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NON-ISOTHERMAL CRYSTALLIZATION OF POLY(L-LACTIDE) (PLLA) UNDER QUIESCENT AND STEADY SHEAR CONDITIONS*

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Abstract The non-isothermal crystallization of poly(L-lactide) (PLLA) under quiescent and steady shear flow conditions was *in situ* investigated by using polarizing optical microscopy (POM) with a hot shear stage and wide-angle X-ray diffraction (WAXD). The shear rate and the cooling rate both play a significant role in the final crystalline morphology and crystallinity. Under quiescent conditions, the morphology assumes different sized spherulites, and its crystallinity dramatically reduces with increasing the cooling rate. On the other hand, the shear flow increases the onset crystallization temperature, and enhances the final crystallinity. When the shear rate is above 5 s^{-1}, cylindrite-like crystals are observed, furthermore, their content depends on the cooling rate.

Keywords: Poly(L-lactide) (PLLA); Non-isothermal crystallization; Shear; Cylindrite-like crystal.

INTRODUCTION

The investigation on poly(lactic acid) (PLA) is attracting a great interest among the researchers because of its bio-degradation, bio-compatibility and good mechanical properties[1–7]. Generally, the term poly(lactic acid) (PLA) includes poly(L-lactide) (PLLA), poly(D-lactide) (PDLA), poly(D,L-lactide) (PDLLA) and poly(*meso*-lactide). PLLA and PDLA are crystalline polymers, showing a melting temperature (T_m) and a glass transition temperature (T_g) around 180°C and 67°C, respectively, while the PDLLA and poly(*meso*-lactide) are amorphous polymers, showing a T_g in the range of 50–60°C, below which, they present hard and rigid. Compared to amorphous PLA, crystalline PLA has higher elastic modulus and strength, but lower plastic deformability. The crystalline morphology not only affects the mechanical properties of PLA, but its degradable rate and permeability[8], *etc*. The perfect crystallization in the crystalline area accounting for the compact arrangement of molecular chains improves mechanical properties[9], delays degradation rate, meanwhile, enhances the film's permeability, heat resistance, thermal stability *etc*. However, the as-processed PLLA products often exhibit a quasi-amorphous phase due to PLLA's slow crystallization rate, resulting in poor physical properties, which consequently limits its application. On the other hand, the products with high crystallinity are hard and rigid, which are not good for secondary processing, meanwhile, they also need long degradable time. Therefore, the understanding of crystallization of PLA is beneficial to controlling its microstructure and guidance of processing and application.

To date, the crystallization behavior of PLA has been extensively investigated. Generally, PLA assumes a spherulitic form from melt crystallization under quiescent condition[9, 10]. Single crystals and twinned crystals can form in solution crystallization[11] while the formation of fibrillar crystals is relevant to flow fields which

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exist in most processing operations (*e.g.* fiber spinning)[12–16]. However, these works are mostly carried out under isothermal crystallization condition, which can avoid the influences of cooling rate and temperature gradient in the samples, leading to simplifying theoretic analysis. In factual polymer processing, such as injection molding and fiber spinning, the molten polymer chains are subjected to non-isothermal gradient flow, in which, the cooling rate and flow usually affect products' structure and morphology, and thus their final performances[17–19]. Flow can induce formation of oriented nuclei, thus accelerating the crystallization kinetics and generating unique crystalline morphology like shish-kebab[20–23]. Therefore, the subject on non-isothermal crystallization behavior of PLA under shear flow has important practical significance for guiding its forming and processing[24]. PLLA is sensitive to processing, altering properties critical to its degradation rate. Weir *et al.* found that upon processing, the crystallinity of the PLLA fell from 61% for the PLLA pellets to 12% and 20% for the compressed and extruded components, respectively. After annealing, crystallinity increased to 43% for the compression-moulded material and 40% for the extruded material. Young's modulus generally increased with increasing crystallinity, and extension at break and tensile strength decreased[25, 26].

The aim of the present work is to investigate the non-isothermal crystallization of poly(L-lactide) (PLLA) under quiescent condition and steady shear flow. The influences of cooling rate and shear rate on the morphology, structure and crystallinity are determined using an polarizing optical microscope with a hot shear stage and ex-situ wide-angle X-ray diffraction (WAXD).

EXPERIMENTAL

Materials

The PLLA (Grade 5051X) used in this work was an injection grade, granular material manufactured by Cargill Dow Co. (Japan). The number-average molecular weight (M_n) was 6.24×10^4 and the weight-average molecular weight (M_w) was 9.32×10^4. The film of 0.1–0.5 mm thickness used for crystallization measurements was prepared by the following procedures: the solution of PLLA with methylene chloride as solvent was cast onto a glass plate placed horizontally, and then the solvent was allowed to evaporate at room temperature for 1 day. The obtained films were dried in vacuum oven at 50°C overnight.

Non-isothermal Crystallization

A Linkam CSS-450 high temperature optical shear stage equipped with video camera coupled to an optical polarizing microscope, Olympus BX51 model, was employed for the observation of the crystallization process under a shear field. The Linkam shear stage has two quartz optical windows, the top window and the bottom window. The top window is fixed while the bottom one can rotate to produce a shear field. The sample was held in the gap between the two windows. The mechanical design of the hot stage provided precise control over various parameters of the shear experiment, such as temperature, cooling/heating rate, gap width, shear strain, rate and duration as well as the shear mode such as steady, step and oscillatory. In all our experiments, the steady mode was selected. The top and bottom flat planes have a constant gap, in which there is a radial distribution of shear rate. Nevertheless, the quartz optical windows are fixed, so the position for observation always has a constant shear rate, which is the reported value.

The sample was placed between the two windows, and the gap width was set to the sample thickness (*ca.* 100 μm). In isothermal crystallization, all the samples were subjected to the following protocol: (1) heating at a rate of 30 K/min from room temperature to 200°C. (2) holding the temperature at 200°C for 2 min to eliminate thermal history. (3) cooling down to 150°C at a rate of 30 K/min. (4) as soon as reaching 150°C, the shear was immediately applied for 60 s. (5) after shear cessation, cooling down to 60°C at a desired cooling rate (0.5, 1, 2, 3, 4, 5 K/min) for observation under the polarizing optical microscope. In order to avoid degradation, in each experiment a new sample was used.

Before describing the POM images, it has to be noted that the number of activated nuclei depends strongly on the zone for observation in the hot stage; however, a picture involving the whole zone is unavailable. Therefore, the results reported are obtained from several experiments performed at the same conditions.

WAXD Measurements

Wide angle X-ray diffraction (WAXD) data were obtained by using an X'pert PRO X-ray diffractometer with the Cu Kα radiation at room temperature. The operating condition of the X-ray source was set at a voltage of 40 kV. The relative crystallinity $X_{\mathrm{c}}^{\mathrm{WAXD}}$ was calculated using the Eq. (1)[27]:

$$X_{\mathrm{c}}^{\mathrm{WAXD}} = \frac{I_{\mathrm{c}}}{I_{\mathrm{c}} + I_{\mathrm{a}}} \times 100\% \tag{1}$$

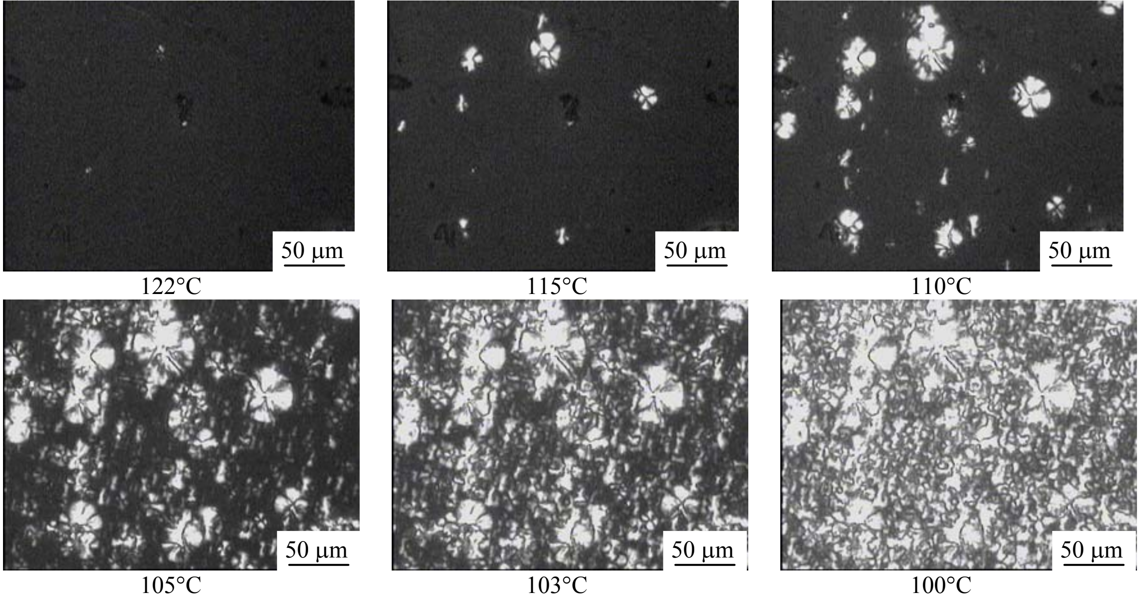
I_{c} — diffraction intensity of the crystalline peak; I_{a} — diffraction intensity of the amorphous peak.

RESULTS AND DISCUSSION

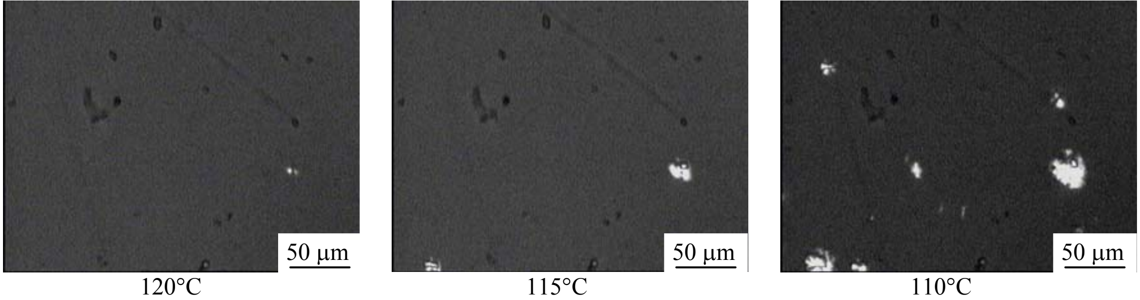
Non-isothermal Crystallization of PLLA under Quiescent Condition

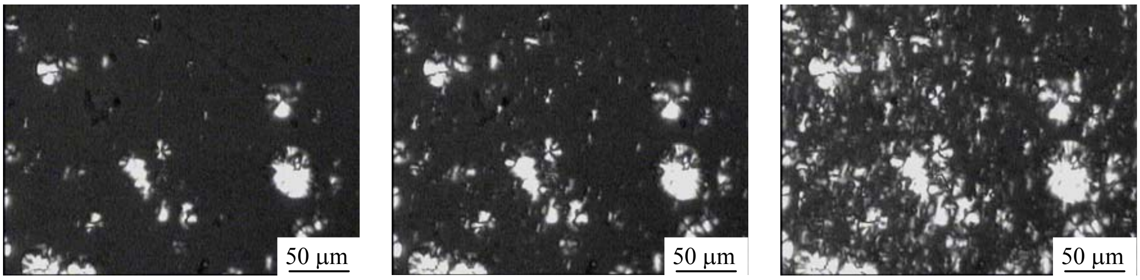
Figure 1 shows the POM images of PLLA non-isothermally crystallized at different cooling rates under quiescent condition. Within the cooling rate range examined, the crystalline morphology is typical spherulites with various sizes. The whole crystallization process upon cooling can be divided into a nucleation controlled stage (higher temperature) and a crystal growth controlled stage (lower temperature). The nuclei formed at higher temperatures can grow fast into larger spherulites, while a large amount of nuclei formed at lower temperatures grow slowly and form small spherulites. The cooling rate, *i.e.*, the supercooling, has a great influence on the size of spherulites, nuclei density, onset crystallization temperature (T_{onset}) and crystallinity. With increasing cooling rate, it seems that the size and nuclei density of crystals reduce.

(a) 0.5 K/min



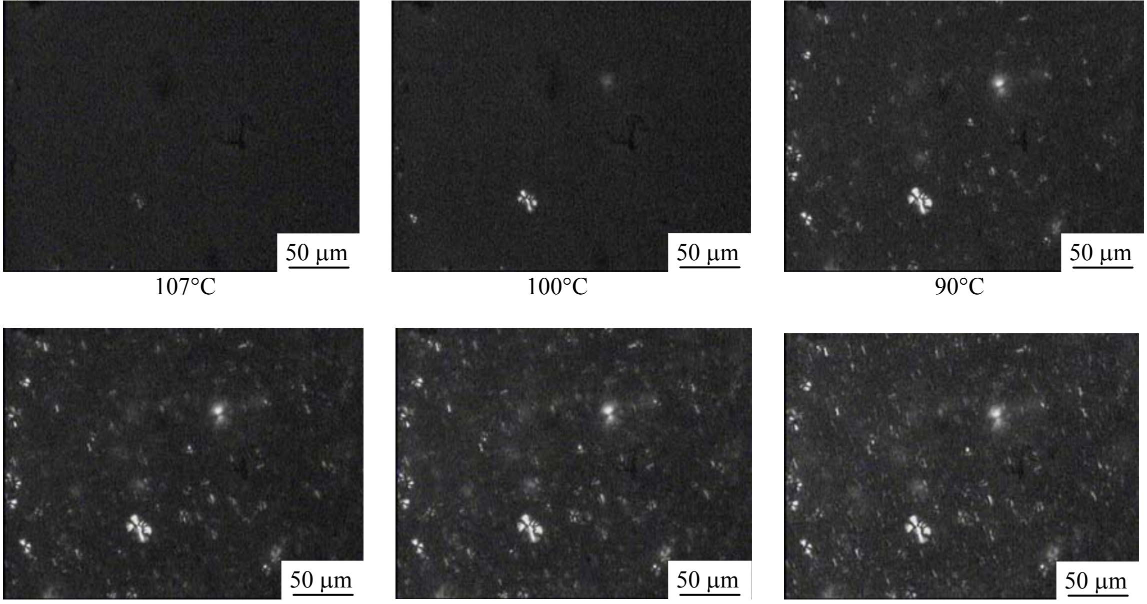
(b) 1 K/min





105°C 103°C 100°C

(c) 2 K/min



107°C 100°C 90°C

85°C 80°C 70°C

Fig. 1 The polarized optical microscopy pictures (POM) of PLLA crystallized at different cooling rates under quiescent condition

The T_{onset} at different cooling rates is shown in Table 1. One can see that the T_{onset} decreases with increasing the cooling rate. Specifically, it declines from 122°C at 0.5 K/min to 107°C at 2 K/min. This result suggests that the rotation and folding of polymer chains are relaxation processes, which need a period of time for molecular chains or segments to arrange into the lattice. At low cooling rates, the T_{onset} is high as a result of the long time for polymer chains to stay at relatively high temperatures, as well as good movement of chains to fold into lattice. High cooling rate makes the temperature down quickly, so there is not enough time for polymer chains to form nuclei; when reduced to a certain cooling degree, there is large enough supercooling to drive the formation of nuclei. Nevertheless, under low temperatures, the growth of crystals declines due to the low movement ability of chains. Therefore, at a rapid cooling rate, nonuniform spherulites with small size and low crystal density are obtained.

Table 1. The values of the onset crystallization temperature of PLLA non-isothermally crystallized at different cooling rates under quiescent condition

Cooling rate (K/min)	0.5	1	2
T_{onset} (°C)	122	120	107

The structure and crystallinity of PLLA crystallized under non-isothermal conditions are examined by X-ray diffraction, as shown in Fig. 2. The diffraction peaks at 2θ = 12.5°, 14.8°, 16.7°, 19.1°, 22.4° ascribed to

(103), (010), (200 or 110), (203), (015) respectively show that the crystal structure under such condition is an α form. The increasing number of diffraction peaks with decreasing cooling rate suggests that low cooling rate favors the generation of perfect structure. The calculated crystallinity from Fig. 2 is presented in Table 2. The crystallinity increases from 0% at 5 K/min to 59.02% at 0.5 K/min, which shows that low cooling rate is in favor of the formation of more perfect structure and higher crystallinity, while the cooling rate is above 5 K/min, PLLA hardly crystallizes.

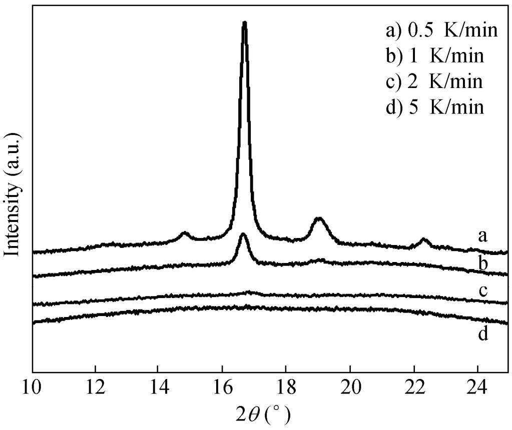


Fig. 2 The WAXD measurements of PLLA non-isothermally crystallized at different cooling rates under quiescent condition

Table 2. The crystallinity of PLLA non-isothermally crystallized at different cooling rates under quiescent condition

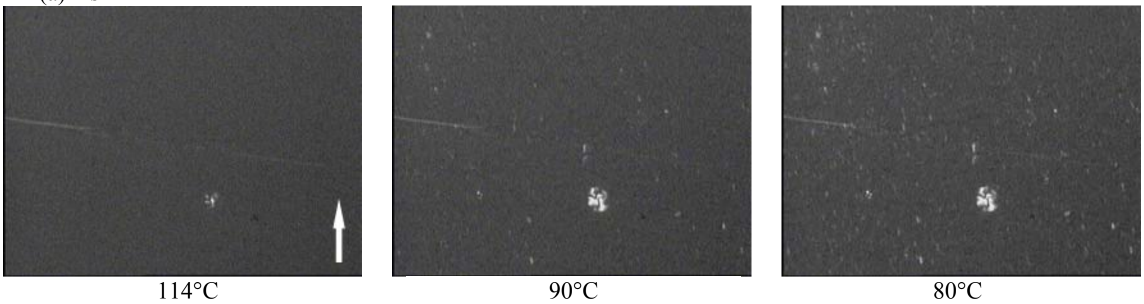
Samples	Crystallinity
0.5 K/min	59.02%
1 K/min	33.51%
2 K/min	9.04%
5 K/min	0%

Non-isothermal Crystallization Behavior of PLLA under Shear Flow

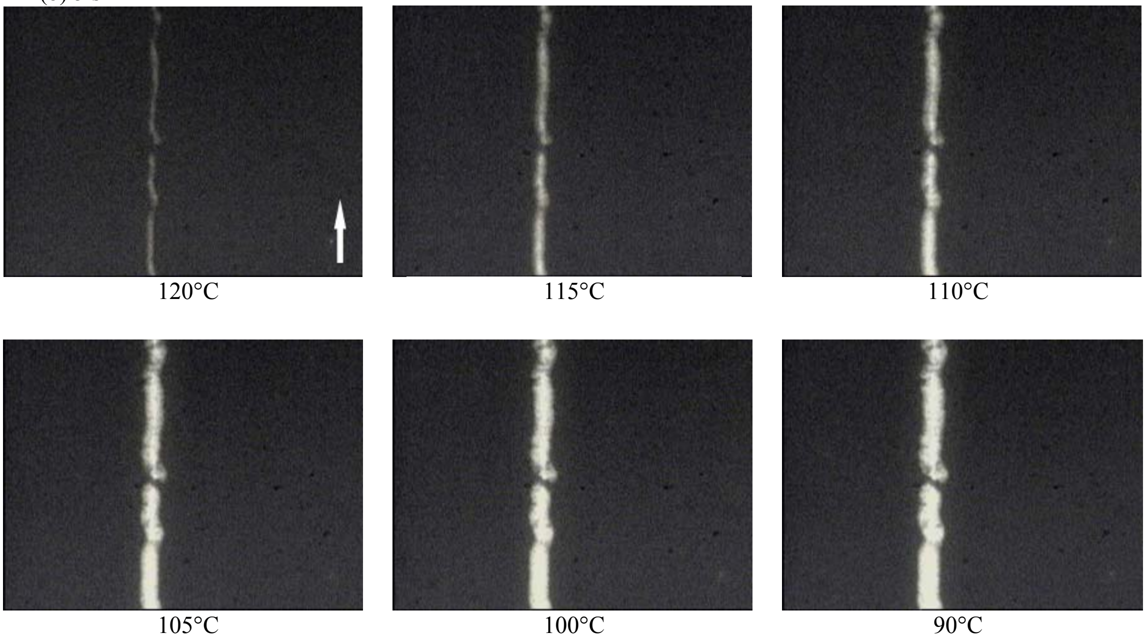
Effect of shear rate

Figure 3 presents the POM images of PLLA non-isothermally crystallized at different shear rates at a cooling rate of 2 K/min. The results show that there is a critical shear rate (5 s^{-1}), above which, the cylindrite-like crystals are generated. Due to the limit of the resolution for POM, one can not certainly identify the microstructre of the cylindrite-like crystals. It seems that the shear flow induced oriented nuclei unevenly grow into deformed spherulites, and then connect in a line along the flow direction. Moreover, their number increases with increasing the shear rate; below which, the crystalline morphology maintains spherulite. The morphology change can be explained by the orientation and relaxation behavior. The high shear rate makes the chains orient along the shear flow to form cylindrite-like crystals, while at low shear rates, the oriented chains have sufficient time to relax, and stable nuclei cannot be formed, therefore, shear has no obvious effect on the nuclei density and crystalline morphology. Generally, flow is responsible for both the orientation of polymer chains, (at shear rates $\dot{\gamma} > 1/\tau_d$, where τ_d is the reptation time) and the stretching of polymer chains (at higher shear rates $\dot{\gamma} > 1/\tau_R > 1/\tau_d$, where τ_R is the longest Rouse time in the melt)[28]. While the first condition could be necessary for the formation of an oriented structure, the second condition ensures strong stretching of molecules into a conformation ideal for crystallization. This, then, suggests that there is a minimum shear rate $\dot{\gamma}_{min} \sim 1/\tau_R$, below which the orientated nuclei cannot be obtained, and therefore, an oriented structure (shish-kebab) is unlikely to be formed in a crystallizing polymer. The T_{onset} at different shear rates is shown in Table 3. It can be seen that the T_{onset} rises rapidly with increasing shear rate (from 104°C at 4 s^{-1} to 133°C at 6 s^{-1}), which is attributed to the decrease of barrier between the melt and crystalline phase caused by the orientation of polymer chains. Thus, the higher the shear rate, the higher the orientation degree of chains, consequently, the higher T_{onset} and the more crystal number.

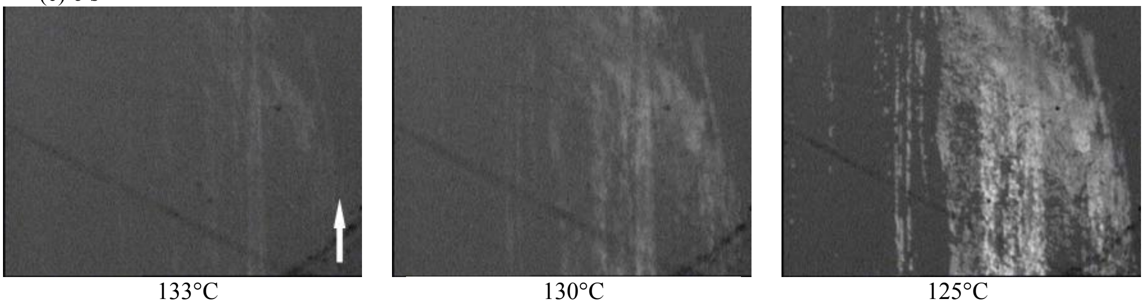
(a) 4 s^{-1}



(b) 5 s^{-1}



(c) 6 s^{-1}



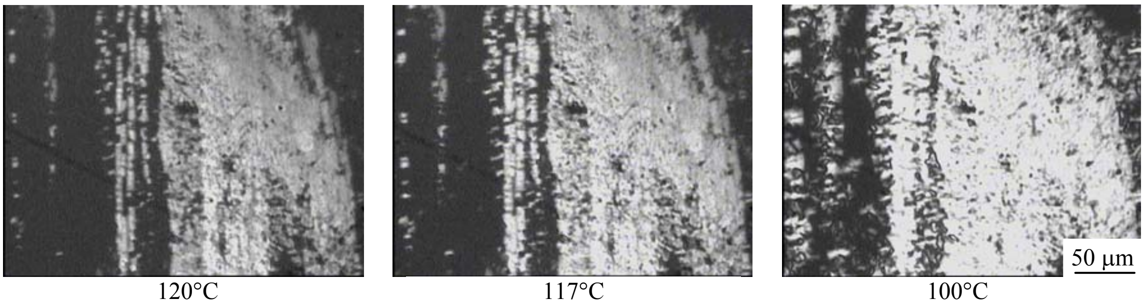


Fig. 3 The non-isothermal crystallization optical pictures of PLLA crystallized at different shear rates for a constant shear duration of 60 s at a cooling rate of 2 K/min
Every image has the same scale, and the arrow in the images shows the flow direction.

Table 3. The values of the onset crystallization temperature of PLLA at different shear rates at 2 K/min

Shear rate (s^{-1})	4	5	6
T_{onset} (°C)	104	120	133

The shear rate affects not only the crystalline morphology, but the perfect degree of crystal structure and the crystallinity, which are shown in Fig. 4, where the peaks at $2\theta = 16.67°$, 19.08° are ascribed to the α form of PLLA. The appearance of 2θ = 19.08° and improvement of peak intensity with the increase of shear rate indicates the more perfect structure and higher crystallinity. The calculated crystalline degrees at different shear rates are shown in Table 4, where the crystalline degree increases slightly with increasing the shear rate when the shear rate is below or above 5 s^{-1}, near such a value, the crystalline degree increases sharply (from 19.99% at 4 s^{-1} to 29.69% at 5 s^{-1}). These results suggest that there is a critical shear rate, below which, the shear only makes a small fraction of chains or segments orient to provide nuclei points, finally the crystallinity increases slightly, while crystalline morphology dose not change; above which, the orientation of chains and segments induces oriented nuclei to form cylindrite-like crystals, and acceleration of crystallization changes slightly resulting in much higher crystallinity than that at low shear rates. The WAXD measurements are consistent with the POM results.

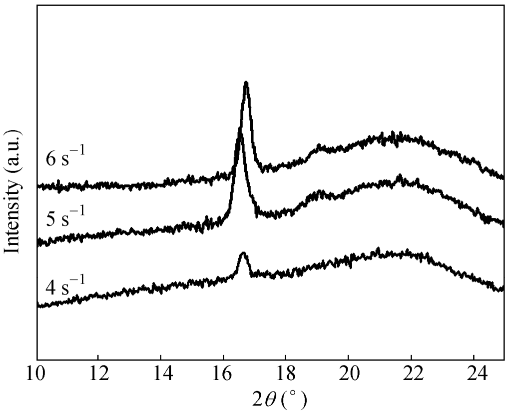


Fig. 4 The WAXD measurements of PLLA non-isothermally crystallized at different shear rates

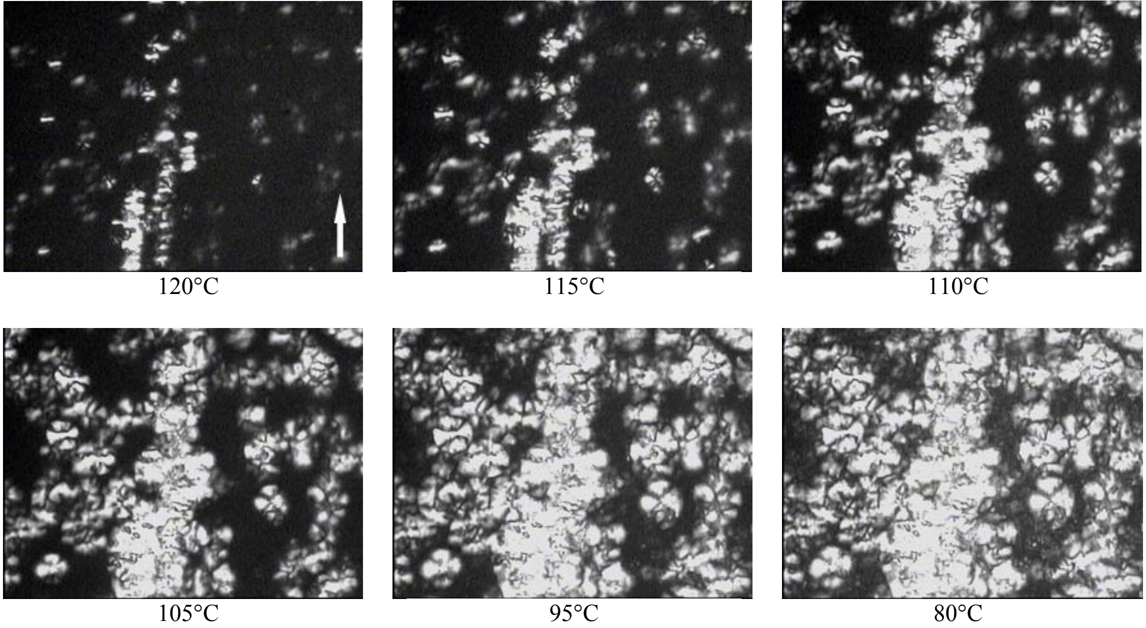
Table 4. The crystallinity of PLLA non-isothermally crystallized at different shear rates at 2 K/min

Shear rate (s^{-1})	4	5	6
Crystallinity (%)	19.99	29.69	31.02

Effect of cooling rate

Figure 5 shows the POM pictures of PLLA non-isothermally crystallized at different cooling rates at 5 s^{-1}. The crystalline morphology can be spherulites or cylindrite-like crystals and depends on the cooling rate. When the cooling rate is 1 K/min, the main crystalline morphology exhibits a large number of spherulites with a few cylindrite-like crystals. With increasing the cooling rate, the sum of cylindrite-like crystals increases, while the spherulite's number decreases, finally, only a few cylindrite-like crystals can be observed. If the cooling rate reaches 5 K/min, no crystals are generated. Generally speaking, the high cooling rate is in favor of maintenance of orientation. However, as we know, it needs enough time for chains or segments to fold into the lattice. Therefore, if the cooling rate is too high, the chains' movement may be frozen before crystallization, consequently, amorphous samples are obtained; if the cooling rate is too low, the oriented chains would relax before crystallization, leading to only spherulite crystals. As shown in Figure 5, when the cooling rate is 1 K/min, the orientation relaxes; between 1 K/min and 5 K/min, the orientation remains, resulting in the formation of cylindrite-like crystals; above 5 K/min, PLLA will not form observable crystals under such condition.

(a) 1 K/min



(b) 3 K/min (c) 4 K/min (d) 5 K/min

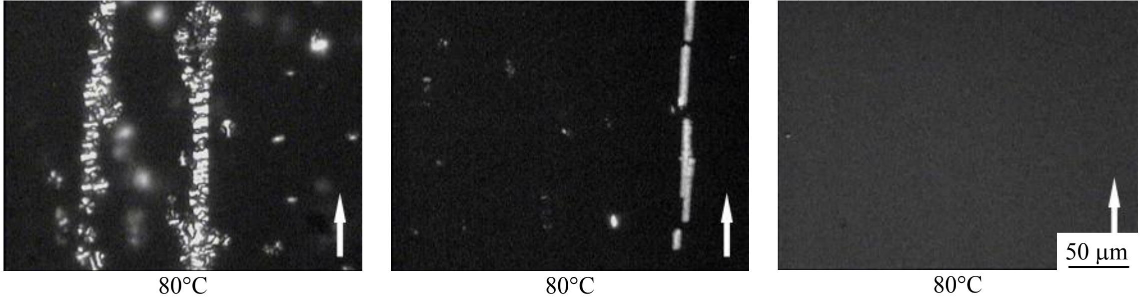


Fig. 5 The non-isothermal crystallization optical pictures of PLLA crystallized at different cooling rates at a constant shear rate of 5 s^{-1} for a shear duration of 60 s
All the images have the same scale, and the arrow in the images shows the flow direction.

Figure 6 presents the one-dimentional WAXD curves of PLLA non-isothermally crystallized at different cooling rates at 5 s^{-1}. The 2θ = 14.8°, 16.67°, 19.08° are ascribed to the α form of PLLA. The calculated crystallinity at different shear rates is shown in Table 5, which shows that the crystalline degree improves dramatically with decreasing the cooling rate (from 0% at 5 K/min to 42.36% at 1 K/min). When the cooling rate is above 5 K/min, PLLA presents amorphous state. Compared with the results under quiescent conditions at the same cooling rate, shear improves the perfectness of crystals and increases the crystallinity.

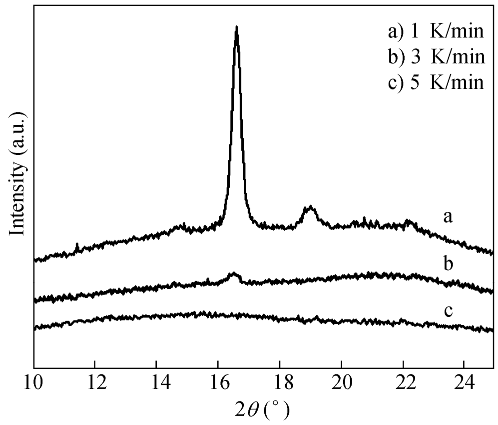


Fig. 6 The WAXD measurements of PLLA non-isothermally crystallized at different cooling rates under a shear rate of 5 s^{-1}

Table 5. The crystallinity of PLLA non-isothermally crystallized at different cooling rates under a shear rate of 5 s^{-1}

Samples	Crystallinity
1 K/min	42.36%
3 K/min	14.54%
5 K/min	0%

CONCLUSIONS

Cooling rate and shear rate have significant influence on the nuclei density, morphology and crystallinity. Under quiescent condition, nuclei density as well as crystallinity increases with decreasing the cooling rate. When the cooling rate is above 2 K/min, the PLLA exhibits amorphous. After application of shear flow, the T_{onset} and crystal density increase owing to the orientation of molecular chains. Above the critical shear rate of *ca.* 5 s^{-1}, the generation of cylindrite-like crystals and their contents, corresponding to crystallinity, are determined by cooling rate and shear rate. The size and number of cylindrite-like crystals decrease with cooling rate resulting from the relaxation of oriented molecular chains; whereas the final crystallinity increases with decreasing cooling rate since the molecular chains have enough time to arrange into crystal lattice. Although high cooling rate is good for maintenance of orientation, it will lead to low crystallinity, even when the cooling rate is above 5 K/min.

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