

INCREASED SPHERULITIC GROWTH RATES OF SEMICRYSTALLINE POLYMER DUE TO ENHANCED LIMITED LOCAL CHAIN SEGMENTAL MOBILITY AT THE INTERFACE OF DOUBLE-LAYER THIN FILMS*

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Abstract In this work the nucleation and growth of spherulites for the below polylactide (PLA) layer in poly(ϵ -caprolactone)/polylactide (PCL/PLA) double-layer films during isothermal crystallization at various temperatures above the melting point of PCL have been investigated by using polarized optical microscopy (POM). It is revealed that two types of spherulitic morphologies are observed in PCL/PLA double-layer films. One is the well defined highly birefringent spherulites, and the other one is the coarse spherulites. It is interesting to find that the spherulitic growth rate of the coarse spherulites is higher than that of the well defined spherulites. It is thought that the coarse spherulites nucleate and grow with the assistance of the interfaces between the PCL and PLA layers, and the well defined highly birefringent spherulites only nucleate and grow in the PLA layer.

Keywords: Polylactide; Poly(ϵ -caprolactone); Interface; Crystallization; Spherulite.

INTRODUCTION

Morphological control through polymer crystallization, which has been studied for several decades, has been always an important and fundamental research topic in polymer physics^[1–4]. During the past decades the surface-induced crystallization of polymers has attracted much attention, which provides an important way for tailoring polymer crystallization kinetics as necessary^[2, 5, 6]. The epitaxial crystallization as the most popular one provides the much useful way to control the crystalline structures and morphologies^[7, 8]. Recently the surface-induced crystallization of semicrystalline polymers through the layer-by-layer method was proposed by our group^[9, 10]. It was found that the top covering molten poly(ethylene oxide) (PEO) layer could greatly accelerate the spherulitic growth rates (G) of the below PLA layer^[9, 10]. The interdiffusion between PEO and PLA layers is the key factor to accelerating the spherulitic growth rates of the below PLA layer. PEO was a typical miscible polymer component for PLA component in that study. Whereas, the case if an immiscible polymer component layer for the PLA layer can be applied or not by the layer-by-layer method has not been studied so far, which will be the main topic in this study.

It is well known that PLA produced from the renewable resources such as corns has been widely studied due to its excellent mechanical properties, biodegradability and biocompatibility^[11, 12]. PCL as a highly

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processable biopolymer that can be hydrolytically or enzymatically degraded has extensive applications in various areas such as medicine and agriculture^[13, 14]. PCL/PLA blends are typical immiscible blends of biocompatible polymers, which have attracted increasing attention in the context of practical applications^[15–16]. Sakai *et al.* investigated immiscible PCL/PLA blend system and claimed that the presence of PCL, which induced local and deep depression of T_g at the interface of PCL domains, enhanced the nucleation of PLA even at low temperatures^[17]. In this study, polarized optical microscopy (POM) was applied to observe the nucleation and growth of spherulites for the below PLA layer in the PCL/PLA double-layer films during isothermal crystallization at various temperatures above the melting point of PCL layer. The results show that two types of spherulitic morphologies can be observed in the PCL/PLA double-layer films, which are the well defined highly birefringent spherulites and the coarse spherulites, respectively. On the basis of the experimental observation, the mechanism for the formation of the different spherulitic morphologies is proposed.

EXPERIMENTAL

Materials

Poly(L-lactide) (PLA, sample code PLA4032D) used in this study was purchased from Nature Works China/Hong Kong, Shanghai, China and had weight-average molecular mass (M_w) of 1.8×10^5 g/mol, number-average molecular mass (M_n) of 1.2×10^5 g/mol, polydispersity index (M_w/M_n) of 1.5, L-isomeric content of 98.7 mol% and density of 1.24 g/cm^3 . Poly(ϵ -caprolactone) was purchased from the Sigma-Aldrich Company, USA and had M_w of 3.1×10^4 g/mol and polydispersity index of 1.5. Size-exclusion chromatography (SEC) coupled with a DAWN HELEOS II multiangle laser light scattering detector, a refractive index (RI) detector Optilab T-rEX and a viscometer ViscoStar II was applied to measure the M_w and M_n values for these two materials. PLA and PCL were dried in vacuum oven for 24 h before further use.

In situ Preparation of PCL/PLA Double-Layer Films and Crystallization Studies by Using Polarized Optical Microscopy (POM)

PCL and PLA were dissolved in chloroform to form 2 wt% solutions, respectively. The solutions were stirred at room temperature for 12 h, and then were cast on cover glasses, respectively. When chloroform was rapidly evaporated, PCL and PLA films formed on cover glasses, which were further dried under vacuum to constant masses. The PLA and PCL film thicknesses were about 15 μm . POM (Olympus BX51, Japan) was used to observe the nucleation and growth of PLA spherulites in the *in situ* prepared PCL/PLA double-layer films. The typical procedure can be described as follows: once a PLA film (cast on a cover glass) was melted on a homemade hot stage set at 180 °C (less than 30 s), a PCL film (cast on a cover glass) was quickly put on the molten PLA film to obtain the *in situ* prepared PCL/PLA double-layer film, the film was further held at 180 °C for 5 min to erase the previous thermal histories, and then was transferred to another hot stage set at a certain crystallization temperature below the melting point of PLA for the isothermal crystallization studies. From the slopes of changes of spherulite radius with crystallization time, the average radial growth rates of PLA spherulites (G) were obtained.

RESULTS AND DISCUSSION

Nucleation and Growth of Spherulites for PCL/PLA Double-layer Films

For PLA crystallization spherulites are the most common morphology^[18–21]. Figure 1 shows the selected POM micrographs during isothermal crystallization for PCL/PLA double-layer films at the crystallization temperatures (T_c) of 100, 110, 115, 120 and 130 °C, respectively. It can be seen that the nucleation density of PLA spherulites in the PCL/PLA double-layer films increases with decreasing crystallization temperature due to increasing supercooling for PLA crystallization. Obviously different PLA spherulitic morphologies can be noticed in the PCL/PLA double-layer films. It will be discussed in the following section.

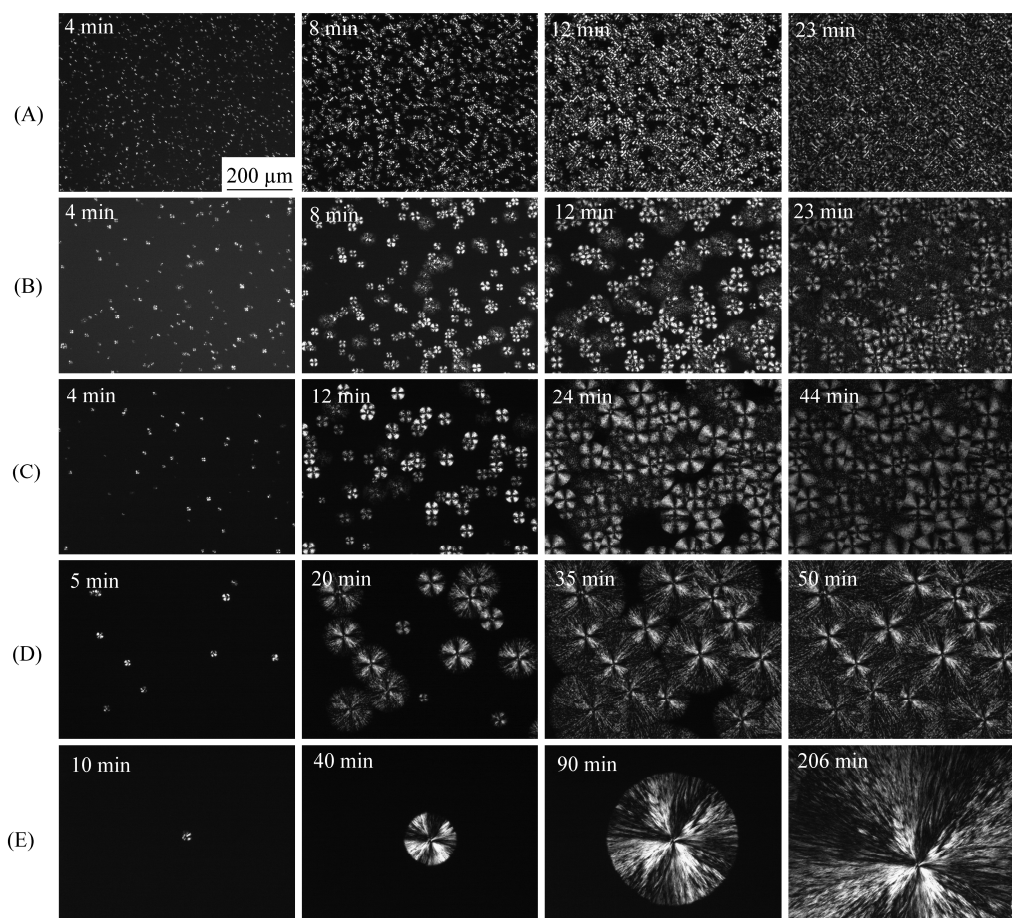


Fig. 1 Selected POM micrographs during isothermal crystallization for PCL/PLA double-layer films at different time and at different temperatures of (A) 100 °C, (B) 110 °C, (C) 115 °C, (D) 120 °C and (E) 130 °C. The scale bar in (A) represents 200 μm and is applied to all the micrographs.

Figure 2 displays the selected POM micrograph for a PCL/PLA double-layer film during isothermal crystallization at T_c of 115 °C for 10 min. Two types of spherulitic morphologies are clearly seen. Some spherulites are well defined with high birefringence, whereas, some spherulites look coarse. More interesting, it can be found that the coarse spherulites look larger than the well defined ones. Figure 3 further shows the changes of spherulite radius with time for the selected spherulites A, B and C as marked in Fig. 2 for the PCL/PLA double-layer film during isothermal crystallization at 115 °C. PLA spherulites all grow with time linearly and the spherulitic growth rates can be obtained from the slopes of the linearly fitted lines. The spherulitic growth rates for both spherulites A and B are evaluated to be 4.3 $\mu\text{m}/\text{min}$. However, the spherulitic growth rate for spherulite C is just 2.0 $\mu\text{m}/\text{min}$. Thus, the PLA spherulitic growth rate for spherulites A and B is about two times of that for spherulite C. Note that spherulites A and B are the coarse ones, while spherulite C is the well defined highly birefringent one. The growth rates for these two types of spherulitic morphologies are apparently much different. The mechanism relating to this difference will be presented in a later section. We further notice that in Fig. 3 the linearly fitted lines point at the different time in the X-axis (see the olive and red color arrows), which indicate the different nucleation induction time for these two spherulitic morphologies. The coarse spherulites need longer nucleation induction time compared with that for the well defined highly birefringent spherulites. Because of the limited miscibility between PCL and PLA layers, local glass transition temperature (T_g) of PLA decreases^[17], which brings out the prolonged nucleation induction time accordingly for PLA at the interface between PCL and PLA layers. We note here that for neat PLA film the above observed

phenomenon could not be found, for which the regular PLA spherulites with high birefringence and with some ring-banded texture were observed. Because the results for neat PLA film are out of the focus in this study, the results for neat PLA film will be presented elsewhere in a future publication.

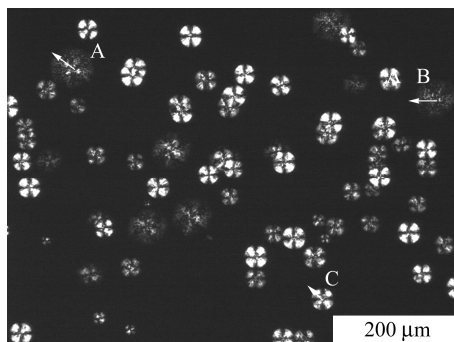


Fig. 2 POM micrograph for a PCL/PLA double-layer film during isothermal crystallization at T_c of 115 °C for 10 min. Three arrows indicate the measured radial directions for the selected spherulites A, B and C, respectively.

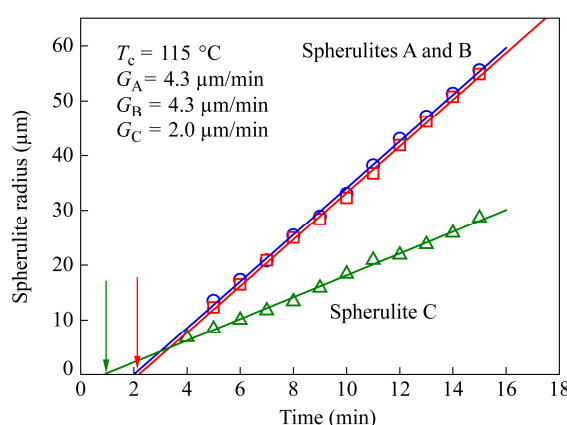


Fig. 3 Changes of spherulite radius with time for the selected spherulites A, B and C as marked in Fig. 2 for PCL/PLA double-layer film during isothermal crystallization at T_c of 115 °C. The arrows point at the time when the nuclei of spherulites A, B and C start to form, respectively.

Figure 4 shows the selected POM micrograph for a PCL/PLA double-layer film during isothermal crystallization at T_c of 120 °C for 20 min. A combination of the above mentioned two types of spherulitic morphologies can be seen from Fig. 4, which can be representatively indicated by spherulite D. For spherulite D, the initial growing part of the spherulite is the well defined highly birefringent one (as marked by the circle on spherulite D), and then the further growing part of the spherulite becomes coarse. In Fig. 4, spherulite E shows similar coarse spherulitic morphology as spherulites A and B shown in Fig. 2. Figure 5 displays the changes of spherulite radius with time for the selected spherulites D and E in the PCL/PLA double-layer film during isothermal crystallization at 120 °C. It is interesting to find that spherulite D shows two obviously different spherulitic growth rates. Before the crystallization time of 19 min, the spherulitic growth rate for spherulite D is $G_{D1} = 2.6 \mu\text{m/min}$, and subsequently spherulite D becomes to grow faster with a growth rate of $G_{D2} = 3.9 \mu\text{m/min}$. The latter growth rate for spherulite D (after 19 min) is close to that for spherulite E ($G_E = 4.0 \mu\text{m/min}$) in the whole crystallization time range. Consistent with the result shown in Fig. 3, the linearly fitted lines for spherulites D and E also point at the different time in the X-axis, indicating the different nucleation induction time for these two types of spherulitic morphologies.

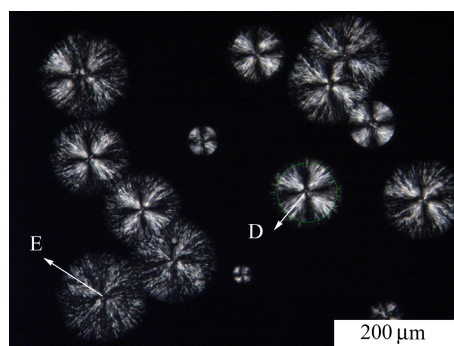


Fig. 4 POM micrograph for a PCL/PLA double-layer film during isothermal crystallization at T_c of 120 °C for 20 min

The circle on spherulite D separates the spherulitic morphology into two parts. The two arrows indicate the measured radial directions for the selected spherulites D and E, respectively.

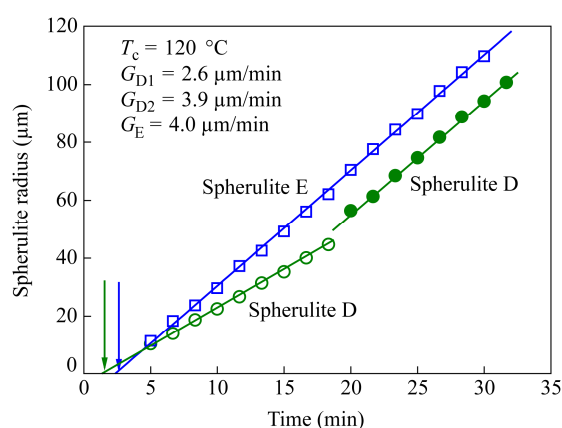


Fig. 5 Changes of spherulite radius with time for the selected spherulites D and E as marked in Fig. 4 for PCL/PLA double-layer film during isothermal crystallization at T_c of 120 °C

The arrows point at the time when the nuclei of spherulites D and E start to form, respectively.

The growth rates of spherulites for the below polylactide (PLA) layer in PCL/PLA double-layer films during isothermal crystallization at various temperatures above the melting point of PCL were all measured. The changes of spherulitic growth rate with isothermal crystallization temperature for the PCL/PLA double-layer film are plotted in Fig. 6. The result for neat PLA film is plotted together in Fig. 6 for the comparison purpose. It is easily found that neat PLA film shows the typical bell-shape spherulitic growth rate as reported in our previous study and in other reports^[9, 22, 23]. Whereas, for the PCL/PLA double-layer film two spherulitic growth rates at the same crystallization temperature can be measured. The slow spherulitic growth rates in the PCL/PLA double-layer film were measured from the well defined highly birefringent spherulites, while the fast spherulitic growth rates in the PCL/PLA double-layer film were measured from the coarse spherulites. The slow spherulitic growth rates for PCL/PLA double-layer films are slightly higher than those for neat PLA films at the same crystallization temperatures. However, the fast spherulitic growth rates for PCL/PLA double-layer films are obviously higher than those for neat PLA films at the same crystallization temperatures. The mechanism for this observed result will be discussed in the next section.

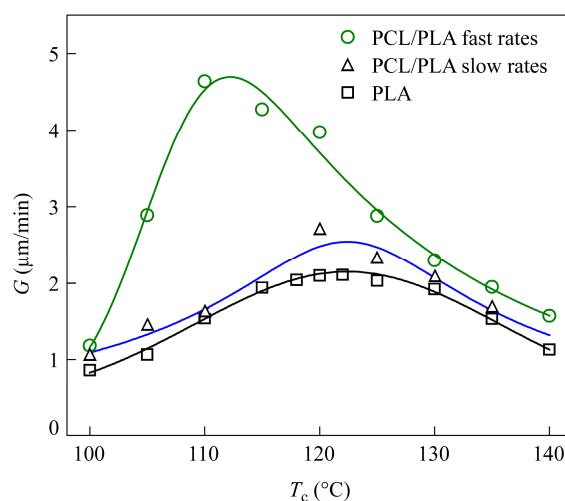


Fig. 6 Changes of spherulitic growth rate G as functions of isothermal crystallization temperature for neat PLA and PCL/PLA double-layer films
Note that the slow and fast spherulitic growth rates coexist in PCL/PLA double-layer films. The solid curves are guides to eyes.

Mechanism for Slow and Fast Spherulitic Growth Rates in PCL/PLA Double-Layer Films

In our previous study, the nucleation and growth of spherulites in the miscible PEO/PLA double-layer film were investigated and the interface between PEO and PLA layers plays a key role for accelerating the spherulitic growth rates of PLA layer^[9]. While for the immiscible polymer pairs, such as the PCL/PLA pair, our experimental results are interesting as well. To provide an explanation for the observed phenomena, the mechanism is described schematically in Fig. 7. Spherulites A and B shown in Fig. 7(a) represent the two types of spherulitic morphologies, the coarse spherulite (A), which nucleates and grows from the PCL/PLA interface, and the well defined highly birefringent spherulite (B), which nucleates and grows in the PLA layer. At the interface between PCL and PLA layers the interaction between PCL and PLA chains activates PLA chain segmental mobility, therefore the coarse spherulite (A) can grow faster. Figure 7(b) schematically demonstrates the growths of these spherulites. A particular case is the growth of spherulite C, which nucleates and grows in the PLA layer, however, the nucleating site is close to the interface between the PCL and PLA layers. With the prolonged crystallization time, when the growth fronts of spherulite C touch with the interface between the PCL and PLA layers, it becomes to grow faster and becomes coarse, which results from that the PCL chains can locally enhance the PLA chain segmental mobility at the interface^[17], although such a kind of enhancement is localized and limited when compared with the miscible polymer pairs, such as the PEO/PLA or PEG/PLA pairs^[9, 10]. It should be noted here that it is worthy of comparing the spherulitic growth rate of PLA in PLA/PCL blends with that in PCL/PLA double-layer film. The result reported from a previous publication^[24] demonstrates that the spherulitic growth rates of PLA in PCL/PLA blends are relatively faster than that in neat PLA, which is consistent with our result in this study. We further emphasize that the slow growth rates in PCL/PLA double-layer film is only slightly higher than that in neat PLA film, which might indicate the interfacial effect from PCL layer at the late stage somehow, because the exact elimination of the interfacial effect due to PCL layer is impossible when we measured the PLA spherulite sizes during the growth. In addition, although the immiscibility between PCL and PLA components in the blends was reported^[10], the sharp interface between PCL and PLA layers might not exist because certain interfacial diffusion between PCL and PLA layers might occur^[25], which causes the slightly increased spherulitic growth rates for PCL/PLA double-layer films compared with neat PLA film.

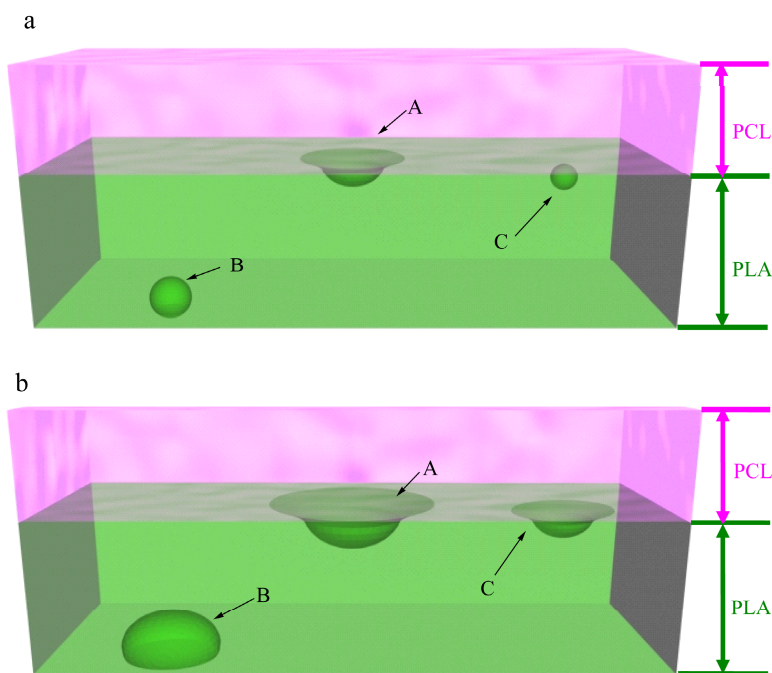


Fig. 7 Schematic illustration for nucleation and growth of PLA spherulites in a PCL/PLA double-layer film at (a) the early stage and (b) the late stage of crystallization: (A) a coarse spherulite, (B) a well defined highly birefringent spherulite and (C) a spherulite with an initial slow growth rate and a later fast growth rate

CONCLUSIONS

In this study POM was applied to investigate the nucleation and growth of spherulites for the below PLA layer in PCL/PLA double-layer films during isothermal crystallization at various temperatures above the melting point of PCL. Two types of spherulitic morphologies are observed in PCL/PLA double-layer films. One is the well defined highly birefringent spherulites, and the other one is the coarse spherulites. Through measuring the changes of spherulite radius with crystallization time, it can be found that the spherulitic growth rates of the coarse spherulites are higher than those of the well defined ones. It is interesting to notice that some spherulites show the combined morphology of the above mentioned spherulitic morphologies, for which the well defined highly birefringent spherulites form at first, and then they become coarse with further increasing crystallization time. Accordingly, these spherulites show two spherulitic growth rates. Although PCL and PLA components are immiscible, the interface between PCL and PLA layers is the key clue to understanding the formation of two types of spherulitic morphologies. It is thought that PCL can enhance the PLA chain segmental mobility at the interface between PLA and PCL layers. Therefore, the coarse spherulites nucleate and grow at the interface of PCL and PLA layers, the well defined highly birefringent spherulites nucleate and grow in the PLA layer, and the spherulites having two spherulitic growth rates nucleate and grow in the PLA layer at first, and then when the growth fronts of the PLA spherulites meet with the interface between the PCL and PLA layers, they continue to grow faster into the coarse ones.

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