



Complete stereo-complexation of enantiomeric polylactides for scalable continuous production



Gangwei Pan^{a,b}, Helan Xu^{a,b,**}, Bingnan Mu^b, Bomou Ma^a, Jing Yang^a, Yiqi Yang^{b,c,d,*}

^a Key Laboratory of Science and Technology of Eco-Textiles, Ministry of Education, Jiangnan University, Wuxi 214122, China

^b Department of Textiles, Merchandising & Fashion Design, University of Nebraska-Lincoln, Lincoln, NE 68583-0802, USA

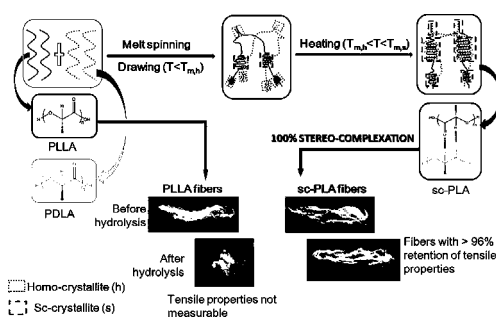
^c Department of Biological Systems Engineering, University of Nebraska-Lincoln, Lincoln, NE 68583-0802, USA

^d Nebraska Center for Materials and Nanoscience, University of Nebraska-Lincoln, Lincoln, NE 68583-0802, USA

HIGHLIGHTS

- A continuous and eco-friendly method for complete stereo-complexation (sc) was proposed.
- Quantitative relationship between ratio of sc-crystallites and hydrolysis resistance was investigated.
- Quantitative relationship between ratio of sc-crystallites and softening point was investigated.
- Sc-PLA fibers had softening point and MW retention rose by up to 61 °C and up to 170%, respectively.
- Improvements of softening point and hydrolysis resistance contributed to industrial application.

GRAPHICAL ABSTRACT



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ABSTRACT

A facile and clean technology for stereo-complexation of polylactides (PLAs) shows potential to be readily incorporated into continuous industrial processes for manufacture of films, fibers and other plastic products. Using this approach, complete stereo-complexation of high-molecular-weight PLAs could be achieved via simple thermal treatment, rendering the production of durable PLA commodities inexpensive and industrially scalable. Currently, due to their high susceptibility to water and heat, PLA products have restricted industrial applications, and cannot compete with their petroleum-derived counterparts. Stereo-complexation of poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA) could effectively decrease water and heat sensitivity of common PLLA products. However, many stereo-complexation processes required harmful solvents or nucleating agents, and thus, were costly, complicated, and had low potential for short-term industrialization. Moreover, complete stereo-complexation was mostly achieved for PLAs with weight-average molecular weight lower than 1×10^5 . In this research, PLLA and PDLA both with viscosity-average molecular weight of 3×10^5 were completely stereo-complexed (sc) via simple thermal treatment. Comparing to PLLA fibers, sc-PLA fibers had softening points 60 °C higher, and their thermal and hydrolytic stability significantly enhanced. Relationship among temperature of thermal treatment, degree of stereo-complexation and performance properties of sc-PLA fibers were also established. This clean technology makes possible industrial-scale production of commercializable biobased plastics.

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* Corresponding author at: Department of Biological Systems Engineering, University of Nebraska-Lincoln, Lincoln, NE 68583-0802, USA.

E-mail addresses: pangangwei@126.com (G. Pan), xuhelan@hotmail.com (H. Xu), bingnan.mu@huskers.unl.edu (B. Mu), mabomou@163.com (B. Ma), 18206178857@163.com (J. Yang), yyang2@unl.edu (Y. Yang).

** Co-corresponding author.

1. Introduction

Due to the continuously increasing population, global demand for plastics is anticipated to reach 335 million tons by 2020 [1]. Production and disposal of fossil-derived plastics create a heavy carbon footprint, which may be a critical cause for unfavorable climate change. To reduce carbon emission, it is imperative to switch feedstock of plastics from non-renewable fossil to renewable bio-based resources [2], such as polysaccharides. polylactide (PLA) is one of the most widely used bioplastics polymerized from lactic acid, which is fermented from starch [3]. PLA has good biodegradability and renewability [4,5]. The past decade has seen a remarkable surge of research interest in developing durable PLA products for applications in automotive, electronics, semi-structural parts and other fields. However, the production and consumption of PLA products are still negligible, comparing to their oil-derived counterparts.

Poor resistance to thermostability and hydrolysis restricts wide industrial applications of PLA products [6,7]. Due to the low softening points (60–70 °C) [8], PLA products are prone to deform under heat, and thus can only be manufactured into products for applications within a small range from room temperature to 65 °C [9,10]. PLA products also degrade readily under wet conditions, especially under heating. Unlike other petroleum-derived polyester fibers, such as polyethylene terephthalate fibers, currently commercial PLA fibers cannot be used in textile products, which are usually dyed and finished under hot and wet conditions [11,12]. In addition, many other plastic products also need to be dyed and thermally processed, or used under wet and hot environments or conditions, disqualifying PLA [13–15]. To render PLA products eligible for large-scale industrial applications, their thermostability and hydrolysis resistance should be substantially improved.

Till now, relevant research was limited to blending, block copolymerization and crosslinking of PLA [16–19]. Reddy et al. [16] blended PLA with polypropylene (PP) for melt spinning to obtain fibers with improved hydrolysis resistance. However, due to the low compatibility of PLA and PP, the blended fibers had poor mechanical properties. Also, due to the non-biodegradable nature, incorporation of PP reduced the eco-friendliness of PLA fibers. Ma and Zhou [17] improved hydrophobicity of PLA fibers via chemical modification, which enhanced hydrolysis resistance moderately, but remarkably decreased their strength. Via molecular modeling, Karst and Yang proposed that blending of poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA) could yield PLA fibers with good hydrolysis resistance [18,19]. However, they did not use experiments to verify the proposition.

Ikada et al. [20] first reported stereo-complexation between PLLA and PDLA polymers in 1987. Stereo-complexation (sc) of enantiomeric PLA polymers is now a major approach to improve hydrolytic and thermal stability of PLA products to expand their commercial applications [21–23]. However, current stereo-complexation methods are difficult to be scaled up and incorporated into existing industrial production processes. PLLA and PDLA were usually co-dissolved in chloroform, dichloromethane, acrylonitrile and other environmentally unfriendly organic solvents for stereo-complexation [24–26]. The dissolution-associated stereo-complexation processes are usually expensive, time-consuming, require complicated equipment for solvent collection and may cause environmental problems due to solvent disposal. Furthermore, nucleating agents, such as carbon nanotube [27], polyethylene glycol [24], aryl amide derivatives [25], zinc phenylphosphonate [26], etc. were also commonly used during stereo-complexation. Addition of these nucleating agents could pose significant difficulty and increase cost of production, and thus is not practical either. Last but not the least, using current stereo-

complexation methods, it was difficult to achieve 100% stereo-complexation for high viscosity-average molecular weight (Mv) PLA polymers, which are usually required in production of high-quality plastics. Complete stereo-complexation of PLA with Mv higher than 3×10^5 has not been found [27–29].

In this research, to seek a clean method for continuous production of polylactide fibers with complete stereo-complexation and investigate the quantitative relationship between ratio of sc-crystallites and hydrolysis resistance and softening temperature of PLA fibers, PLLA and PDLA polymers both with Mv of 3×10^5 were stereo-complexed via a facile thermal treatment. The sc-polymers are intentionally developed into textile fibers to verify the potential for the treatment to be introduced into commercial production lines. PLLA and PDLA pellets were directly mixed, melt spun and annealed into fibers with crystalline regions composed of stereo-complexed structures. Different degrees of stereo-complexation were controlled via post-spun thermal treatment. The ratio of sc-crystallites, thermal properties and hydrolysis resistance of PLLA/PDLA fibers were characterized by Wide Angle X-Ray Diffraction, Differential Scanning Calorimetry, Dynamic Mechanical Analyzer and correlated.

2. Materials and methods

2.1. Materials

PLLA ($M_v = 3 \times 10^5 \text{ g mol}^{-1}$) was purchased from a company. PDLA ($M_v = 3 \times 10^5 \text{ g mol}^{-1}$) was synthesized via ring-opening polymerization of D-lactides provided by Xinning Biomaterial Co. Ltd., Zhejiang, China. The pilot-scale reaction catalyzed by stannous octoate was performed at 140–180 °C for 6 h under vacuum. As measured by differential scanning calorimetry (DSC), melting temperatures (T_m) of PLLA and PDLA were 175 °C and 176 °C, respectively; and glass transition temperatures (T_g) were 62 °C and 63 °C, respectively. Chloroform (99%) and hexafluoro-2-propanol (HFIP) (99%) were purchased from Sigma-Aldrich, St. Louis, MO, USA. Sodium dihydrogen phosphate and sodium hydroxide were purchased from Alfa Aesar, Haverhill, MA, USA.

2.2. Sample preparation and stereo-complexation

Pellets of PLLA and PDLA were dried at 80 °C in a vacuum oven overnight before being grinded and mixed to prepare blend of PLLA and PDLA (50:50, wt%) in a laboratory mixing extruder (Dynisco, Franklin, MA, USA). In the same extruder, the PLLA/PDLA blend and PLLA were heated at 240 °C and 220 °C, respectively, and extruded through a die with inner diameter of 0.5 mm at 230 °C and 200 °C, respectively. The fibers were taken up at 200 m min⁻¹. The as-spun PLLA/PDLA fibers were drawn for 3 times at a temperature between 60 °C and 140 °C. Glass transition temperature of PLLA or PDLA was around 60 °C, making the fibers glassy and unable to be drawn below 60 °C. Above 140 °C, the fibers tended to melt and could not be drawn either. For stereo-complexation via annealing, the drawn PLLA/PDLA fibers were heated in a chamber at 160 °C, 180 °C and 200 °C for 5 min under tension of 10 MPa. The PLLA fibers were drawn for 3 times at 80 °C and annealed at 100 °C for 5 min, based on a widely accepted protocol [16]. In this research, PLLA/PDLA fibers without annealing were named as PLLA/PDLA fibers, while those after annealing were named as sc-PLA fibers.

2.3. Hydrolysis

To evaluate the effect of practical industrial process on fiber properties, PLLA fibers and sc-PLA fibers were hydrolyzed in pH 5

buffer solution with a fiber-to-liquid ratio of 1:50 at 130 °C for 60 min in sealed bottles [30]. Here, 130 °C and 60 min are typical temperature for polyester dyeing, and holding time after reaching the dyeing temperature, respectively. Subsequently, the fibers were withdrawn, washed with distilled water and dried under ambient conditions. All the fibers were then conditioned in the standard testing atmosphere (65% Relative Humidity, 21 °C) for at least 24 h before testing.

2.4. Characterization

2.4.1. Thermal behavior

Thermal analysis was carried out using a Mettler Toledo D822^e Differential Scanning Calorimeter (Mettler Toledo Inc., Columbus, OH, USA) under a nitrogen atmosphere. The fibers were heated at a rate of 10 °C min⁻¹ from 25 °C to 250 °C [31]. Crystallization temperature (T_c), T_g , T_m and enthalpy of glass transition, crystallization and melting (ΔH_g , ΔH_c and ΔH_m , respectively) of fibers were determined. $\Delta H_{m,H}$ and $\Delta H_{m,S}$ are ΔH_m of homo-crystallites and sc-crystallites, respectively.

2.4.2. Crystallinity

Fractions of homo-crystallites and sc-crystallites of the PLLA and sc-PLA fibers were determined using Wide Angle X-Ray Diffraction (WAXD). The WAXD measurements were performed at 25 °C using a Rigaku SmartLab Diffractometer (Rigaku, Tokyo, Japan) with a Cu-K α source. Diffractograms of the fibers were obtained at 40 kV and 44 mA with scanning angles of 5° to 40° at a scanning rate of 3° min⁻¹ [32]. The X-ray diffraction patterns were analyzed using Jade 5.0 software (Materials Date, Livermore, CA, USA). The crystalline peak areas for sc-crystallites and homo-crystallites relative to the total area between the diffraction profile and the baseline were used to estimate the degree of sc-crystallites ($X_{c,S}$) and degree of homo-crystallites ($X_{c,H}$), respectively, according to the following Eqs. (1)–(3):

$$X_{c,S} (\%) = 100S_{sc}/(S_{sc} + S_{hc} + S_a) \quad (1)$$

$$X_{c,H} (\%) = 100S_{hc}/(S_{sc} + S_{hc} + S_a) \quad (2)$$

$$\%SC = X_{c,S}/(X_{c,S} + X_{c,H}) \quad (3)$$

Where, S_{sc} , S_{hc} and S_a are diffraction peak areas of sc-crystallites, homo-crystallites and amorphous regions, respectively. %sc is degree of stereo-complexation, a.k.a., fraction of sc-crystallites in both sc-crystallites and homo-crystallites.

2.4.3. Tensile properties

All fibers were conditioned in a standard testing atmosphere of 21 °C and 65% Relative Humidity for at least 24 h before testing. An Instron 4400 tensile tester (Instron Co., Canton, MA, USA) equipped with a 5 N load cell was used to determine tensile strength, breaking elongation and Young's modulus of PLLA and sc-PLA fibers before and after treatments, according to ASTM standard 3822. A gauge length of 1 inch with a cross-head speed of 50 mm min⁻¹ was used. About 20 replicates were tested for each condition, and the average and standard error were reported. Tensile properties of PLA fibers prepared under various conditions were tested to verify the effect of stereo-complexation on improving resistance of PLA fibers to hydrolysis. % retention of mechanical properties is the ratio of tensile properties, including tensile strength and breaking elongation of PLA fibers after hydrolysis over the values of the same properties of the same fibers before hydrolysis.

2.4.4. Molecular weight

Viscosity-average molecular weight (M_v) of the fibers was measured by the viscosity method using an Ubbelohde capillary

viscometer. The intrinsic solution viscosity $[\eta]$ was determined in chloroform containing 10 vol% of HFIP at 25 °C [33]. The M_v was calculated from the $[\eta]$ using the Mark-Houwink equation given as [34]

$$[\eta] = 0.0153 \times M_v^{0.759} \quad (4)$$

2.4.5. Softening temperature

Softening temperature (T_s) of a fiber is defined as the temperature at which the strain reaches 2% in the temperature-strain curves with a constant load of 0.01 N. Thermomechanical tests were carried out in a Q800 Dynamic Mechanical Analyzer (DMA) (TA Instruments, New Castle, DE, USA). The temperature was raised from 40 to 150 °C at a heating rate of 2 °C min⁻¹ in a nitrogen atmosphere. The samples were tested in tension mode.

2.4.6. Morphology

The surface morphologies of the sc-PLA fibers before and after annealing at 200 °C were observed using a Nikon Ti-S optical microscope (Nikon, Tokyo, Japan). Magnification of images was 40 $\times$.

2.5. Statistical analysis

Data generated was analyzed using Tukey's multiple-pair wise comparison using SAS program (SAS Institute, Raleigh, NC, USA). A significance level of $\alpha = 0.05$ was considered as statistically significant.

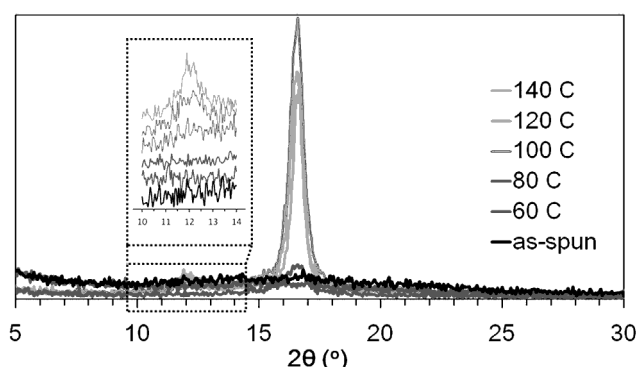


Fig. 1. WAXD patterns of PLLA/PDLA fibers as spun and drawn for 3 times at 60 °C, 80 °C, 100 °C, 120 °C and 140 °C, respectively.

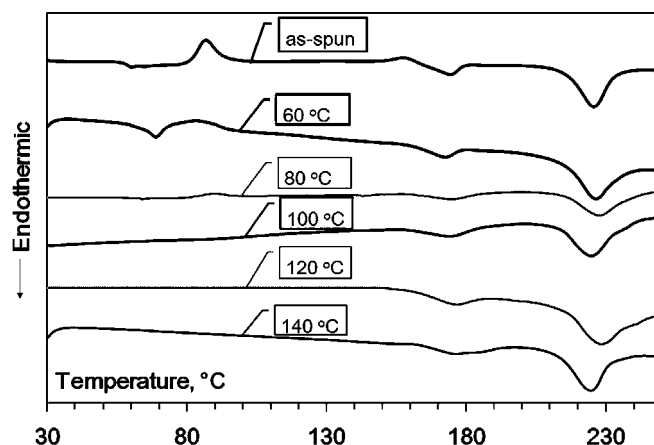


Fig. 2. DSC thermograms of PLLA/PDLA fibers as spun and drawn for 3 times at 60 °C, 80 °C, 100 °C, 120 °C and 140 °C, respectively.

Table 1

Characteristics of thermal properties of PLLA/PDLA fibers as spun and drawn for 3 times at 60 °C, 80 °C, 100 °C, 120 °C and 140 °C, respectively.

Fiber Type	T_D^a (°C)	T_g^b (°C)	$T_{cc}/\Delta H_c^c$ (°C)/(J/g)	$T_{m,H}/\Delta H_{m,H}^d$ (°C)/(J/g)	$T_{m,S}/\Delta H_{m,S}^e$ (°C)/(J/g)
PLLA/PDLA	–	60	87/21.59	174/15.68	226/48.28
	60	64	84/7.54	172/9.68	226/43.20
	80	–	90/3.82	175/9.00	228/40.94
	100	–	–	175/14.92	228/57.47
	120	–	–	177/14.27	228/58.06
	140	–	–	176/14.87	225/50.29

^a Drawing temperature.

^b Glass transition temperature.

^c Cold crystallization temperature (T_{cc}) and melting enthalpy (ΔH_c).

^d Melting temperature ($T_{m,H}$) and melting enthalpy ($\Delta H_{m,H}$) of homo-crystallites.

^e Melting temperature ($T_{m,S}$) and melting enthalpy ($\Delta H_{m,S}$) of sc-crystallites.

3. Results and discussion

3.1. Effects of drawing

3.1.1. Effect of drawing on crystalline structures of PLLA/PDLA fibers

Fig. 1 shows WAXD spectra of PLLA/PDLA fibers to demonstrate the effect of drawing and drawing temperature on their crystalline structures and crystallinity. The diffraction peaks at 12° and 16.7° indicate formations of sc-crystallites of PLLA and PDLA, and homo-crystallites of individual PLLA or PDLA [35,36]. In the as-spun PLLA/PDLA fibers and PLLA/PDLA fibers drawn at 60 °C, none of these two peaks appeared, suggesting that these fibers contained only amorphous phases. As the drawing temperature increased to 80 °C and 100 °C, diffraction peaks at 16.7° arose, demonstrating homocrystallization of individual PLLA or PDLA. As the drawing temperature reached 120 °C and 140 °C, peaks at both 12° and 16.7° appeared, indicating presence of homo-crystallites and sc-crystallites after drawing. In summary, as the drawing temperature increased, the percentage of homo-crystallites decreased while that of sc-crystallites increased. Raising drawing temperature could enhance mobility of individual PLLA and PDLA macromolecules, and facilitate their mixing. Subsequently, PLLA and PDLA molecules could re-combine into more regularly arranged sc-crystallites, resulting in increased degree of crystallinity.

3.1.2. Effect of drawing on thermal structures of PLLA/PDLA fibers

Fig. 2 demonstrates DSC thermograms of PLLA/PDLA fibers to illustrate the effect of drawing temperature on their thermal properties. Melting peaks of homo-crystallites and sc-crystallites appear at the temperature ranges of 140–180 °C and 210–240 °C, respectively [37–41]. The as-spun and 60 °C drawn PLLA/PDLA fibers had obvious glass transition behaviors, indicated by the peaks between 60 °C and 70 °C, attributed to the total amorphous phase of the two types of PLLA/PDLA fibers (Fig. 1). However, no such peak could be detected in the thermograms of any PLLA/PDLA fibers drawn between 80 °C and 140 °C, attributed to the increased amounts of crystallites (Fig. 1).

As temperature increased to 80–100 °C, exothermic peaks appeared in the thermograms of PLLA/PDLA fibers drawn under 60 °C and 80 °C, demonstrating formation of homo-crystallites in the total amorphous structures. Similar phenomenon was also reported by Furuhashi et al. [42–44]. However, no peaks around 70 °C existed in the PLLA/PDLA fibers drawn under 100–140 °C. In these fibers, homo-crystallites and sc-crystallites already formed during fiber drawing, leaving limited amounts of free PLLA and PDLA molecules available for crystallization at around 70 °C.

Thermograms of all PLLA/PDLA fibers showed two endothermic peaks at around 175 °C and 225 °C, indicating melting of homo-crystallites and sc-crystallites, respectively (Table 1). However, as indicated in XRD results (Fig. 1), both PLLA/PDLA fibers without

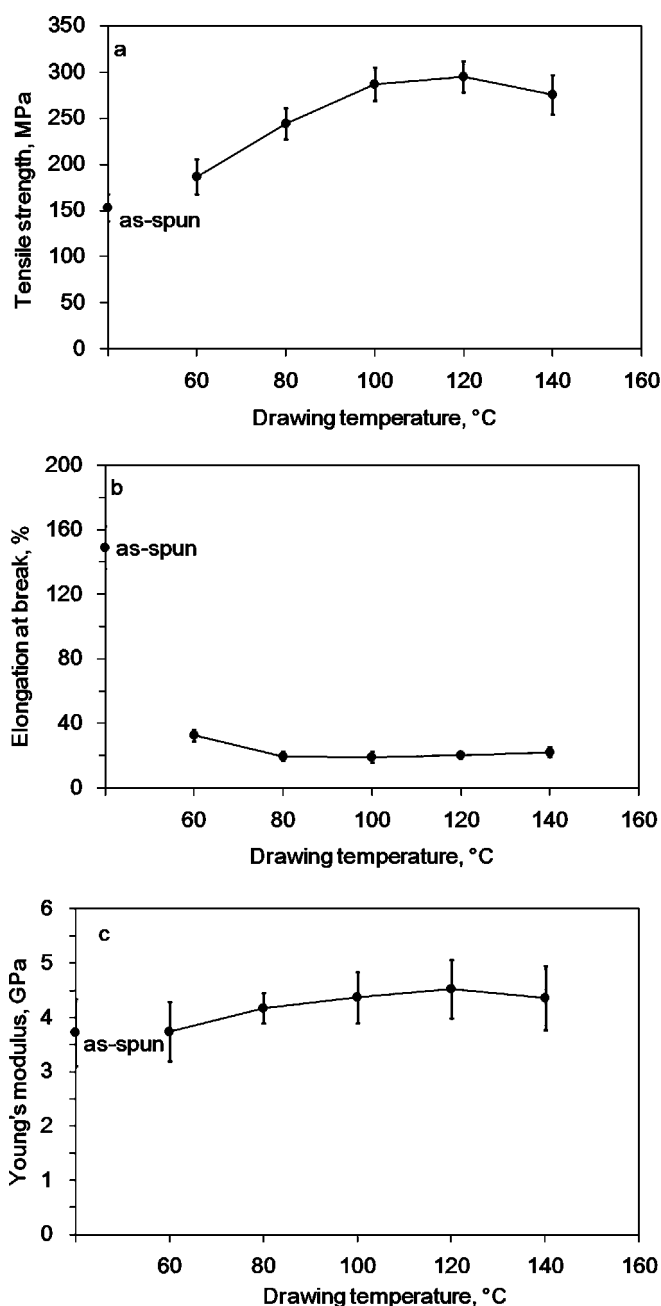


Fig. 3. (a) Tensile strength, (b) elongation at break, and (c) Young's modulus of PLLA/PDLA fibers as spun and drawn for 3 times at 60 °C, 80 °C, 100 °C, 120 °C and 140 °C, respectively. Linear densities of the as-spun and drawn PLLA/PDLA fibers were 11.2 D and 3.5 D, respectively.

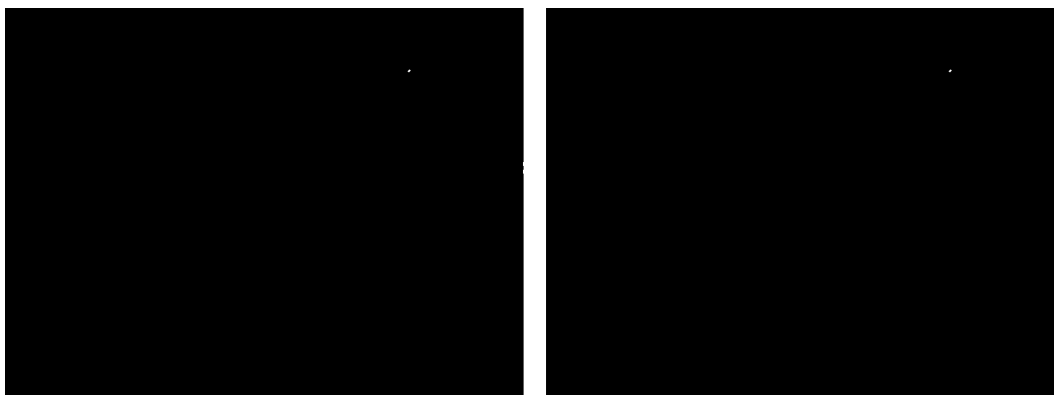


Fig. 4. Optical photomicrographs of sc-PLA fibers before (a) and after (b) annealing at 200 °C.

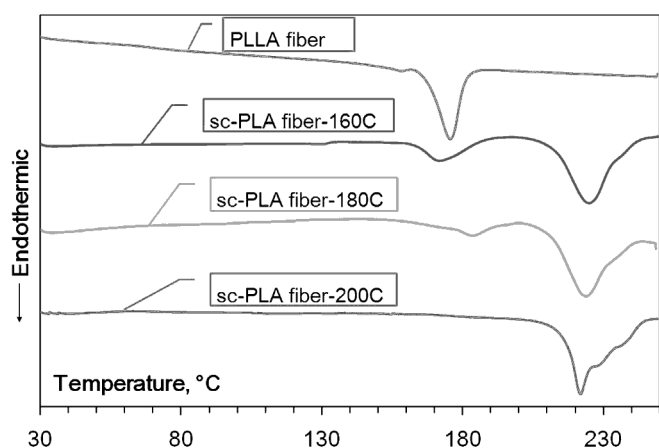


Fig. 5. DSC thermograms of PLLA fibers and sc-PLA fibers annealed at 160 °C, 180 °C and 200 °C for 5 min. All fibers were hydrolyzed in pH 5 buffer solution with a fiber-to-liquid ratio of 1:50 at 130 °C for 60 min in sealed bottles.

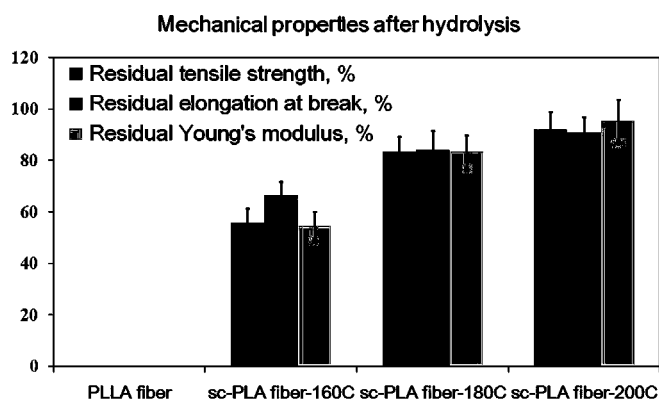


Fig. 6. Post-hydrolysis tensile properties of PLLA fibers and sc-PLA fibers annealed at 160 °C, 180 °C and 200 °C for 5 min. All fibers were hydrolyzed in pH 5 buffer solution with a fiber-to-liquid ratio of 1:50 at 130 °C for 60 min in sealed bottles.

drawing and those drawn under 60 °C were amorphous. The crystallites detected in these fibers might be formed via recrystallization of melted molecules during the heating process of DSC analysis.

3.1.3. Effect of drawing on mechanical properties of PLLA/PDLA fibers

Fig. 3 presents tensile properties of PLLA/PDLA fibers as spun and drawn at 60 °C, 80 °C, 100 °C, 120 °C and 140 °C, respectively.

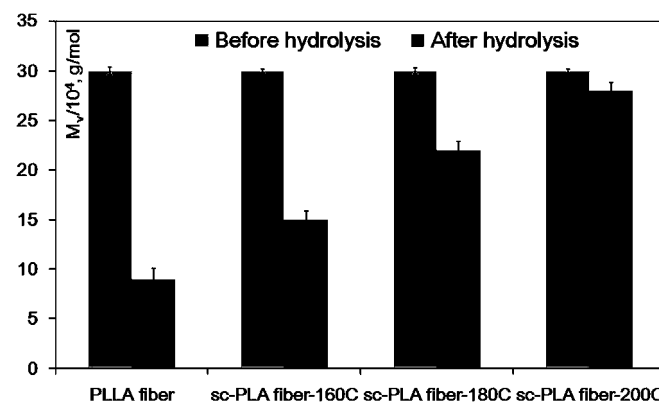


Fig. 7. Molecular weights of PLLA fibers and sc-PLA fibers annealed at 160 °C, 180 °C and 200 °C for 5 min before and after hydrolysis. All fibers were hydrolyzed in pH 5 buffer solution with a fiber-to-liquid ratio of 1:50 at 130 °C for 60 min in sealed bottles.

Comparing with as-spun PLLA/PDLA fibers, tensile strength, Young's modulus and elongation of the drawn fibers were higher, the same, and much lower, respectively. The difference might be ascribed to drawing, which could align PLA crystalline regions in the fibers to achieve better orientation. Comparing with the drawn fibers, the tensile strength increased as the drawing temperature increased from 60 °C to 100 °C, and did not change as the temperature continued to increase. The elongation first decreased and then increased. There was no difference among the Young's modulus as the drawing temperature changed.

3.2. Effects of annealing

3.2.1. Effect of annealing on morphologies of PLLA fibers and sc-PLA fibers

Annealing did not obviously change width of sc-PLA fibers. As shown in Fig. 4, there was no significant difference in diameters (30.38 μm VS 30.09 μm) of sc-PLA fibers before and after annealing at 200 °C. Sc-crystallites, which already existed in sc-PLA fibers before annealing assisted in maintaining the fiber morphologies and were not affected by the annealing process.

3.2.2. Effect of annealing on thermal properties of PLLA fibers and sc-PLA fibers

Fig. 5 demonstrates the DSC thermograms of PLLA fibers and sc-PLA fibers drawn at 120 °C and annealed under different temperatures. PLLA fibers only had a sharp melting peak of homocrystallites at 175 °C, which shrunk until disappeared as the

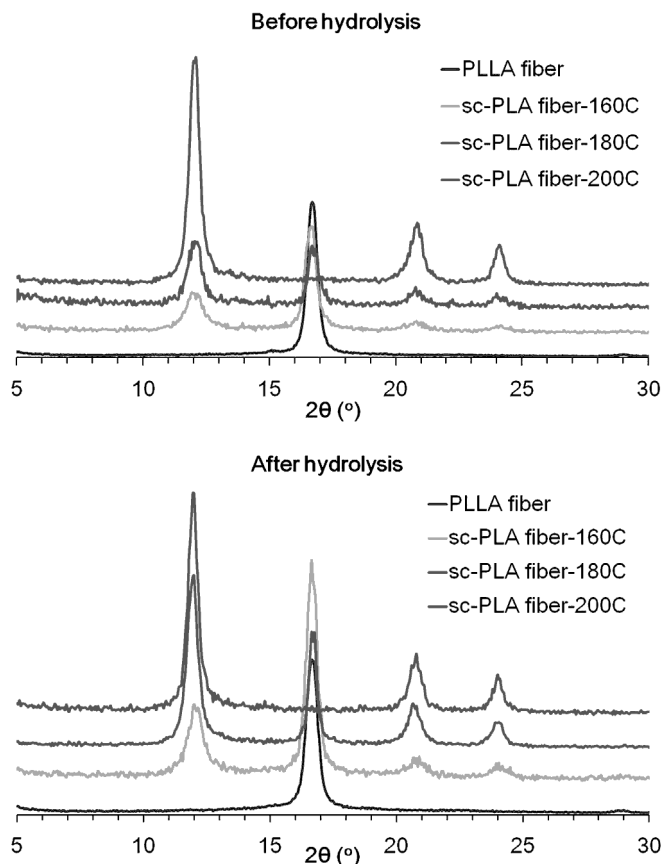


Fig. 8. WAXD patterns of PLLA fibers and sc-PLA fibers annealed at 160 °C, 180 °C and 200 °C for 5 min before and after hydrolysis. All fibers were hydrolyzed in pH 5 buffer solution with a fiber-to-liquid ratio of 1:50 at 130 °C for 60 min in sealed bottles.

annealing temperature increased from 160 °C to 200 °C in sc-PLA fibers. The crystallites in sc-PLA fibers annealed at 200 °C were 100% stereo-complexed. Meanwhile, the peak at 225 °C indicating melting of sc-crystallites enlarged accordingly as the annealing temperature increased from 160 °C to 200 °C. Since T_m of PLLA or PDLA is 175 °C, annealing at 160 °C could only liberate PLLA and PDLA molecules in the amorphous regions, leading to formation of small amounts of sc-crystallites. By increasing the annealing temperature to 180 °C, which is slightly higher than the T_m , homo-crystallites could be melted and form sc-crystallites. As the annealing temperature further increased to 200 °C, which is substantially higher than the T_m , all homo-crystallites could be melted, leading to formation of 100% sc-crystallites in the crystalline regions of sc-PLA fibers. There are double peaks and triple peaks for sc-PLA fibers annealed at 225 °C. The sc-crystallites in sc-PLA

fibers might have different aggregation sizes, accounting for the slight differences among melting temperatures. This phenomenon is consistent with many other reports [45–47]. It could be seen that, annealing played a much more important role in stereo-complexation comparing to drawing.

3.2.3. Effect of annealing on mechanical properties of PLLA fibers and sc-PLA fibers after hydrolysis

As shown in Fig. 6, after treated in water at 130 °C for 60 min, tensile properties of PLLA fibers were not testable due to severe hydrolysis, while that of sc-PLA fibers did not decrease significantly. Percent retention of tensile strength, breaking elongation and Young's modulus of sc-PLA fibers annealed at 160 °C were 56%, 67% and 55%, respectively, while the values of sc-PLA fibers annealed at 200 °C were 92%, 91% and 96%, respectively. The higher the percentage of sc-crystallites, the higher the % retention of mechanical properties of sc-PLA fibers due to better resistance to hydrolysis.

3.2.4. Effect of annealing on molecular weights of PLLA fibers and sc-PLA fibers after hydrolysis

Changes in molecular weight retention of PLLA fibers and sc-PLA fibers inferred the critical role stereo-complexation played in enhancing resistance of sc-PLA fibers to hydrolysis. Fig. 7 indicates that, the higher the percentage of sc-crystallites in fibers, the higher the M_v of PLA after hydrolysis. Before hydrolysis, PLLA and PDLA in both PLLA fibers and sc-PLA fibers had M_v of 3×10^5 , which decreased to M_v too small to be tested for the PLLA fibers, and for less than 10% to M_v of around 2.7×10^5 for the sc-PLA fibers annealed at 200 °C with 100% of crystalline regions stereo-complexed. The sc-PLA fibers annealed at 180 °C and 200 °C might have higher crystallinity than PLLA fibers and sc-PLA fibers annealed at 160 °C. Hydrolysis of PLA fibers could be divided into two stages, fast hydrolysis of amorphous regions and slow hydrolysis of crystalline regions, due to the high and low diffusion rates of water molecules in these two regions, respectively [48–50]. With more amorphous regions, the fibers were more easily to react with water and had polymers scissored. Thus, sc-PLA fibers annealed at 200 °C and 180 °C were more resistant to hydrolysis comparing to PLLA fibers and sc-PLA fibers annealed at 160 °C both with less sc-crystallites (Fig. 5). Homo-crystallites are more easily to be hydrolyzed comparing to sc-crystallites, due to their weaker intermolecular force. Thus, sc-PLA fibers annealed at 200 °C with 100% of sc-crystallites in crystalline regions were more resistant to hydrolysis, comparing to sc-PLA fibers annealed at 180 °C with less sc-crystallites.

3.2.5. Effect of annealing on crystalline structures of PLLA fibers and sc-PLA fibers before and after hydrolysis

Fig. 8 demonstrates WAXD spectra of PLLA fibers and sc-PLA fibers before and after hydrolysis. As shown in Fig. 8a, before

Table 2

Characteristics of melting temperature and crystallinity of PLLA fibers and sc-PLA fibers annealed at 160 °C, 180 °C and 200 °C for 5 min before and after hydrolysis. All fiber samples were hydrolyzed in pH 5 buffer solution with a fiber-to-liquid ratio of 1:50 at 130 °C for 60 min in sealed bottles.

Sample	Annealing Temperature (°C)	Total degree of crystallinity (%)			Crystallinity of homo-crystallites (%)			Crystallinity of sc-crystallites (%)			% of sc-crystallites in both homo-crystallites and sc-crystallites	
		Before	After	% Increase	Before	After	% Increase	Before	After	% Increase	Before	After
PLLA fiber	100	53.9	74.4	38.0	53.9	74.4	38.0	0	0	–	0	0
sc-PLA fiber-160	160	60.1	74.6	24.1	36.8	46.1	25.3	23.3	28.5	22.3	38.8	38.2
sc-PLA fiber-180	180	66.7	72.8	9.2	16.1	19.2	19.3	50.6	53.6	5.9	75.9	73.6
sc-PLA fiber-200	200	60.6	61.8	2.0	0	0	–	60.6	61.8	2	100	100

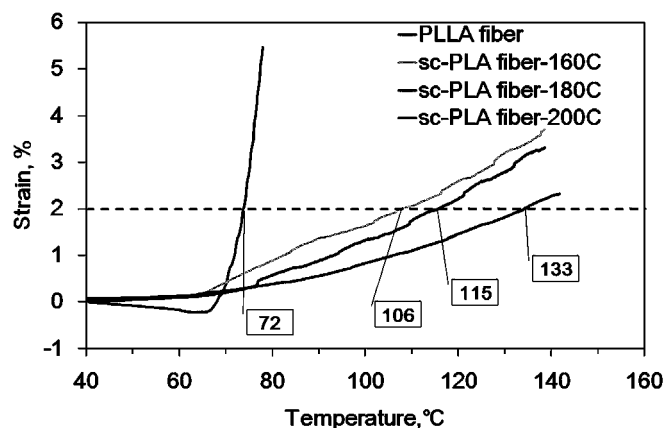


Fig. 9. Softening temperatures of PLLA fibers and sc-PLA fibers annealed at 160 °C, 180 °C and 200 °C for 5 min.

hydrolysis, sc-PLA fibers annealed at 160 °C and 180 °C had peaks at 12°, 16.7° and 24°, while sc-PLA fibers annealed at 200 °C had peaks at 12°, 21° and 24°, and PLLA fibers only had one peak at 16.7°. The crystalline regions in PLLA fibers, 160 °C and 180 °C annealed sc-PLA fibers, and 200 °C annealed sc-PLA fibers contained only homo-crystallites, both homo-crystallites and sc-crystallites, and only sc-crystallites, respectively. The XRD results were consistent with DSC results (Fig. 5), suggesting that annealing at higher temperature increased the amount of sc-crystallites and simultaneously decreased that of homo-crystallites. As shown in Fig. 8b, hydrolysis did not change peak positions, but changed intensities, indicating variation in the percentages of homo-crystallites or sc-crystallites in PLLA fibers or sc-PLA fibers.

Changes in degrees of crystallinity of PLLA fibers and sc-PLA fibers annealed at different temperatures before and after hydrolysis are listed in Table 2. The % increase of crystallinity degree due to hydrolysis was highest for PLLA fibers, due to easier elimination of amorphous regions, which was the highest among all the fibers. Though the crystallinity of PLLA fibers was similar to that of 160 °C annealed sc-PLA fibers, the % increase of crystallinity of the latter was lower, probably because the interaction between PLLA molecules and PDLA molecules might be stronger than that among PLLA molecules. The % increase of crystallinity degree of sc-PLA fibers gradually decreased as the percentage of sc-crystallites increased. The 160 °C annealed sc-PLA fibers had larger increase in crystallinity degree than the 180 °C annealed sc-PLA fibers. For 200 °C annealed sc-PLA fibers which contained 100%

sc-crystallites in crystalline regions, change in degree of crystallinity was not detected after hydrolysis. With higher amount of sc-crystallites, PLLA and PDLA molecules in both amorphous and crystalline regions could be better protected from hydrolysis due to enhanced intermolecular forces and reduced contact with water molecules. The changing trend of crystallinity degree was also in consistence with that of tensile properties fibers (Fig. 6), and Mv of PLLA and PDLA polymers (Fig. 7). For sc-PLA fibers annealed at 160 °C, the percentage the homo-crystallite peak at 16.7° increased to a larger extent than the sc-crystal peak at 12°. On contrast, for sc-PLA fibers annealed at 180 °C, the percentage the homo-crystallite peak at 16.7° increased to a smaller extent than the sc-crystal peak at 12°. Further research is needed to explain the difference in the change of peak intensity.

3.3. Softening temperatures of PLLA fibers and annealed sc-PLA fibers

Fig. 9 shows the T_s of PLLA fibers and sc-PLA fibers obtained from temperature-strain curves. Comparing to PLLA fibers with T_s at 72 °C, sc-PLA fibers annealed at 160 °C, 180 °C and 200 °C softened at substantially higher temperatures of 106 °C, 115 °C and 133 °C, respectively. Higher annealing temperature resulted in higher percentage of sc-crystallites in the sc-PLA fibers, and subsequently better thermal stability due to stronger intermolecular interaction between PLLA and PDLA molecules comparing to among PLLA molecules. Thus, the sc-PLA fibers had good potential for applications in textile and other industries, which contain multiple thermal and hydro-thermal treatments in their processing procedures.

3.4. Mechanism of stereo-complexation of PLLA and PDLA polymers via annealing

Fig. 10 shows the stereo-complexation process of sc-PLA fibers from melt spinning/drawing to annealing. Melting spinning of PLLA and PDLA polymers at 240 °C without drawing generated blended PLLA/PDLA fibers with totally amorphous structures (Fig. 1). Drawing under temperatures from 80 °C to 140 °C, which was higher than T_g of PLA, could rearrange the PLA molecules which were slightly mobilized in amorphous regions. Thus, the quantities of homo-crystallites (16.7°) increased to large extents, and that of sc-crystallites (12°) started to exist, though in almost negligible amounts, as shown in Fig. 1. Since the drawing temperatures were still much lower than T_m (175 °C) of PLA homo-crystallites, stereo-complexation requiring completely mobilized PLLA and PDLA polymers could merely occur.

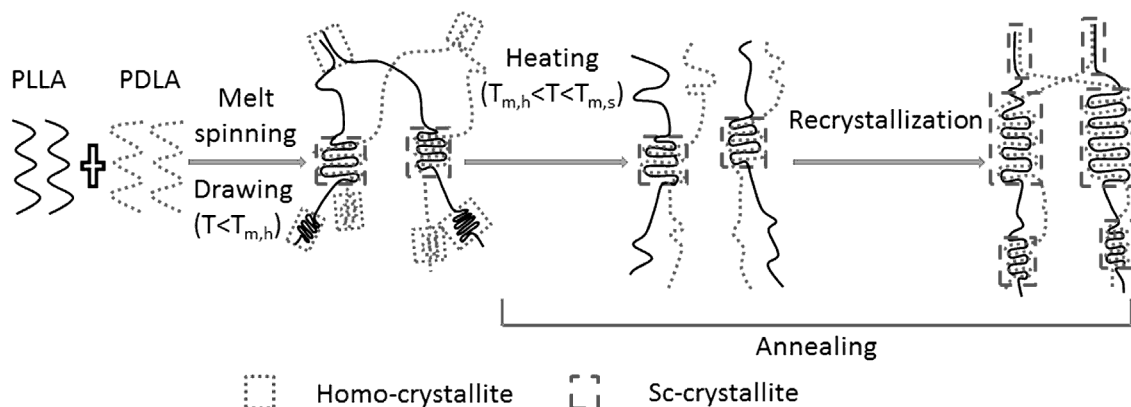


Fig. 10. Schematic of crystallization process of sc-crystallites at high temperature ($T_{m,h}$ is the melting temperature of homo-crystallites, $T_{m,s}$ is the melting temperature of sc-crystallites).

Via subsequent annealing at 200 °C, or other temperatures higher than T_m of homo-crystallites (175 °C, Fig. 5), but lower than T_m of sc-crystallites (225 °C, Fig. 5), the PLLA or PDLA homo-crystallites in PLLA/PDLA fibers melted. The sc-PLA crystallites, with a majority formed during post-spinning annealing and a minority formed during fiber drawing functioned as nucleation centers to promote stereo-complexation of the molten PLLA and PDLA polymers.

Temperature is of vital importance for effective stereo-complexation. Under optimal temperature, the crystalline regions in PLLA/PDLA fibers could be all stereo-complexed. If the temperature is too low, PLLA and PDLA molecules are not sufficiently mobile to move to vicinities of their enantiomers. Resultantly, only a small quantity of sc-structures could be formed. On the contrary, if the temperature is too high, sc-crystallites which function as nucleation centers might melt, and thus could not function as nucleation centers, preventing formation of new sc-structures.

4. Conclusions

In this research, via a facile process, controllable stereo-complexation was achieved for enantiomeric PLAs with high M_v to obtain satisfactory hydrolytic and thermal resistance. Thermal treatments at 160 °C, 180 °C and 200 °C increased the %sc of PLLA/PDLA fibers from 0 to 38.8%, 75.9% and 100%, respectively. The 100% sc-PLA fibers had the highest softening point of 133 °C, and retained the highest percentages of their tensile strength, breaking elongation and Young's modulus after being treated under a hot-wet textile dyeing condition. The satisfactory performance properties made the PLA products suitable for a wider range of industrial applications for replacement of non-biodegradable synthetic polymers. This clean and inexpensive approach for complete stereo-complexation of high-molecular-weight PLAs could be readily incorporated into current continuous industrial-scale production lines for manufacturing of thermoplastics.

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References

- [1] S.D.A. Sharuddin, F. Abnisa, W. Daud, M.K. Aroua, A review on pyrolysis of plastic wastes, *Energ. Convers. Manage.* 115 (2016) 308–326.
- [2] F.A. Leibfarth, N. Moreno, A.P. Hawker, J.D. Shand, Transforming polylactide into value-added materials, *J. Polym. Sci. Pol. Chem.* 50 (2012) 4814–4822.
- [3] Z. Li, X. Zhao, L. Ye, P. Coates, F. Caton-Rose, M. Martyn, Fibrillation of chain branched poly(lactic acid) with improved blood compatibility and bionic structure, *Chem. Eng. J.* 279 (2015) 767–776.
- [4] L.T. Lim, R. Auras, M. Rubino, Processing technologies for poly(lactic acid), *Prog. Polym. Sci.* 33 (2008) 820–852.
- [5] P. Zhang, R. Tian, R. Lv, B. Na, Q. Liu, Water-permeable polylactide blend membranes for hydrophilicity-based separation, *Chem. Eng. J.* 269 (2015) 180–185.
- [6] L. Gardella, D. Furfaro, M. Galimberti, O. Monticelli, On the development of a facile approach based on the use of ionic liquids: preparation of PLLA (sc-PLA)/high surface area nano-graphite systems, *Green Chem.* 17 (2015) 4082–4088.

- [7] L. Zhang, Y. Li, H. Wang, Y. Qiao, J. Chen, S. Cao, Strong and ductile poly(lactic acid) nanocomposite films reinforced with alkylated graphene nanosheets, *Chem. Eng. J.* 264 (2015) 538–546.
- [8] K.M. Nampoothiri, N.R. Nair, R.P. John, An overview of the recent developments in polylactide (PLA) research, *Bioresour. Technol.* 101 (2010) 8493–8501.
- [9] L. Wang, Y. Wang, Z. Huang, Y. Weng, Heat resistance, crystallization behavior, and mechanical properties of polylactide/nucleating agent composites, *Mater. Design* 66 (2015) 7–15.
- [10] A.R. Kakroodi, Y. Kazemi, M. Nofar, C.B. Park, Tailoring poly(lactic acid) for packaging applications via the production of fully bio-based in situ microfibrillar composite films, *Chem. Eng. J.* 308 (2017) 772–782.
- [11] D. Karst, M. Hain, Y. Yang, Mechanical properties of polylactide after repeated cleanings, *J. Appl. Polym. Sci.* 108 (2008) 2150–2155.
- [12] S. Xu, J. Chen, B. Wang, Y. Yang, Molecular surface area based predictive models for the adsorption and diffusion of disperse dyes in polylactic acid matrix, *J. Colloid Interf. Sci.* 458 (2015) 22–31.
- [13] S. Xu, J. Chen, B. Wang, Y. Yang, Sustainable and hydrolysis-free dyeing process for polylactic acid using nonaqueous medium, *ACS Sustain. Chem. Eng.* 3 (2015) 1039–1046.
- [14] D. Karst, D. Nama, Y. Yang, Effect of disperse dye structure on dye sorption onto PLA fiber, *J. Colloid Interf. Sci.* 310 (2007) 106–111.
- [15] Y. Yang, S. Huda, Comparison of disperse dye exhaustion, color yield, and colorfastness between polylactide and poly(ethylene terephthalate), *J. Appl. Polym. Sci.* 90 (2003) 3285–3290.
- [16] N. Reddy, D. Nama, Y. Yang, Polylactic acid/polypropylene polyblend fibers for better resistance to degradation, *Polym. Degrad. Stab.* 93 (2008) 233–241.
- [17] M. Ma, W. Zhou, Improving the hydrolysis resistance of poly(lactic acid) fiber by hydrophobic finishing, *Ind. Eng. Chem. Res.* 54 (2015) 2599–2605.
- [18] D. Karst, Y. Yang, Molecular modeling study of the resistance of PLA to hydrolysis based on the blending of PLLA and PDLA, *Polymer* 47 (2006) 4845–4850.
- [19] D. Karst, Y. Yang, Effect of arrangement of L-lactide and D-lactide in poly (L-lactide)-co-(D-lactide) on its resistance to hydrolysis studied by molecular modeling, *Macromol. Chem. Phys.* 209 (2008) 168–174.
- [20] H. Tsuji, T. Tsuruno, Accelerated hydrolytic degradation of poly(L-lactide)/poly(D-lactide) stereocomplex up to late stage, *Polym. Degrad. Stab.* 95 (2010) 477–484.
- [21] Y. Ikada, K. Jamshidi, H. Tsuji, S. Hyon, Stereocomplex formation between enantiomeric poly(lactides), *Macromolecules* 20 (1987) 904–906.
- [22] Z. Zhang, X. Gao, Z. Hu, Z. Yan, J. Xu, L. Xu, G. Zhong, Z. Li, Inducing stereocomplex crystals by template effect of residual stereocomplex crystals during thermal annealing of injection-molded polylactide, *Ind. Eng. Chem. Res.* 55 (2016) 10896–10905.
- [23] Z. Xiong, G. Liu, X. Zhang, T. Wen, S. Vos de, C. Joiasse, D. Wang, Temperature dependence of crystalline transition of highly-oriented poly (L-lactide)/poly (D-lactide) blend: in-situ synchrotron X-ray scattering study, *Polymer* 54 (2013) 964–971.
- [24] R. Bao, W. Yang, X. Wei, B. Xie, M. Yang, Enhanced formation of stereocomplex crystallites of high molecular weight poly(L-lactide)/poly(D-lactide) blends from melt by using poly(ethylene glycol), *ACS Sustain. Chem. Eng.* 2 (2014) 2301–2309.
- [25] Z. Xiong, X. Zhang, R. Wang, S. Vos de, R. Wang, C.A.P. Joiasse, D. Wang, Favorable formation of stereocomplex crystals in poly(L-lactide)/poly(D-lactide) blends by selective nucleation, *Polymer* 76 (2015) 98–104.
- [26] L. Han, P. Pan, G. Shan, Y. Bao, Stereocomplex crystallization of high-molecular-weight poly(L-lactic acid)/poly(D-lactic acid) racemic blends promoted by a selective nucleator, *Polymer* 63 (2015) 144–153.
- [27] S. Yang, G. Zhong, J. Xu, Z. Li, Preferential formation of stereocomplex in high-molecular-weight polylactic acid racemic blend induced by carbon nanotubes, *Polymer* 105 (2016) 167–171.
- [28] P. Pan, L. Han, J. Bao, Q. Xie, G. Shan, Y. Bao, Competitive stereocomplexation, homocrystallization, and polymorphic crystalline transition in poly(L-lactic acid)/poly(D-lactic acid) racemic blends: molecular weight effects, *J. Phys. Chem. B* 119 (2015) 6462–6470.
- [29] Q. Xie, L. Han, G. Shan, Y. Bao, P. Pan, Polymorphic crystalline structure and crystal morphology of enantiomeric poly(lactic acid) blends tailored by a self-assemblable aryl amide nucleator, *ACS Sustain. Chem. Eng.* 4 (2016) 2680–2688.
- [30] Y. Yang, S. Huda, Dyeing conditions and their effects on mechanical properties of polylactide fabric, *AATCC Rev.* 3 (2003) 56–61.
- [31] G. Gao, M.A. Karaaslan, J.F. Kadla, F.K. Ko, Enzymatic synthesis of ionic responsive lignin nanofibres through surface poly(N-isopropylacrylamide) immobilization, *Green Chem.* 16 (2014) 3890–3898.
- [32] B.K. Ahn, H. Wang, S. Robinson, T.B. Shrestha, D.L. Troyer, S.H. Bossmann, X.S. Sun, Ring opening of epoxidized methyl oleate using a novel acid-functionalized iron nanoparticle catalyst, *Green Chem.* 14 (2012) 136–142.
- [33] O. Monticelli, M. Putti, L. Gardella, D. Cavallo, A. Basso, M. Prato, S. Nitti, New stereocomplex PLA-based fibers: effect of POSS on polymer functionalization and properties, *Macromolecules* 47 (2014) 4718–4727.
- [34] M.J.A. van den Oever, B. Beck, J. Muessig, Agrofibre reinforced poly(lactic acid) composites: effect of moisture on degradation and mechanical properties, *Compos. Part A-Appl. Sci.* 41 (2010) 1628–1635.
- [35] J. Shao, S. Xiang, X. Bian, J. Sun, G. Li, X. Chen, Remarkable melting behavior of PLA stereocomplex in linear PLLA/PDLA blends, *Ind. Eng. Chem. Res.* 54 (2015) 2246–2253.

- [36] J. Shao, J. Sun, X. Bian, Y. Cui, Y. Zhou, G. Li, X. Chen, Modified PLA homochiral crystallites facilitated by the confinement of PLA stereocomplexes, *Macromolecules* 46 (2013) 6963–6971.
- [37] V. Arias, K. Odelius, A. Hoglund, A.-C. Albertsson, Homocomposites of polylactide (PLA) with induced interfacial stereocomplex crystallites, *ACS Sustain. Chem. Eng.* 3 (2015) 2220–2231.
- [38] S.R. Andersson, M. Hakkarainen, S. Inkinen, A. Sodergard, A.C. Albertsson, Polylactide stereocomplexation leads to higher hydrolytic stability but more acidic hydrolysis product pattern, *Biomacromolecules* 11 (2010) 1067–1073.
- [39] H.T. Oyama, S. Abe, Stereocomplex poly(lactic acid) alloys with superb heat resistance and toughness, *ACS Sustain. Chem. Eng.* 3 (2015) 3245–3252.
- [40] Y. Li, X.S. Sun, Preparation and characterization of polymer-inorganic nanocomposites by in situ melt polycondensation of L-lactic acid and surface-hydroxylated MgO, *Biomacromolecules* 11 (2010) 1847–1855.
- [41] Y. Li, F.K. Ko, W.Y. Hamad, Effects of emulsion droplet size on the structure of electrospun ultrafine biocomposite fibers with cellulose nanocrystals, *Biomacromolecules* 14 (2013) 3801–3807.
- [42] Y. Furuhashi, N. Yoshie, Stereocomplexation of solvent-cast poly(lactic acid) by addition of non-solvents, *Polym. Int.* 61 (2012) 301–306.
- [43] Y. Furuhashi, Y. Kimura, N. Yoshie, H. Yamane, Higher-order structures and mechanical properties of stereocomplex-type poly(lactic acid) melt spun fibers, *Polymer* 47 (2006) 5965–5972.
- [44] Y. Furuhashi, Y. Kimura, H. Yamane, Higher order structural analysis of stereocomplex-type poly(lactic acid) melt-spun fibers, *J. Polym. Sci. B Polym. Phys.* 45 (2007) 218–228.
- [45] P. Pan, W. Kai, B. Zhu, T. Dong, Y. Inoue, Polymorphous crystallization and multiple melting behavior of poly(L-lactide): Molecular weight dependence, *Macromolecules* 40 (2007) 6898–6905.
- [46] D. Sawai, M. Tamada, T. Kanamoto, Development of oriented morphology and mechanical properties upon drawing of stereo-complex of poly(L-lactic acid) and poly(D-lactic acid) by solid-state coextrusion, *Polym. J.* 39 (2007) 953–960.
- [47] S. Saeidlou, M.A. Huneault, H. Li, P. Sammut, C.B. Park, Evidence of a dual network/spherulitic crystalline morphology in PLA stereocomplexes, *Polymer* 53 (2012) 5816–5824.
- [48] H. Tsuji, A. Mizuno, Y. Ikada, Properties and morphology of poly(L-lactide). III. effects of initial crystallinity on long-term in vitro hydrolysis of high molecular weight poly(L-lactide) film in phosphate-buffered solution, *J. Appl. Polym. Sci.* 77 (2000) 1452–1464.
- [49] C.A.P. Joiasse, D.W. Grijpma, J.E. Bergsma, F.W. Cordewener, R.R.M. Bos, A.J. Pennings, The influence of morphology on the (hydrolytic degradation of as-polymerized and hot-drawn poly (L-lactide)), *Colloid Polym. Sci.* 276 (1998) 968–975.
- [50] G.L. Siparsky, K.J. Voorhees, F.D. Miao, Hydrolysis of polylactic acid (PLA) and polycaprolactone (PCL) in aqueous acetonitrile solutions: autocatalysis, *J. Environ. Polym. Degrad.* 6 (1998) 31–41.