Enhancement of Stain-Induced Crystallization in Polylactide via Thermal Preannealing

Bing Na, Jie Zhu, Ruihua Lv, Peng Zhang, Qingxian Liu

Fundamental Science on Radioactive Geology and Exploration Technology Laboratory, School of Biology, Chemistry and Materials Science, East China Institute of Technology, Nanchang, 330013, People's Republic of China
Correspondence to: B. Na (E‑mail: bna@ecit.edu.cn and bingnash@163.com)

ABSTRACT: Stretching of amorphous polylactide above glass transition temperature can lead to strain-induced crystallization, which is mainly determined by stretching rate and temperature. This study demonstrates that thermal annealing prior to stretching is alternative to enhance strain-induced crystallization of a given polylactide at the identical stretching conditions. The local order generated during thermal annealing acts as physical crosslinks to effectively alleviate molecular relaxation and thus facilitates the advent of strain-induced crystallization. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2013**, *000*, 39993.

INTRODUCTION

Much attention is focused on polylactide in recent years since it is a biodegradable thermoplastic polyester with superior properties.[1–3] The crystallization rate of polylactide is rather low and under normal processing conditions little crystallization is induced.[4–6] This largely deteriorates the strength and thermal resistance of polylactide. A facile route to resolve this problem is to stretch polylactide above glass transition temperature where strain-induced crystallization occurs.[7–12] The alignment of molecular chains can accelerate cold crystallization of polylactide and results in highly oriented texture, responsible for the improved mechanical strength and thermal resistance.

So far, stretching temperature and rate are two main factors concerned as regarding strain-induced crystallization of a given polylactide.[7,9] At low stretching temperatures or high stretching rates, molecular chains can be well aligned but crystallization is inhibited due to limited molecular mobility. On the contrary, significant chain retraction at high stretching temperatures or low stretching rates does not favor chain alignment and thus retards strain-induced crystallization.

In this study, it is indicated that formation of local order (not crystals), achieved by thermal annealing of amorphous poly(L-lactide) (PLLA) above glass transition temperature, is helpful for molecular orientation and thus strain-induced crystallization at the identical stretching conditions. It suggests that thermal annealing prior to stretching, in addition to stretching temperature and rate, is another factor regulating strain-induced crystallization of polylactide.

EXPERIMENTAL

Material and Sample Preparation

PLLA, purchased from Natureworks, had a number-average and weight-average molecular weight of 56 and 74 kg/mol, respectively. Films with thickness of about 100 μm were melt-compressed in a hot press at 190°C, followed by quenching into ice water. The films were first thermally annealed at 82°C for 0, 25, and 55 min, respectively, and then cut into rectangle stripes (10 mm in width and 20 mm in gauge length) for stretching. Of note, at this annealing temperature it was easy to tailor the extent of cold crystallization because of moderate crystallization rate. Stretching of the strips was carried out by a mini-stretcher coupled with a temperature-regulated oven at 82°C. After pre-conditioning the strips for 5 min they were stretched at a rate of 50 mm/min to various true strains (determined from the separation of preprinted ink marks), followed by rapid cooling in air together with the mini-stretcher. It is noted that the total annealing time prior to stretching at 82°C was 5, 30, and 60 min, respectively, which was also adopted by the samples without stretching for direct characterizations.

Characterizations

Polarized Fourier transform infrared spectroscopy (FTIR) measurements were conducted by a Thermo Nicolet IR microscope coupled with a FTIR spectrometer at room temperature. Polarized IR spectra, parallel and perpendicular to stretching direction, respectively, were collected with a resolution of 4 cm^{-1} and a total of 32 scans were added. In addition, an attenuated total reflection accessory was coupled with the FTIR spectrometer to obtain ATR-FTIR spectra. Differential scanning
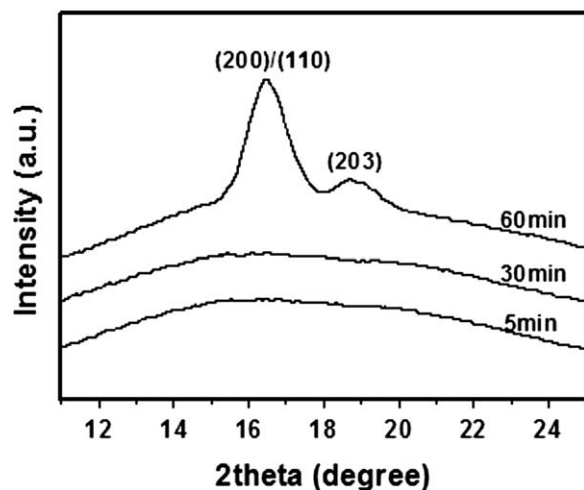
Figure 1. XRD profiles of PLLA after being annealed at 82°C for the indicated period.

calorimetry (DSC) measurements were recorded at a heating rate of 10 °C/min in a nitrogen atmosphere using a Perkin–Elmer Pyris-1 DSC instrument. Room temperature X-ray diffraction patterns were obtained from an in-house setup with a 30 W micro X-ray source (Incoatec, GmbH) that provides highly parallel beam of monochromatic Cu Kα radiation ($\lambda = 0.154$ nm). The diffraction intensity was collected by a multi-wire proportional chamber detector (Bruker Hi-star) with a resolution of 1024 × 1024 pixels. One-dimensional X-ray diffraction (XRD) profiles were integrated over the patterns by subtracting the background diffractions.

RESULTS AND DISCUSSION

Thermal annealing of amorphous films at 82°C is possible to induce cold crystallization of PLLA because enough molecular mobility is gained above glass transition temperature (~60°C).[13] It is the fact observed for samples annealed for 60 min, as shown by the XRD profiles in Figure 1. The generated crystals are manifested by the characteristic diffraction peaks at 16.4° and 18.7° that is contributed by (200)/(110) and (203) of α′ crystals, respectively.[14] In contrast, no crystallization occurs in the samples even annealed for 30 min. It suggests that this annealing time is located in the induction period of cold crystallization of PLLA at 82°C. As argued in the previous studies,[15,16] in the induction period molecular chains could rearrange themselves toward ordering state through intra- and intermolecular interactions. In such a sense, local order (not crystals) could be generated especially in the samples annealed for 30 min.

This speculation is verified by the DSC and ATR-FTIR results in Figure 2. The DSC heating trace in Figure 2(a) exhibits an exothermic peak at about 116°C in the as-quenched samples (without annealing), which arises from the cold crystallization of PLLA. Upon thermal annealing cold crystallization shifts to lower temperatures and becomes significant with increasing annealing periods. For instance, cold crystallization temperature is about 107°C for samples annealed for 30 min. It strongly implies that local order was produced during thermal annealing and acts as nuclei to accelerate the cold crystallization. Similarly,
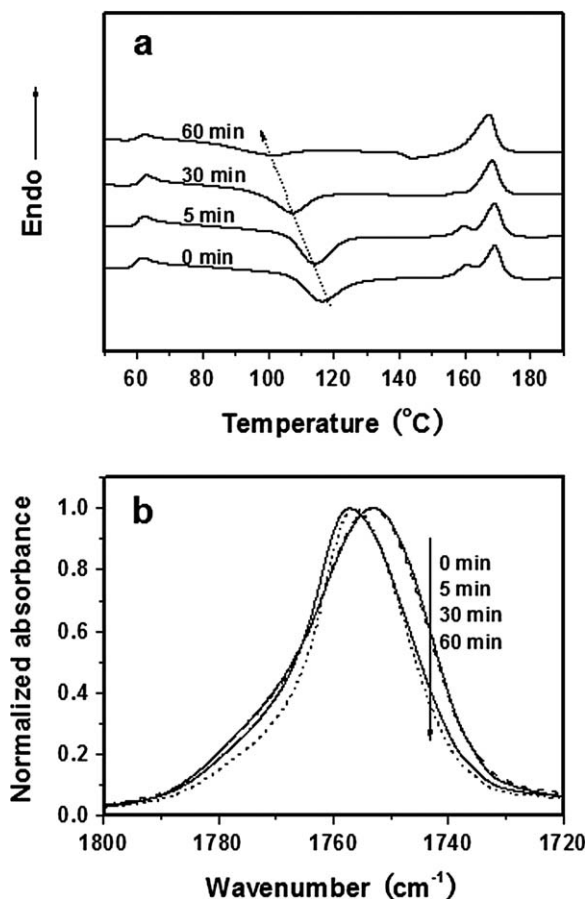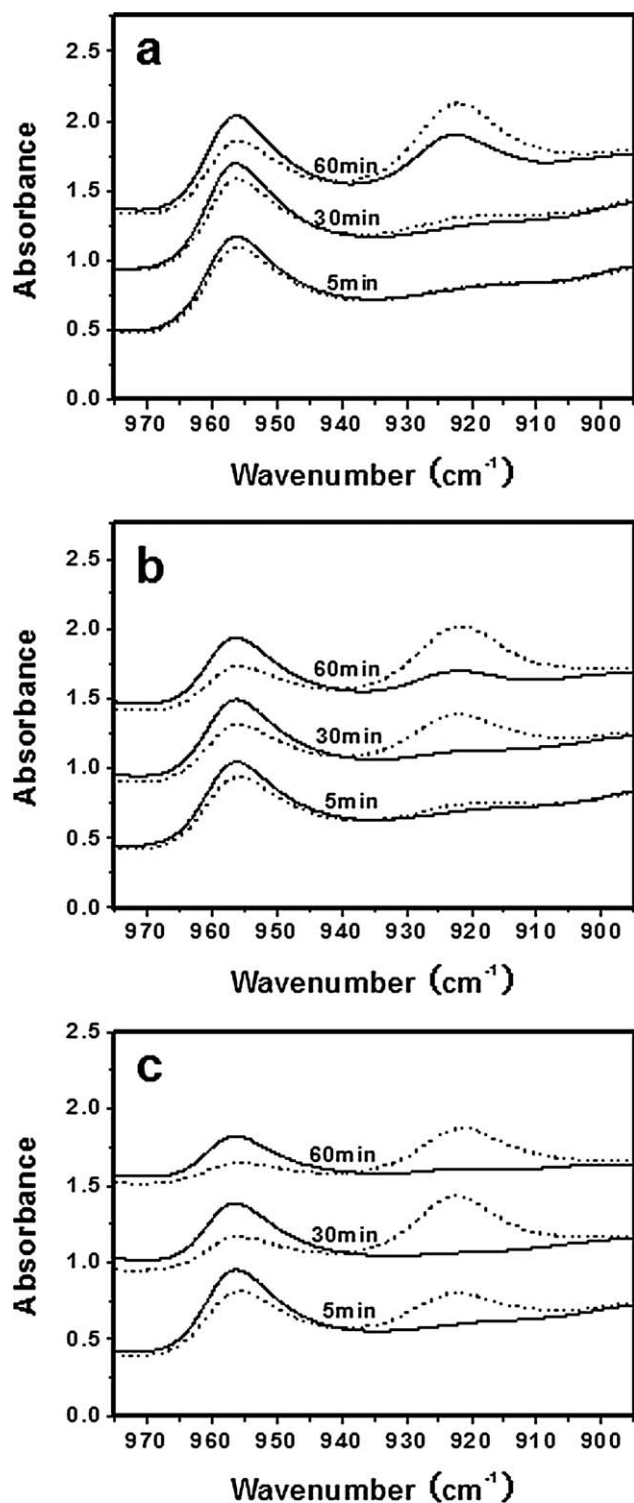

Figure 2. DSC heating traces (a) and ATR-FTIR (b) of PLLA after being annealed at 82°C for the indicated period.

the crystals generated during thermal annealing are responsible for the rapid cold crystallization from the remained amorphous phase in the samples annealed for 60 min, and an exothermic peak at about 100°C is presented.
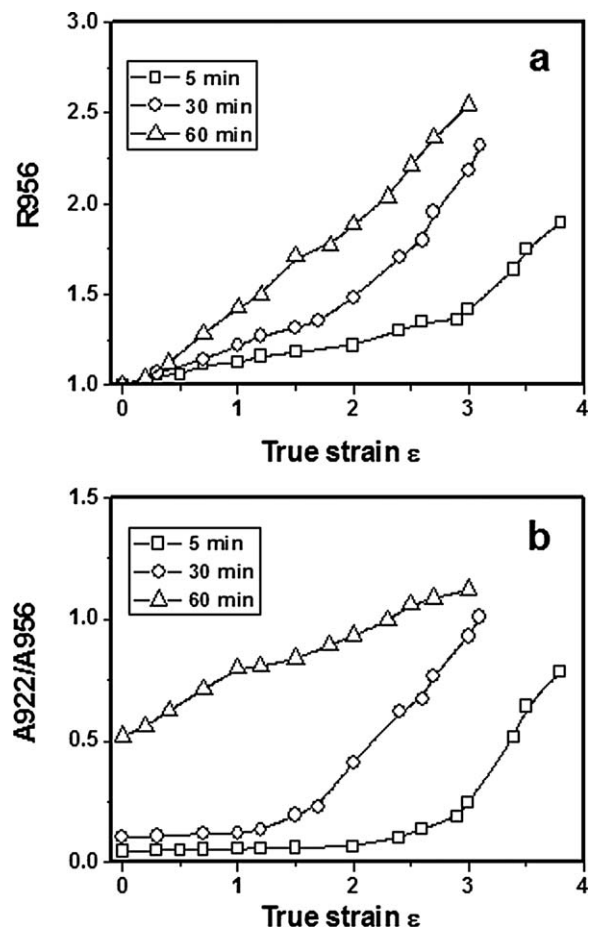
Remarkable formation of local order in the samples annealed for 30 min is further confirmed by the ATR-FTIR spectra in Figure 2(b). The absorption band in the wavenumber range between 1800 and 1720 cm^{-1} is assigned to the stretching vibration of carbonyl group that is sensitive to the intermolecular ordering of PLLA.[17,18] This absorption band remains at a lower wavenumber in the samples annealed for 0 and 5 min, and shifts to a higher wavenumber in the samples annealed for 30 min due to strong dipole–dipole interactions in the densely packed domains. It is very similar to that observed in the samples annealed for 60 min with partial crystallization, albeit a narrower absorption band is exhibited by the latter. The local order generated during thermal annealing has significant influence on the strain-induced crystallization of PLLA, as shown in the following section.

Figure 3 gives typical polarized FTIR spectra of PLLA annealed for 5, 30, and 60 min, respectively, after being stretched to various true strains at 82°C. In the desired wavenumber range, the absorption bands at 956 and 922 cm^{-1} are assigned to the amorphous phase and 10_3 helix of crystals, respectively.[16–18] For all samples, stretching induces the distinct absorption in the parallel and perpendicular direction due to molecular

Figure 4. Evolution of (a) amorphous orientation R956 and (b) relative helix amount A922/A956 with respect to true strains in the annealed PLLA after being stretched at 82°C.

Moreover, strain-induced crystallization depends on the period of thermal annealing and occurs at lower true stains in the samples annealed for 30 min.

To quantitatively analyze the structural evolution during stretching, the following equations were adopted to calculate dichroic ratio, R, and structural absorbance, A.

$$R = A_{//}/A_{\perp} \qquad (1)$$

$$A = \left(A_{//} + 2A_{\perp}\right)/3 \qquad (2)$$

where $A_{//}$, $A_{\perp}$ is the parallel and perpendicular absorbance of a desired absorption band, respectively.

As shown in Figure 4(a), molecular orientation of amorphous phase, represented by the dichroic ratio of the 956 cm^{-1} band ($R956$), increases with true strains for all samples. However, at the same true stain molecular orientation of amorphous phase becomes higher in the samples annealed for more periods. Stretching at temperatures above glass transition temperature inevitably suffers from chain retraction due to high molecular mobility. The presence of physical crosslinks, for instance crystals in the samples annealed for 60 min, can effectively alleviate chain relaxation during stretching and thus results in high molecular orientation of amorphous phase

Figure 3. Polarized FTIR spectra of annealed PLLA after being stretched at 82°C to a true strain of (a) 1, (b) 2, and (c) 3, respectively. Solid and dashed lines represent spectra parallel and perpendicular to the stretching direction, respectively.

orientation, which becomes significant with increasing true stains. On the other hand, in the samples annealed for 5 and 30 min, stretching leads to remarkable appearance of the 922 cm^{-1} band at large strains, as a result of strain-induced crystallization.

during stretching. In such a sense, local order in the samples annealed for 30 min has the similar effects to that of crystals in enhancing molecular orientation. It is responsible for the earlier advent of strain-induced crystallization in the samples annealed for 30 min than that in those annealed for 5 min, since strain-induced crystallization requires a certain molecular orientation. As indicated by Figure 4(b), relative amount of the 10_3 helix to amorphous phase (A922/A956) shows a sharp increase before true strain reaches 2 in the samples annealed for 30 min. On the contrary, in the samples annealed for 5 min significant increase in A922/A956 just appears at a true strain of around 3. Note that the use of A922/A956 rather than A922 is to exclude the effect of sample thickness.

To give further insights into strain-induced crystallization, X-ray diffraction measurements were conducted and corresponding results are collected in Figures 5 and 6. Consistent with above polarized FTIR results, stretching of PLLA annealed for 5 min results in weak diffractions from crystals at a true strain of 3, below which only amorphous diffraction is observed. In contrast, strain-induced crystallization becomes significant at a true strain of 2 in the samples annealed for 30 min. It further confirms that the generation of local order during thermal annealing is helpful for the advent of strain-induced crystallization at the identical stretching conditions (same stretching temperature and rate). As for the partially crystallized samples, i.e. annealing for 60 min,
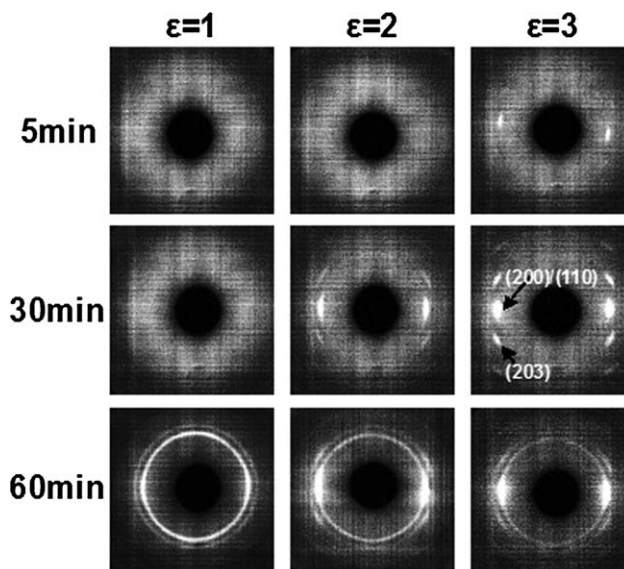
Figure 5. XRD patterns of annealed PLLA after being stretched at 82°C to the indicated true strain. The stretching direction is nearly vertical.

plastic deformation of the crystals dominates the stretching process at large strains. The diffraction circles are gradually concentrated in the equator, i.e. perpendicular to the stretching direction.
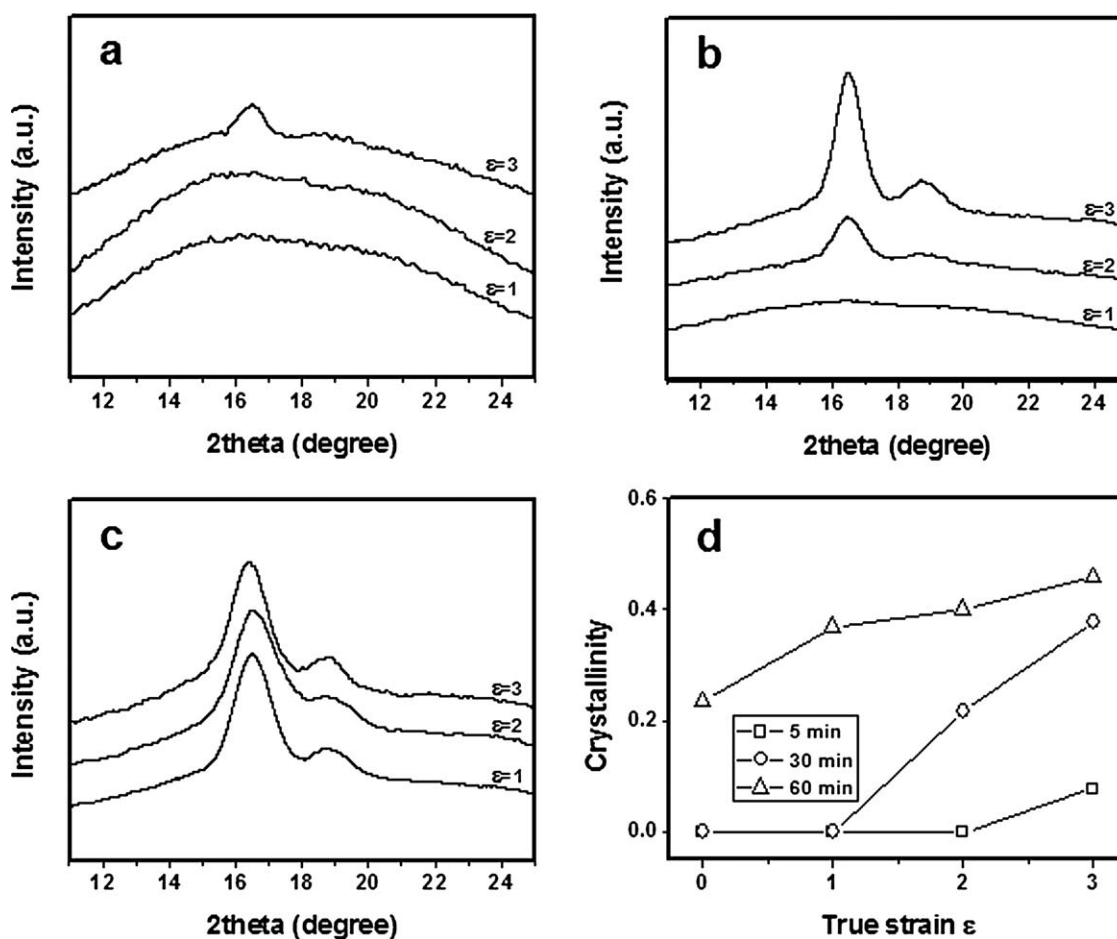
Figure 6. The deduced XRD profiles of annealed PLLA after being stretched to the indicated true stain: (a) 5 min, (b) 30 min, (c) 60 min. The evolution of crystallinity with true strains is included in (d).

However, the orientation of crystals induced by plastic deformation is less significant than that of crystals generated by strain-induced crystallization. The diffraction width of crystal planes along the azimuthal direction is much broader in the samples annealed for 60 min than that that in the samples annealed for 30 min. It makes sense that strain-induced crystallization begins with highly stretched amorphous strands,[7] whereas plastic deformation of crystals involves gradual crystal fragmentation and reorientation of fragments along the stretching direction.

CONCLUSION

Thermal annealing of amorphous polylactide can produce local order rather than crystals by regulating annealing period. The local order has similar effects in enhancing molecular orientation to that of crystals, responsible for the significant enhancement of strain-induced crystallization at the identical stretching conditions. It could open a new way to tailor the structure and properties of stretched polylactide.

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