



Complete stereo-complexation of enantiomeric polylactides for scalable continuous production



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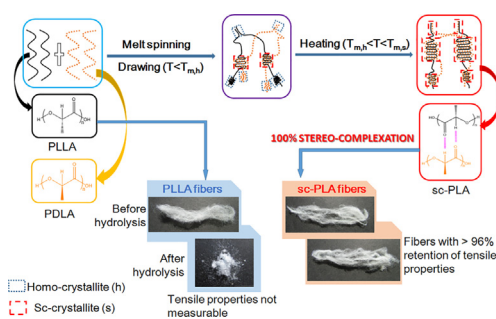
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HIGHLIGHTS

- 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



ARTICLE INFO

Article history:

Received 5 April 2017

Received in revised form 18 June 2017

Accepted 12 July 2017

Available online 13 July 2017

Keywords:

Continuous process

Poly lactide

Stereo-complexation

Hydrolysis resistant

Softening temperature

Poly lactic acid

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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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 (M_v) PLA polymers, which are usually required in production of high-quality plastics. Complete stereo-complexation of PLA with M_v 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 M_v 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 = 3×10^5 g mol⁻¹) was purchased from a company. PDLA (M_v = 3×10^5 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

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