temperature and the melting temperature, respectively. Before melting (Fig. 1a), it can be observed that spherulites are distributed throughout most regions. However, some regions (such as the arrow-labeled region) are black without birefringence, which is a feature of amorphous structures. After melting at 190 °C (Fig. 1b), the crystallization region is no longer evident and the sample has a relatively uniform structure with some droplets (labeled with arrows). To further determine the phase structures of the blend in the melt, an image in another region with obvious heterogeneity was also taken (Fig. 1c). The image can be divided into two parts: one with outlined regions of an irregular shape and another with uniform structures that have liquid drops with the same morphology observed in Fig. 1(b). Thus, the melt of the PLLA/PTMC blend has an obvious heterogeneous structure. Comparing Figs. 1(a), 1(b), and 1(c), it can be inferred that the outlined regions in Fig. 1(c) are PTMC-rich regions.

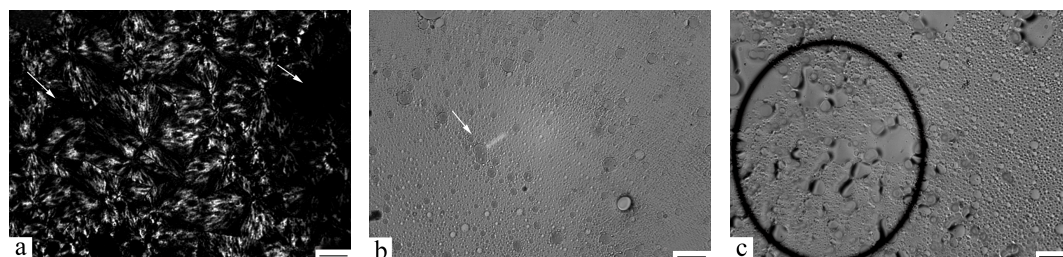


Fig. 1 Optical micrographs of PLLA/PTMC 60/40 taken at different temperatures after isothermal crystallization at 120 °C for 24 h: (a) at room temperature under polarized mode, (b) and (c) at 190 °C under parallel mode (The scale bar is 10 μ m.)

The miscibility of the PLA/PTMC blends was further studied by DSC. Figure 2 shows the DSC heating curves of the blends at a heating rate of 10 K/min from the amorphous state. It can be observed that neat PTMC shows only one T_g at approximately -14 °C and no endothermic or exothermic peaks, suggesting that PTMC is

amorphous. While the DSC trace of neat PLLA shows a T_g at approximately 58 °C, a crystallization peak at 125 °C, a one melting peak at 150 °C. Both the PLLA/PTMC blend samples 80/20 and 60/40 show two values for T_g : one at -14 °C, corresponding to the T_g of PTMC, and another at approximately 58 °C, which is the same as the T_g of PLLA. Consequently, the T_g of PTMC and PLLA in the blends are the same as those of neat components. Therefore, it can be determined from the T_g data that the PLLA/PTMC blends are immiscible.

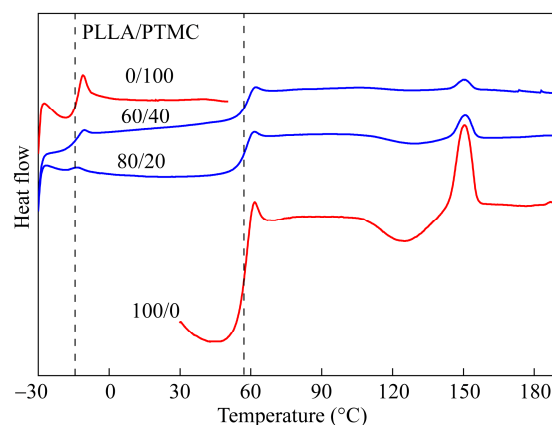


Fig. 2 DSC heating traces of PLLA/PTMC blends at a rate of 10 K/min after quenching from melt at a rate of 80 K/min

In addition, for PLLA/PTMC 80/20, the DSC curve shows a crystallization peak at 126 °C and a melting peak at 150 °C. Because the PLLA content was lower in PLLA/PTMC 60/40, the crystallization peak is not obvious and the melting peak at 150 °C is very weak. Therefore, the crystallization behavior of PLLA/PTMC will be discussed in the following section by virtue of investigations of isothermal crystallization.

Isothermal Crystallization of Polymer Blends

Figure 3 shows the isothermal crystallization traces of PLLA/PTMC blends with different weight ratios at 120 °C. The exothermic area of the blends decreased linearly with an increase in the PTMC content, which indicates the decreasing of crystallinity of blends with the increase of PTMC components. Interestingly, the time of exothermic peak (t_p) varied with the weight ratio of the blends at the same crystallization temperature. For example, the t_p value of neat PLLA is at 9.1 min and that of PLLA/PTMC 80/20 is 8.4 min, while that of PLLA/PTMC 50/50 is 21.4 min. The nonlinear changes of the t_p values suggest that the crystallization rate of PLLA/PTMC blends varied nonlinearly.

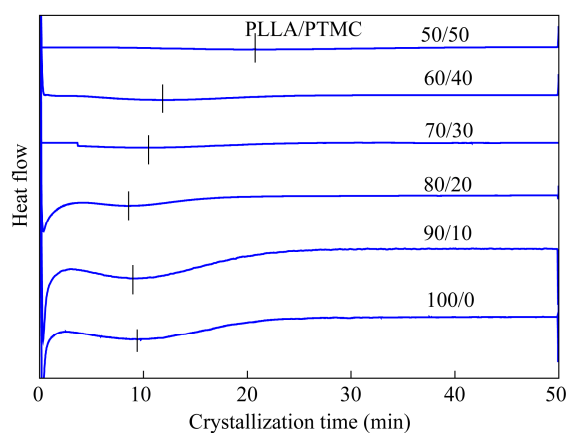


Fig. 3 Heat flow versus time for the isothermal crystallization of PLLA/PTMC blends with different weight ratios at 120 °C

To further investigate the crystallization rate of the blends and to clarify the influence of PTMC on the crystallization behavior of PLLA, PLLA/PTMC 80/20 and 60/40 were chosen to investigate the crystallization behavior at different temperatures. As a comparison, the isothermal crystallization of neat PLLA was also investigated. Because the melt crystallization rate of PLLA is very low, the isothermal cold crystallization kinetics were studied from 120 °C to 130 °C according to the Avrami equation^[22, 23]:

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

X_t represents the relative crystallinity, k is the crystallization rate constant in relation to the nucleation and growth process, and n is the Avrami index dependent on the nature of nucleation and spatial dimensions of crystal growth. Relative crystallinity (X_t) values versus crystallization time for neat PLLA and the PLLA/PTMC blends are shown in Fig. 4. For the same sample and same X_t , the crystallization time increased with increasing isothermal crystallization temperature, which suggests that the crystallization rate decreased with increasing crystallization temperature between 120 °C and 130 °C. It was attributed to the nucleation rate decreasing with increasing crystallization temperature.

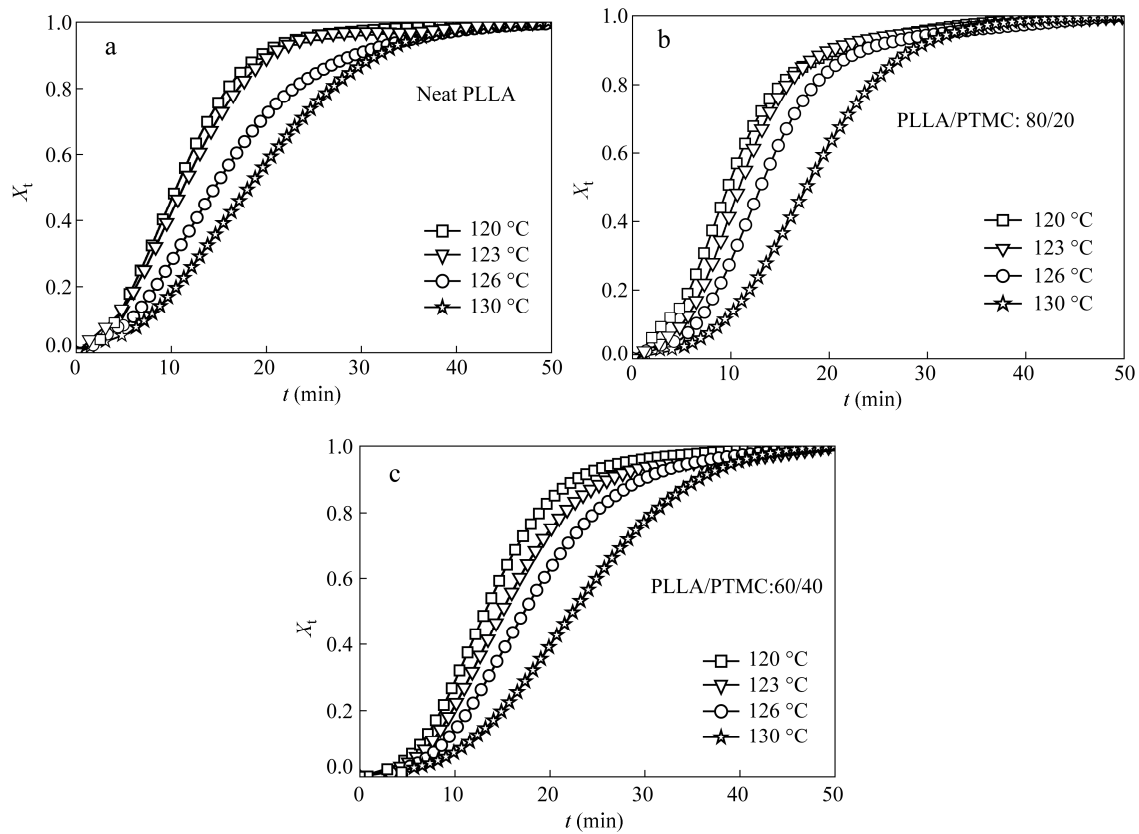


Fig. 4 Plots of relative degree of crystallinity versus crystallization time for (a) Neat PLLA, (b) PLLA/PTMC 80/20 and (c) PLLA/PTMC 60/40

To analyze the isothermal crystallization of neat PLLA and PLLA/PTMC in detail, parameters K , n , and $t_{0.5}$ calculated from Eqs. (1) and (2) are listed in Table 1.

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

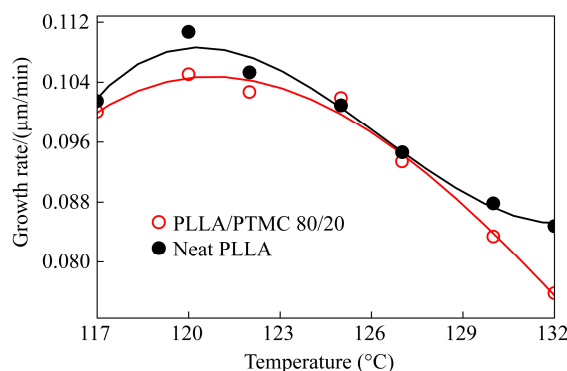
Table 1. Isothermal crystallization kinetics parameters of neat PLLA and PLLA/PTMC blend obtained by Avrami fit

Samples	T_c (°C)	n	K (min ⁻ⁿ)	$t_{0.5}$ (min)
Neat PLLA	120	2.1	6.3×10^{-3}	10.7
	123	2.1	6.3×10^{-3}	10.9
	126	2.1	3.1×10^{-3}	14.4
	130	2.2	1.4×10^{-3}	18.4
PLLA/PTMC 80/20	120	2.1	5.4×10^{-3}	9.8
	123	2.4	2.1×10^{-3}	10.9
	126	2.5	1.1×10^{-3}	13.4
	130	2.4	6.6×10^{-4}	17.9
PLLA/PTMC 80/20	120	2.5	1.3×10^{-3}	12.2
	123	2.5	7.7×10^{-4}	15.3
	126	2.6	3.8×10^{-4}	17.6
	130	2.7	2.1×10^{-4}	22.4

The values of n for neat PLLA and the blends are between 2.1 and 2.5, indicating that the crystallization may correspond to three-dimensional truncated sphere growth with athermal nucleation^[24]. In addition, the differences in the n values are very small, which suggests that the crystallization mechanism of PLLA did not change by incorporating PTMC.

However, the $t_{0.5}$ value suggests that the crystallization rate varied nonlinearly for blends with different compositions. The crystallization rate of the PLLA/PTMC 80/20 blend was faster whilst that of PLLA/PTMC 60/40 was noticeably slower than that of neat PLLA. The nonlinear changes in the crystallization rate are consistent with the t_p values of the PLLA/PTMC blends (as seen in Fig. 3). Therefore, it can be inferred that when the PTMC content is low (< 20%), the crystallization rate of PLLA is improved, whereas when it is high, the crystallization rate decreased significantly. What is the reason that caused this kind of strange changes for crystallization kinetics?

POM with a hot stage was used to observe the nucleation and growth process of the blends to determine the cause of the strange crystallization kinetics of the PLLA/PTMC blends. The growth rates of spherulites were first determined by following the diameter of spherulites over 3 h. The data of crystal growth rates after nucleation were investigated. Therefore, Fig. 5 was calculated from the process of spherulite growth after forming a spherulites of about 0.1 μm and did not include the primary nucleation process. Additionally, the boundary of the spherulites in PLLA/PTMC 60/40 was too fuzzy to distinguish; therefore, only the growth rates of spherulites of neat PLLA and PLLA/PTMC 80/20 were determined. It can be observed in Fig. 5 that the growth rate decreases with increasing the temperature from 120 °C to 130 °C (consistent with Table 1). However, it was found that the growth rate of the blend is smaller than that of neat PLLA. The decrease in the growth rate can be attributed to a dilution effect in the crystalline/amorphous blends.

**Fig. 5** The growth rates of neat PLLA and PLLA/PTMC 80/20 blend spherulites after about 0.1 μm in size

Then, what is the reason that causes the high overall crystallization rate of PLLA/PTMC 80/20? The nucleation rate was further studied. Figure 6 shows the POM images of neat PLLA, PLLA/PTMC 80/20, and PLLA/PTMC 60/40 at 120 °C for 60 min. Figures 6(a₁), 6(b₁), and 6(c₁) show the images of the initial samples at 120 °C. Figures 6(a₂), 6(b₂), and 6(c₂) show the images of the first nucleation appearing. The following images were taken at 30 and 60 min, respectively. It is evident that the time of first nucleation increased with increase in the PTMC content. This is an usual phenomenon since the amorphous component has dilution effects that cause a decrease in the nucleation rate of the crystalline component. However, the number of nuclei in neat PLLA, PLLA/PTMC 80/20, and PLLA/PTMC 60/40 are 43, 68, and 90 at 60 min, respectively. It suggests that the time for inducing nucleation in the blends increased with the addition of PTMC. However, the number of spherulites in the blends increased with PTMC content. These results infer that although the immiscible amorphous component in PLLA/PTMC blends plays a diluting role (increases the time of nucleation), the number of nuclei still increases in the long crystallization process. The increase of nuclei could be attributed to the boundary of PLLA/PTMC which supplies many nucleating points and increases the number of nuclei. Figure 7 shows a typical spherulite that grows from the interface of PLLA and PTMC. The outlined region shows that some

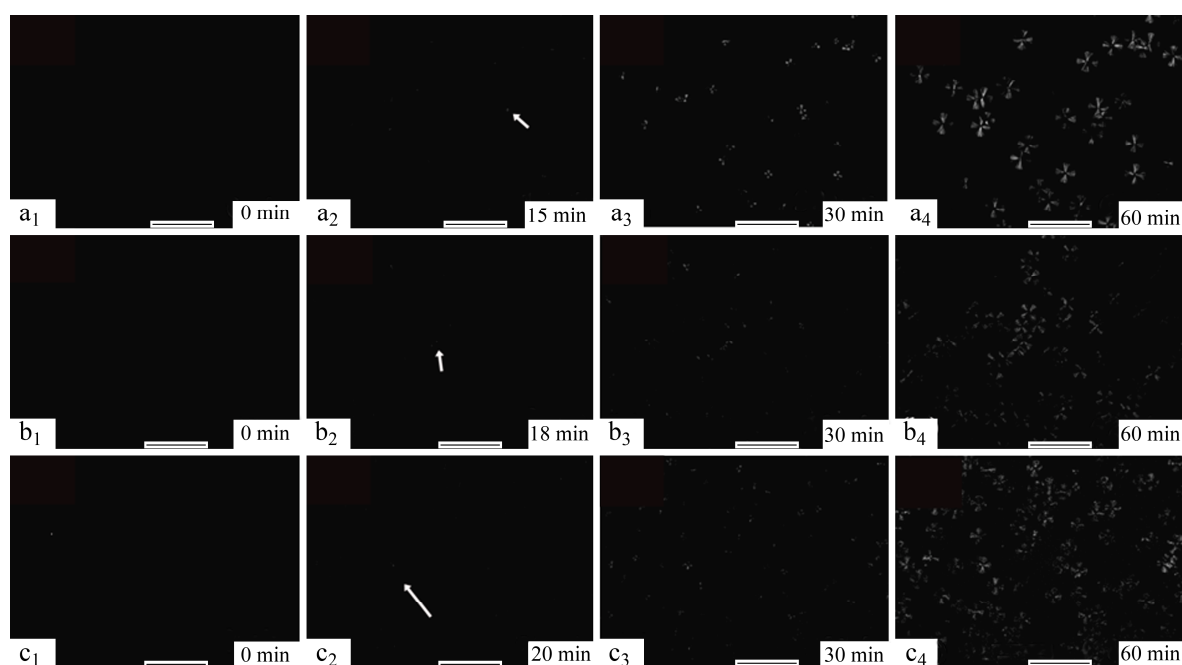


Fig. 6 Polarized optical micrographs in the first one hour of neat PLLA and blends during isothermal crystallization at 120 °C (The scale bar is 10 μ m.)

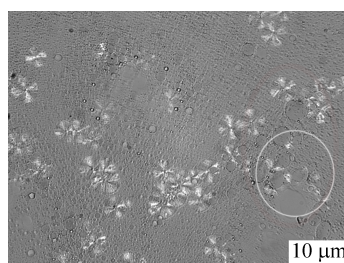


Fig. 7 Optical micrographs of PLLA/PTMC 60/40 morphology during isothermal crystallization at 120 °C. The scale bar is 10 μ m. Outlines indicate areas where crystals grew from boundaries.

spherulites grow from the boundary of the two components. Moreover, a large number of boundaries could not be identified with optical microscopy. In immiscible crystalline/amorphous blends, since the interfacial tension is high and interface is very sharp, it rarely induces new nucleus. However, in immiscible PP/PS blends, Wenig *et al.* reported the effect of heterogenous surface nucleation at PP/PS interfaces^[25]. This type of nucleation may relate with the surface features, which are suitable for a crystalline chain to deposit on. But what is the specific properties is a question that needs further investigation.

By combining the results of Fig. 5, it can be determined that the changes in the crystallization kinetics of PLLA are caused by the effects of PTMC on the nucleation and growth process during PLLA crystallization. The existence of PTMC has two effects on the crystallization behavior of PLLA. First, PTMC decreases the growth rate of PLLA after nucleation because of a dilution effect. Second, the boundaries in immiscible blends induce a large number of nuclei in long time. Therefore, when the PTMC content is low (PLLA/PTMC 80/20), the boundary effect is dominant and the crystallization rate is higher than that of neat PLLA. However, when the PTMC content is high (PLLA/PTMC 60/40), although more nuclei can be formed after a long time, the dilution effect is large enough to significantly decrease the crystal growth rate. Thus, a combination of nucleation and growth processes induced a decrease in the overall crystallization rate.

Crystallization Morphology of PLLA/PTMC

Figure 8 shows the POM images of PLLA/PTMC blends with different weight ratios after isothermal crystallization at 120 °C for 24 h. It can be observed that, although both neat PLLA and the blends formed Maltese-cross spherulites, the intensity of the birefringence of the spherulites decreases with increasing PTMC content. Additionally, a comparison of Figs. 8(a) and 8(b) shows that there are many black dots in the spherulites of the blends, while the surface of neat PLLA is very clear. Therefore, the black dots can be determined as amorphous PTMC without birefringence. In PLLA/PTMC 60/40, the amorphous PTMC enlarged into big black regions that caused the birefringence intensity to decrease significantly.



Fig. 8 Polarized optical micrographs of PLLA/PTMC blends with different PLLA/PTMC ratios: (a) 0/100, (b) 80/20 and (c) 60/40 (The scale bar is 10 μm .)

In Fig. 8, the spherulite sizes also varied with the PTMC content. For example, the diameters of neat PLLA spherulites were approximately 13 μm , while those of PLLA/PTMC 80/20 were approximately 7 μm . With a PTMC content of 40%, it was difficult to determine the exact diameters of spherulites because many of the spherulites did not form clear boundaries. However, the size of the spherulites in PLLA/PTMC 60/40 looked smaller than that of neat PLLA and PLLA/PTMC 80/20. The change in the morphology agrees with the crystallization kinetics results. For PLLA/PTMC 80/20, the number of nuclei is more than that of neat PLLA, which was caused by nucleation at the boundaries. In addition, the spherulite growth of PLLA/PTMC 80/20 is slower than that of PLLA. Therefore, PLLA/PTMC 80/20 formed a greater number of spherulites with smaller diameters. When the PTMC content is high (PLLA/PTMC 60/40), there is a large amount of amorphous PTMC, which is immiscible with PLLA. Therefore, the spherulite growth region is limited by PTMC and the shape of PLLA spherulites is not well defined. As previously discussed, the number of nuclei for PLLA/PTMC 60/40 is large; therefore, the decrease in the spherulite diameter and increase in the spherulite number are reasonable. These changes in the morphology further supported the crystallization kinetics results.

CONCLUSIONS

The miscibility and crystallization behaviors of PLLA/PTMC blends were investigated by DSC and POM. Heterogeneity of the OM images and a constant T_g suggested that PLLA was immiscible with PTMC. Isothermal crystallization studies showed that PTMC had a large effect on the crystallization kinetics and morphology of PLLA. When the PTMC content was low, although the spherulite growth rate decreased with the dilution effect of PTMC, the crystallization rate did not decrease. It was attributed to an increase in the number of nuclei forming at the interface of the immiscible component. When the PTMC content was high, although more nuclei can be formed in long time, the diluting effect was sufficiently large to greatly decrease the crystal growth rate, leading to a significant decrease in the overall crystallization rate. The morphologies of the blends also confirmed the results obtained from the crystallization kinetics studies. In PLLA/PTMC 80/20, a large number of small spherulites formed as the nucleation number increased and the growth rate decreased, whilst in blends with a high PTMC content (PLLA/PTMC 60/40), most spherulites were not intact because amorphous PTMC regions limit PLLA spherulite growth.

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