

Miscibility and Crystallization Behavior of Biodegradable Poly(ϵ -caprolactone)/Tannic Acid Blends

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ABSTRACT: Miscibility, isothermal melt crystallization kinetics, spherulitic morphology and growth rates, and crystal structure of completely biodegradable poly(ϵ -caprolactone) (PCL)/tannic acid (TA) blends were studied by differential scanning calorimetry, polarized optical microscopy, and wide angle X-ray diffraction in detail in this work. PCL and TA are miscible as evidenced by the single composition dependent glass transition temperature over the whole compositions range and the depression of equilibrium melting point of PCL in the PCL/TA blends. Isothermal melt crystallization kinetics of neat PCL and an 80/20 PCL/TA blend was investigated and analyzed by the Avrami equation. The overall crystallization rates of PCL decrease with increasing crystallization temperature

for both neat PCL and the PCL/TA blend; moreover, the overall crystallization rate of PCL is slower in the PCL/TA blend than in neat PCL at a given crystallization temperature. However, the crystallization mechanism of PCL does not change despite crystallization temperature and the addition of TA. The spherulitic growth rates of PCL also decrease with increasing crystallization temperature for both neat PCL and the PCL/TA blend; moreover, blending with TA reduces the spherulitic growth rate of PCL in the PCL/TA blend. It is also found that the crystal structure of PCL is not modified in the PCL/TA blend. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 4409–4415, 2012

Key words: biodegradable; blends; crystallization

INTRODUCTION

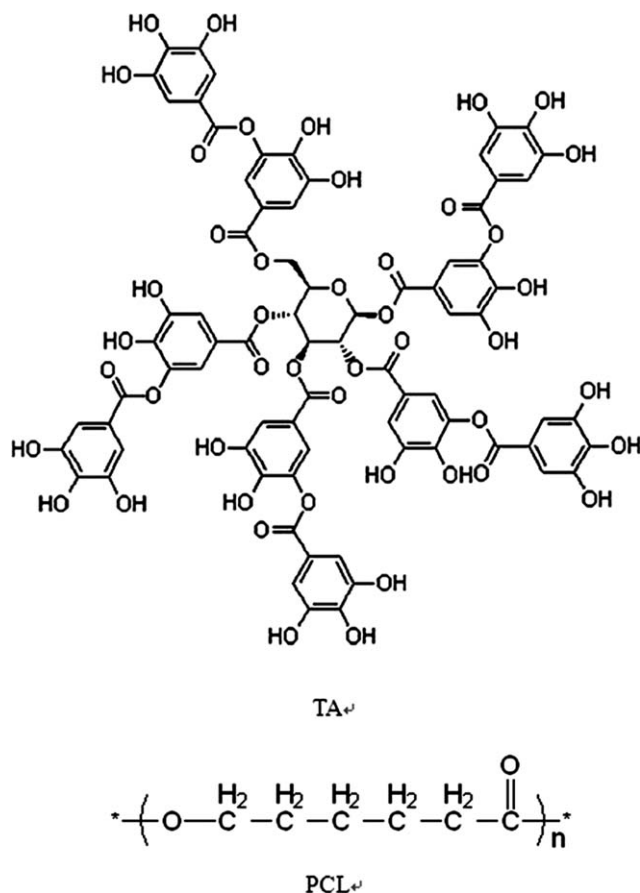
More and more attention has recently been paid to biodegradable and biocompatible poly(ϵ -caprolactone) (PCL); however, its disadvantages, including low glass transition temperature, low melting temperature, low modulus, etc., have limited its wider practical application. Polymer blending is a simple and economic way to modify the physical properties and extend the practical application fields of biodegradable polymers.¹ On one hand, PCL is found to be immiscible with some semicrystalline polymers, such as poly(3-hydroxybutyrate), poly(butylene succinate), Poly(3-hydroxybutyrate-co-hydroxyvalerate), and poly(ethylene oxide).^{2–6} On the other hand, PCL is found to be miscible with some polymers, such as poly(vinyl phenol), bisphenol-A polycarbonate, and phenoxy.^{7–9} Inoue and coworker have studied the PCL based polymer blends with natural polymers, such as chitin, chitosan, and catechin⁷ that contain hydroxyl groups as an electron-donor.^{10–12}

Tannic acid (TA) is a high molecular weight polyphenolic compound and is fully biodegradable. TA is able to bind with biopolymers through noncovalent interactions.^{13–15} Woo and coworker have recently studied the specific interactions and miscibility of a series of binary miscible blend comprising of biodegradable polyesters, such as PCL, poly(ethylene adipate), poly(butylene adipate) (PBA), and TA. The appearance of a single composition-dependent glass transition temperature indicated that TA is miscible with PCL, PBA, and PEA over the whole compositions range, respectively; moreover, fourier transform infrared spectroscopy confirmed the presence of specific intermolecular hydrogen bonding interactions between the carbonyl groups of polyesters and the phenolic hydroxyl groups of TA.¹⁶

Although, Woo and coworker have studied the miscibility and specific interaction of PCL/TA blends, less attention has been paid to crystallization behavior of this newly found miscible crystalline/amorphous polymer blends; however, such study must be of great interest and importance for a better understanding of the structure and properties relationship of biodegradable polymer blends from both academic research and practical application viewpoints. Therefore, in the present work we studied the miscibility, isothermal melt crystallization kinetics, spherulitic morphology and growth rates, and crystal structure of PCL/TA blends in detail.

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Scheme 1 Chemical structures of PCL and TA.

EXPERIMENTAL

Materials

PCL ($M_n = 80,000$ g/mol) and TA ($M_w = 1,721$ g/mol) were purchased from Sigma-Aldrich Company. Both samples were used as received without any further purification. The chemical structures of PCL and TA are shown in Scheme 1.

Sample preparation

PCL/TA blends were prepared via a solution and casting method in this work with a mutual solvent of 1,4-dioxane at room temperature. The solution (0.01 g/ml) was first stirred for 24 h and then cast on a petri dish at room temperature. The solvent was allowed to evaporate slowly in a controlled air stream for 48 h. The resulting films were further dried in a vacuum oven at 40°C for 72 h to ensure total removal of solvent. The PCL/TA blends were prepared with various compositions ranging from 100/0, 80/20, 60/40, 40/60, 20/80 to 0/100 in weight ratio, with the first number referring to PCL.

Characterization

Glass transition temperature (T_g) and melting temperature (T_m) of the melt-quenched PCL/TA blends

were measured by a TA Instruments differential scanning calorimetry (DSC) Q100 with a Thermal Analyst 2000 at 20°C/min. In the case of T_g study, all the samples were first annealed at 100°C for 3 min to erase any thermal history and subsequently quenched to -80°C at 60°C/min. In the case of isothermal melt crystallization kinetics study, neat PCL and an 80/20 blend are only studied because PCL does not crystallize or crystallize too slowly when the TA content is above 20 wt % in the PCL/TA blends. The samples were heated to 100°C first, held for 3 min to erase any thermal history and then cooled to various crystallization temperatures ranging from 28 to 46°C. The exothermal curves of heat flow as a function of temperature were recorded and analyzed.

A polarized optical microscope (Olympus BX51) equipped with a first order retardation plate and a temperature controller (Linkam THMS 600) was used to investigate the spherulitic morphology and growth rates of neat PCL and the PCL/TA blend. The samples were first melted at 100°C for 3 min to erase any thermal history and then quenched to the desired crystallization temperature at 60°C/min.

Wide angle X-ray diffraction experiments were performed on a Rigaku D/Max 2500 VB2+/PC X-ray Diffractometer at 40 kV and 200 mA. The samples for the WAXD experiments were prepared as follows. The samples were first pressed into films with thickness of around 1 mm on a hot stage at 100°C and then transferred into a vacuum oven at 40°C for 3 days.

RESULTS AND DISCUSSION

Miscibility of PCL/TA blends

Figure 1 shows the DSC traces of the quenched samples for neat PCL, neat TA, and their blends. Neat

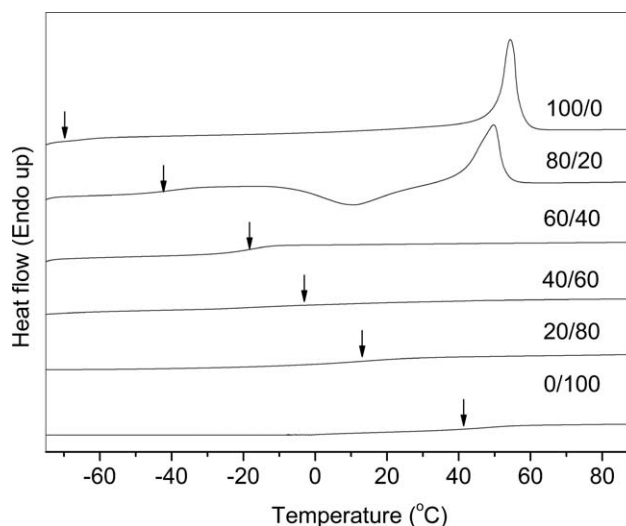


Figure 1 DSC heating curves of neat and blended PCL for the melt-quenched samples at a heating rate of 20°C/min.

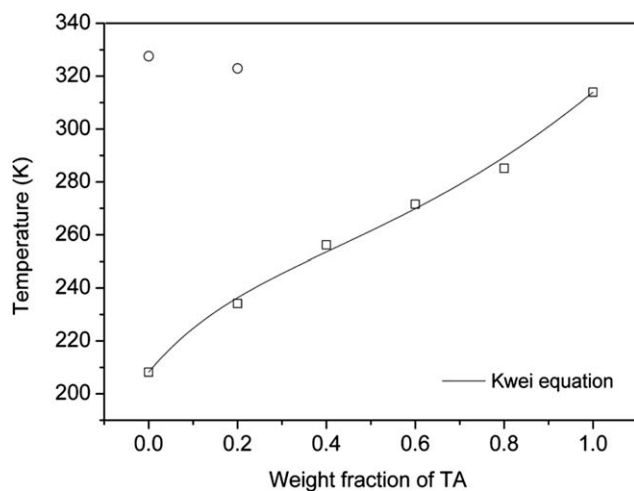


Figure 2 Variation of T_g and T_m of PCL/TA blends as a function of the weight fraction of TA. (The solid line is based on the Kwei equation).

PCL is a semicrystalline polymer with a T_g of about -65°C and a T_m of about 54°C , while neat TA is an amorphous polymer with a T_g of about 42°C . All the PCL/TA blends exhibit a single composition dependent T_g between those of the two individual polymers, and the values of T_g increase with the TA content in the blends, suggesting that PCL is miscible with TA over the entire composition range. T_m of PCL also shifts to lower temperature range upon the addition of TA in the blends. With the amorphous TA content above 20 wt % in the blends, T_m of PCL can not be detected.

Figure 2 summarizes the composition dependence of T_g for the PCL/TA blends. Moreover, the composition dependent T_m of PCL is also shown in Figure 2. It is clear from Figure 2 that PCL shows good miscibility with TA as evidenced by the composition dependence of T_g of the blends and the depression of T_m of PCL.

The Kwei equation is applied in this work to fit the variation of T_g as a function of composition. The Kwei equation is as follows:

$$T_g = \frac{W_1 T_{g1} + kW_2 T_{g2}}{W_1 + kW_2} + qW_1 W_2 \quad (1)$$

where W_1 and W_2 are the weight fraction of two pure components, T_{g1} and T_{g2} are the respective T_g of the neat component, q is a parameter corresponding to the strength of hydrogen bonding in the blends, reflecting a balance between the breaking of the self-association and the forming of the inter-association hydrogen bonding, and k is a fitting constant.¹⁷ As shown in Figure 2, the Kwei equation fits T_g of the PCL/TA blends very well with a q of -100.8 and a k of 2.88 .

The depression of melting point of crystalline polymer in the crystalline/amorphous polymer blends

provides important information of its miscibility. However, melting point of a crystalline polymer is affected not only by the thermodynamic factors but also by the morphological factors such as crystalline lamellar thickness and perfection. Therefore, equilibrium melting point (T_m^o) is introduced to separate the morphological effect from the thermodynamic effect in discussing the melting point depression as described by the Nishi–Wang equation.¹⁸ T_m^o can be derived from the Hoffmann–Weeks equation:

$$T_m = \eta T_c + (1 - \eta) T_m^o \quad (2)$$

where T_m is apparent melting point, T_c is crystallization temperature, and η may be regarded as a measure of the stability.¹⁹ Figure 3(a) shows the melting behavior of an 80/20 blend crystallized isothermally at various T_c s. It is clear from Figure 3(a) that T_m increases with increasing T_c . Neat PCL shows the similar melting behavior. For brevity, the results are

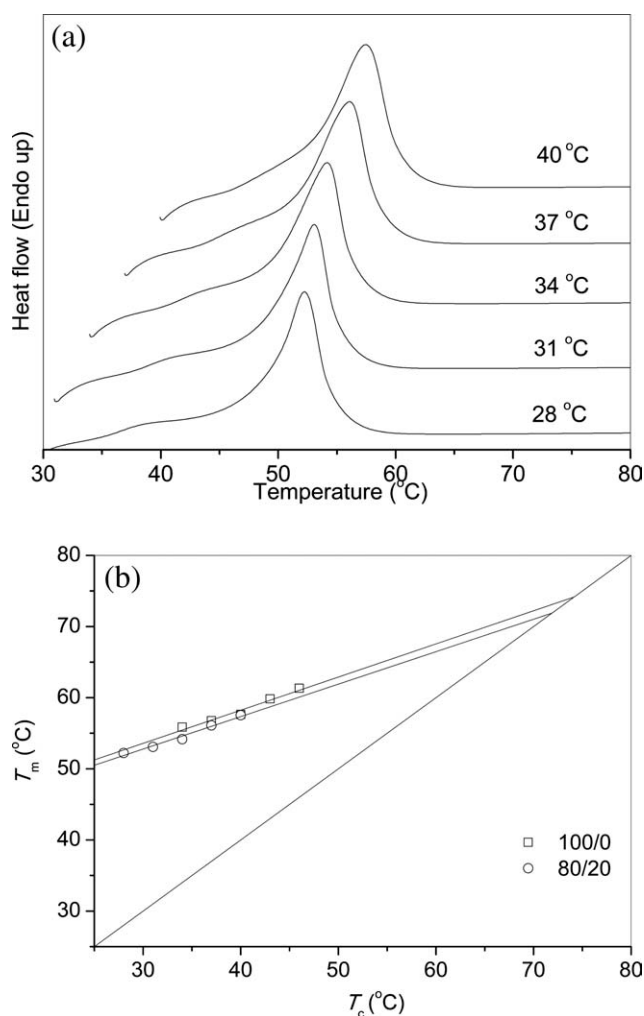


Figure 3 (a) Melting behavior of 80/20 crystallized isothermally at various T_c s from the melt and (b) Hoffman–Weeks plots of neat and blended PCL for the estimation of equilibrium melting points.

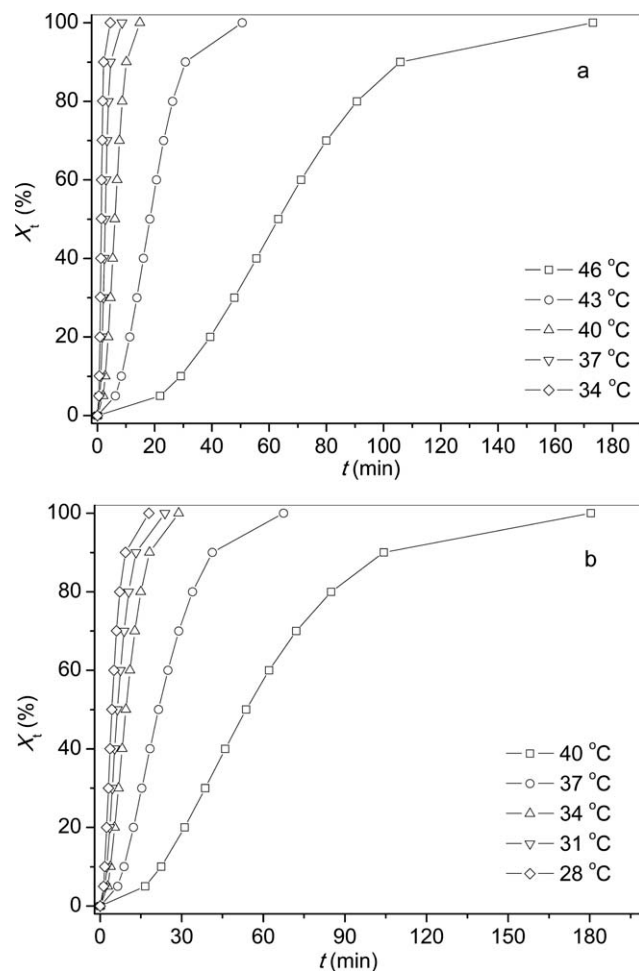


Figure 4 Development of relative crystallinity with crystallization time for (a) 100/0 and (b) 80/20.

not shown here. Figure 3(b) shows the Hoffman-Weeks plots for neat and blended PCL. From Figure 3, T_m^o s is determined to be 74.2 and 71.9°C for neat PCL and the 80/20 blend, respectively. It is clear that T_m^o of PCL decreases with the addition of TA. The depression of T_m^o indicates again that PCL and TA are miscible polymer blends. In addition, the η values are determined to be around 0.46 for both neat PCL and 80/20, indicating that the presence of TA shows little effect on the stability of crystals.

Crystallization behavior of neat PCL and the PCL/TA blend

Isothermal melt crystallization kinetics of neat PCL and the 80/20 PCL/TA blend was further investigated with DSC. Figure 4 shows the variation of relative crystallinity with crystallization time for neat and blended PCL. It can be seen that the crystallization isotherms display the characteristic sigmoidal shape; moreover, the crystallization time prolongs with increasing crystallization temperature for both neat and blended PCL.

The Avrami equation is usually used to analyze the isothermal crystallization kinetics of crystalline polymers, which describes the development of relative degree of crystallinity (X_t) with crystallization time (t) as

$$1 - X_t = \exp(-kt^n) \quad (3)$$

where k is the crystallization rate constant depending on nucleation and growth rate, and n is the Avrami exponent depending on the nature of nucleation and growth geometry of the crystals.²⁰⁻²²

Figure 5 shows the Avrami plots of neat and blended PCL. It can be seen that a series of straight lines are obtained, indicating that the Avrami method can describe the development of the relative degree of crystallinity as a function of crystallization time very well. Accordingly, the Avrami parameters n and k were obtained from the slopes and intercepts, respectively. The values of n and k for neat and blended PCL are summarized in Table I for comparison. The values of n are between 2.3 and 2.5 for neat PCL, while those for the 80/20 blend are around 2.0, suggesting that the crystallization of PCL may correspond to three-dimensional truncated

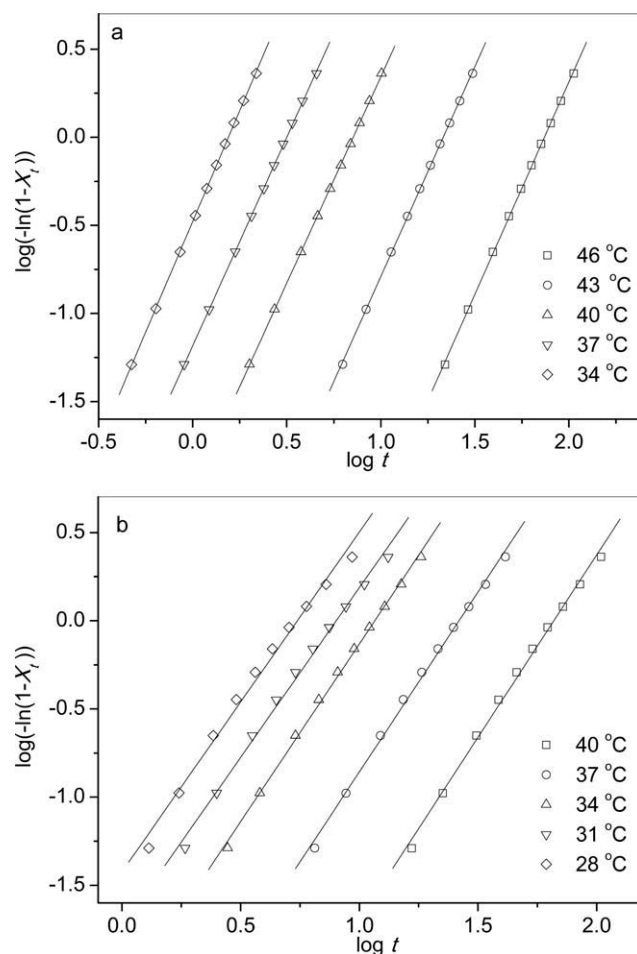


Figure 5 Avrami plots of (a) 100/0 and (b) 80/20.

TABLE I
The Crystallization Kinetics Parameters of Neat and Blended PCL Crystallized at Different Temperatures

Samples	T_c (°C)	n	k (min ⁻ⁿ)	$t_{0.5}$ (min)
100/0	34	2.5	3.3×10^{-1}	1.3
	37	2.4	6.6×10^{-2}	2.7
	40	2.3	1.0×10^{-2}	6.3
	43	2.4	6.6×10^{-4}	18.1
	46	2.4	3.1×10^{-5}	64.9
80/20	28	1.9	3.8×10^{-2}	4.6
	31	1.9	1.8×10^{-2}	6.8
	34	2.0	7.2×10^{-3}	9.8
	37	2.0	1.3×10^{-3}	23.5
	40	2.1	1.7×10^{-4}	52.1

spherulitic growth with a thermal nucleation.²³ It is clear that the crystallization mechanism of PCL remains unchanged despite crystallization temperature and the addition of TA in the blend.

The crystallization half-time ($t_{0.5}$), defined as the time required to half completion of the final crystallinity, can be obtained by the eq. (4). The overall crystallization rate can thus be simply represented by $1/t_{0.5}$.

$$t_{0.5} = \left(\frac{\ln 2}{k} \right)^{1/n} \quad (4)$$

On the basis of the values of n and k , the values of $t_{0.5}$ and $1/t_{0.5}$ were calculated. Table I summarizes the $t_{0.5}$ values for both neat and blended PCL, too. It is obvious that $t_{0.5}$ increases with increasing T_c for both neat and blended PCL. Moreover, it is also found that $t_{0.5}$ is smaller in neat PCL than in the blend at a given T_c , indicating that the crystallization rate of PCL becomes slower in the presence of TA.

To show the effects of crystallization temperature and the addition of TA on the overall crystallization rate of PCL clearly, Figure 6 summarizes the temper-

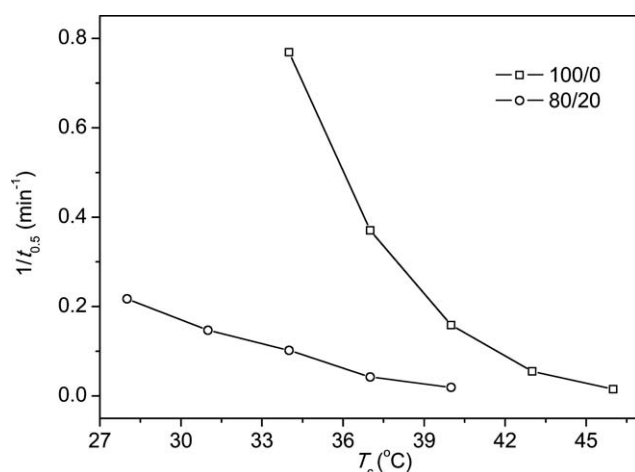


Figure 6 Crystallization temperature dependence of $1/t_{0.5}$ for neat and blended PCL.

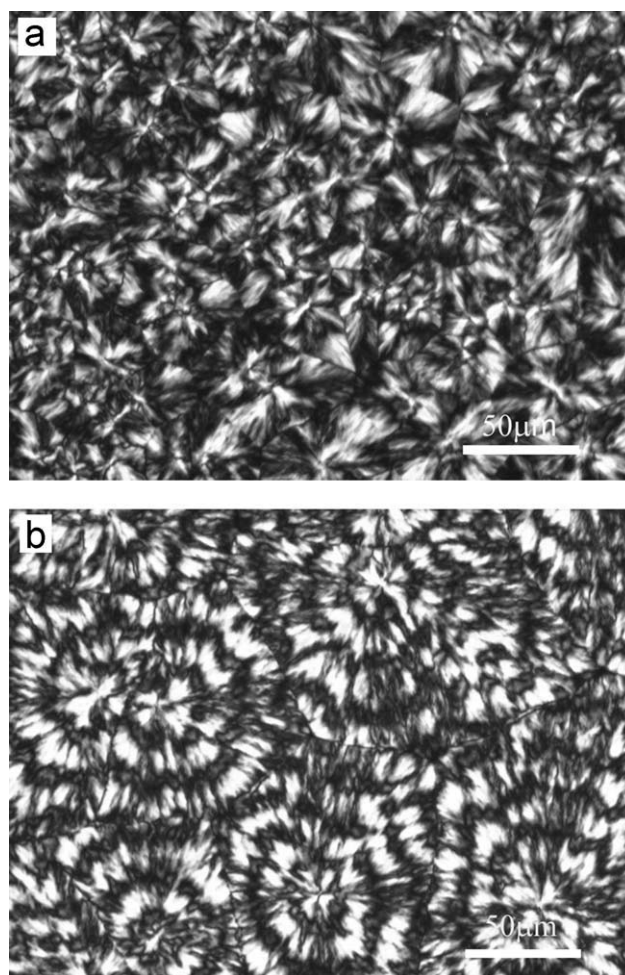


Figure 7 POM images of the spherulitic morphology of (a) 100/0 and (b) 80/20 crystallized at 40°C.

ature dependence of $1/t_{0.5}$ for neat and blended PCL. From Figure 6, the overall isothermal melt crystallization rates of PCL decrease with increasing T_c for both neat and blended PCL because of the difficulty in nucleation at higher T_c . On the other hand, the overall isothermal melt crystallization rates of PCL is reduced in the PCL/TA blend relative to neat PCL at a given T_c , indicating that blending with amorphous TA retards the crystallization of PCL in the blends. The reduction of the overall isothermal melt crystallization rate of PCL in the blend may be attributed to the following factors. First, the addition of high T_g component TA increases T_g of the PCL/TA blend, resulting in the decrease of the mobility of PCL relative to neat PCL. Second, T_m^0 of blended PCL was lower than that of neat PCL, which drops the thermodynamic driving force required for the crystallization of PCL. Third, the addition of TA may play a role of a diluent to the crystallization of PCL in the miscible blend.^{24–26}

The spherulitic morphology and growth rates of neat and blended PCL were studied in this work in a wide crystallization temperature range of 31–43°C. Figure 7

shows the spherulitic morphology of neat and blended PCL crystallized at 40°C as an example. The PCL/TA blend shows banded spherulites morphology, while neat PCL shows normal spherulites morphology, indicating that the addition of TA has a significant influence on the spherulitic morphology of PCL in the PCL/TA blend. Banded spherulites are believed to arise from the twisting of lamellae.^{27–30} However, it is still an open question about the origin of lamellar twisting. The spherulitic growth rates of neat and blended PCL were measured by following the development of radius with time. Both neat and blended PCL spherulites showed a linear growth till contacting other spherulites during the crystallization process. Figure 8 shows the temperature dependence of the spherulitic growth rates of neat and blended PCL. The spherulitic growth rates of PCL decrease with increasing T_c for both neat and blended PCL in the investigated crystallization temperature range. In addition, the spherulitic growth rate is reduced in the PCL/TA blend relative to neat PCL at a given T_c . The variation of spherulitic growth rates with T_c and the addition of PCL is similar to that of the overall isothermal melt crystallization rates reported in the aforementioned section. The reduction of spherulitic growth rate of PCL in the PCL/TA blend may also be attributed to the decreased mobility, depression of equilibrium melting point, and the diluent role of TA.

It is also of interest to study the effect of TA on the crystal structure of PCL. Figure 9 shows the WAXD patterns of neat and blended PCL crystallized at 40°C for 3 days. It can be seen from Figure 9 that neat PCL presents three strong reflections at 21.2°, 21.8°, and 23.4°, corresponding to the (110), (111), and (200) planes, respectively.¹ In the case of the PCL/TA blend, the similar diffraction peaks shift to higher diffraction angle slightly relative to neat PCL, indicative of the small variation of the cell parameters. In brief, blending with a small amount of

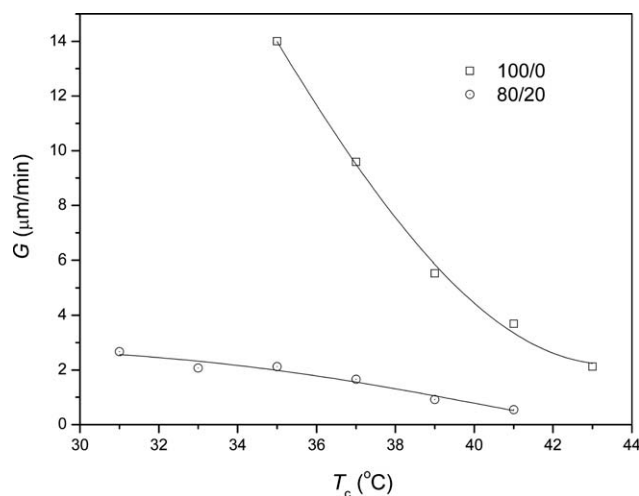


Figure 8 Temperature dependence of the spherulitic growth rates of neat and blended PCL.

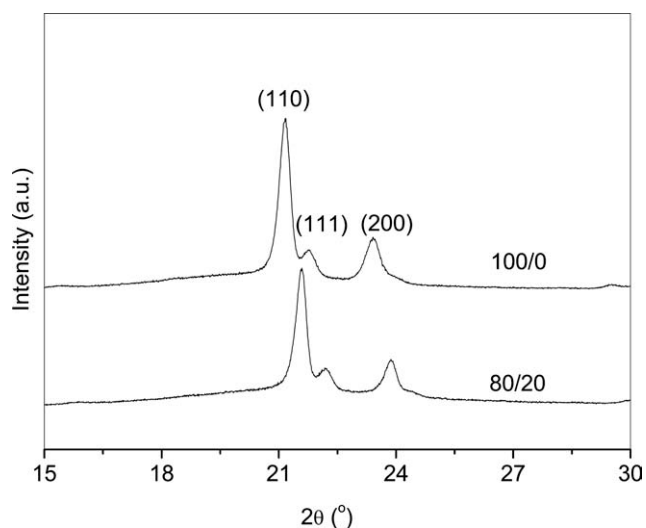


Figure 9 WAXD patterns of neat and blended PCL.

TA does not modify the crystal structure of PCL in the PCL/TA blend.

CONCLUSIONS

In this study, the biodegradable PCL/TA blends were prepared via a solution and casting method. PCL is miscible with TA as evidenced by the single composition dependent glass transition temperature over the whole blend compositions; moreover, the miscibility between PCL and TA is further supported by the depression of equilibrium melting point of PCL in the PCL/TA blend. Isothermal melt crystallization kinetics, spherulitic morphology and growth rates and crystal structure of an 80/20 PCL/TA blend were investigated in detail with various techniques and compared with those of neat PCL. Both the overall isothermal melt crystallization rates and the spherulitic growth rates of PCL decrease with increasing crystallization temperature for both neat PCL and the PCL/TA blend; moreover, they are both reduced in the PCL/TA blend relative to neat PCL at a given crystallization temperature. However, the crystallization mechanism and crystal structure of PCL do not change in the blend.

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