



A clean approach for potential continuous mass production of high-molecular-weight polylactide fibers with fully stereo-complexed crystallites

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ABSTRACT

A clean and cost-effective method for 100% stereo-complexation in polylactide (PLA) fibers with molecular weight (MW) as high as 6×10^5 demonstrates good potential for industrial-scale continuous manufacture. Polylactide, a widely recognized biodegradable and renewable biopolymer, has a negligible share of plastic markets due to its poor hydrolytic and thermal resistance. Stereo-complexation is effective in overcoming these challenges. However, current stereo-complexation approaches usually require solvents and/or external nucleation reagents, and are expensive and complicated. Moreover, high-MW PLAs favored for developing durable products are difficult to be stereo-complexed. In this research, enantiomeric PLAs both with MW up to 6×10^5 were completely stereo-complexed via a facile thermal treatment on pilot-scale devices. Neither solvent nor nucleation agent was used. For poly(L-lactide) (PLLA) fibers with MW of 6×10^5 , percentage retention of MW and percentage retention of tensile strength after hydrolysis under simulated textile dyeing condition increased from 39% to 93% and from 20% to 89%, respectively, after complete stereo-complexation. The melting point, softening point and percentage retention of MW after hydrolysis of stereo-complexed PLA (sc-PLA) fibers were up to 51 °C, up to 59 °C and up to 183% higher than that of PLLA fibers with the same MW, respectively. The mechanism of thorough stereo-complexation in high-MW PLA fibers was proposed and verified. It is promising to use this approach to broaden industrial applications of renewable and degradable biopolymers for sustainable development of material industries.

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1. Introduction

Polylactide (PLA) is one of the most promising synthetic biopolymers derived from renewable biobased materials to replace petroleum-based counterparts (Brockhaus et al., 2016; Rocca-Smith et al., 2017; Spiridon et al., 2016; Tian et al., 2017). However, ester linkages in PLA are easily cleaved under alkaline or acid conditions (Andersson et al., 2010). Heat could further accelerate the

hydrolytic degradation of PLA (Ma and Zhou, 2015). Due to the poor hydrolytic and thermal stability (Hussain et al., 2015; Karst et al., 2008; Nagarajan et al., 2016; Xu et al., 2015c), PLA products are not durable, and cannot withstand many industrial processes, and thus, cannot compete with non-degradable synthetic polymers. For example, textile industry, which consumes about 67 million tons of synthetic polymers for fiber production in 2015 (Aizenshtein, 2012), have many processes under high temperature, high humidity, strong acid or strong alkaline conditions (Karst et al., 2007; Xu et al., 2015b; Yang and Huda, 2003). Thus, it is imperative to improve hydrolytic resistance for broader uses of PLA in textile and many other areas. Many approaches, including blending with non-degradable polymers (Reddy et al., 2008), copolymerization (Fukushima et al., 2007) and crosslinking (Xiong et al., 2016), have been extensively reported, but show limited effectiveness.

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Stereo-complexation has been proved efficacious in enhancing hydrolytic and thermal stability of products from PLA and many other biopolymers. Karst and Yang (2006, 2008) verified the effectiveness of blending of poly(L-lactide) (PLLA) and its enantiomer poly(D-lactide) (PDLA) for enhancing hydrolytic stability of PLA fibers via molecular modeling. The blended PLLA and PDLA polymers were stereo-complexed into crystallites with significantly stronger and more stable intermolecular hydrogen bonds, comparing to H-bonds in homo-crystallites. Complete stereo-complexation of PLA in relevant products was preferred in developing durable eco-friendly products.

Poly lactides with high molecular weight (MW) are favored for development of degradable products with durability, but are difficult to be completely stereo-complexed, as reported in several publications. For example, Pan et al. (2015) and Xie et al. (2016) indicated that, enantiomeric PLA with MW lower than 2.0×10^4 and higher than 8.0×10^4 tended to form both stereo-complexed crystallites (sc-crystallites) and homo-crystallites, respectively. Shao et al. (2015) studied crystallization of PLLA/PDLA blended films and stated that low MW could facilitate stereo-complexation. Purnama and Kim (2014) blended PLLA and PDLA at different MWs (8.7×10^4 – 4.4×10^5), and also found coexistence of sc-crystallites and homo-crystallites in high-MW ($\geq 2.1 \times 10^5$) PLLA/PDLA. Small MW facilitates stereo-complexation of PLA, attributing to the high mobility of relatively short polymers in melt or solution. Nevertheless, the relevant products from small-MW biopolymers were intrinsically brittle, and could not be as durable as common plastic products. On the contrary, high MW could enhance the ductility and other performance properties of stereo-complexed PLA (sc-PLA) products. But the stereo-complexation processes for high MW PLAs were more time- and energy-consuming, as the high MW polymers are much less mobile.

Till now, durable PLA products have not been industrially produced, as it remains challenging to include the step of stereo-complexation into industrial processes. Current stereo-complexation strategies usually use external solvent for blending of racemic PLAs (Furuhashi and Yoshie, 2012; Tsuji and Yamamoto, 2011), or harmful nano-sized nucleation agents to accelerate stereo-complexation (Cao et al., 2016; Xu et al., 2015a). These approaches have not been introduced into continuous production lines, probably due to the complexity of including feeding/separation systems of solvent or feeding systems of nucleation agents, hazard of solvents and nucleation agents, and resultant high costs (Wang et al., 2015).

In this work, equimolar PLLA and PDLA with the same MW ranging from 1×10^5 to 6×10^5 were melt-spun and completely stereo-complexed via post-spinning thermal treatment. To study the relationship between MW and fiber properties, as well as that between degree of stereo-complexation (%sc) and fiber properties, crystalline structures, thermal behavior and thermal mechanical properties of the sc-PLA fibers were investigated and analyzed using Wide-Angle X-ray Diffraction (WAXD), Differential Scanning Calorimeter (DSC) and Dynamic Mechanical Analysis (DMA), respectively. This stereo-complexation approach could notably facilitate continuous cleaner mass production of materials with durability from renewable and degradable PLAs. Overall, the sc-PLA products could provide enhanced competitiveness over petro-products, and subsequently become an alternative solution to current sustainable issues associated with non-degradability of petroleum derived products.

2. Material and methods

2.1. Materials

PLLA pellets were purchased from a US company. D-lactides (racemic purity of 98%, water content of 200 mg/L) were supplied by

Table 1

Viscosity average molecular weights and thermal properties of PLLA and PDLA used in this study.

Sample ^a	$M_v (\times 10^5 \text{ g mol}^{-1})^b$	$T_g (\text{°C})^c$	$T_m (\text{°C})^d$
L1	1.0	62	163
L2	2.1	62	171
L3	3.0	64	175
L6	6.2	65	179
D1	1.0	63	161
D2	2.0	62	168
D3	3.2	65	174
D6	6.1	65	179

^a PLLA and PDLA are abbreviated as L and D, respectively.

^b M_v : viscosity-average molecular weight.

^c T_g : Glass transition temperature.

^d T_m : Melting temperature.

Xinning Biobased Material Company, Ltd. (Zhejiang, China). Catalyzed with stannous octoate, PDLA was synthesized in our lab on pilot scale via ring-opening polymerization under vacuum condition at 140–180 °C. Table 1 lists key parameters of PLLA and PDLA. Chloroform (99%) and hexafluoro-2-propanol (HFIP) (99%) were purchased from Sigma-Aldrich, USA. Sodium dihydrogen phosphate and sodium hydroxide were purchased from Alfa Aesar, USA.

2.2. Fiber preparation

The PLLA and PDLA were dried at 80 °C in a vacuum oven for 12 h before melt blending. PLLA/PDLA (50:50, wt%) pellets and pure PLLA pellets were melt spun on a MATE-V spinning device (Ube, Japan). The molten pellets were extruded (as shown in Fig. 1 left) at temperatures ranging from 230 °C to 250 °C and from 200 °C to 220 °C, respectively, and then taken up at 200 m min^{-1} into fibers (Fig. 1 right). The PLLA were drawn at a drawing ratio of 3 times at 80 °C and annealed at 100 °C (Reddy et al., 2008). The as-spun PLLA/PDLA fibers were drawn at a drawing ratio of 3 times at 120 °C (Pan et al., 2017). To generate 100% stereo-complexed crystallites in PLLA/PDLA fibers, the as-spun PLLA/PDLA fibers was annealed on a home-made continuous fiber thermal stereo-complexing device (schematic diagram as shown in Fig. 2) at 200 °C, which was higher than 170 °C, the T_m of individual PLLA or PDLA, and lower than 230 °C, the T_m of sc-PLA, for a certain time under 10 MPa in tension. Dimensions (L × W × H) of the home-made continuous fiber thermal stereo-complexing device are 4.0 m × 2.0 m × 1.5 m with a processing temperature ranging from 100 to 250 °C. Temperature is automatically controlled by an electronic sensor.



Fig. 1. MATE-V melt spinning device. Left: the extrusion portion; Right: the fiber winding portion.

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