Polymer 140 (2018) 47–55

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Disentanglement induced by uniaxial pre-stretching as a key factor for toughening poly(L-lactic acid) sheets

Yunjing Chen [a, b], Lijing Han [a, *], Dandan Ju [a], Tingting Liu [a], Lisong Dong [a, **]

[a] *Key Laboratory of Polymer Ecomaterials, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, PR China*
[b] *University of Science and Technology of China, Hefei, 230026, PR China*

ARTICLE INFO

Article history:
Received 13 December 2017
Received in revised form
5 February 2018
Accepted 14 February 2018
Available online 15 February 2018

Keywords:
Poly(L-lactic acid)
Pre-stretching
Toughness

ABSTRACT

Poly(L-lactic acid) (PLLA) sheets with dramatic improvement of mechanical properties, especially toughness, were obtained by uniaxial pre-stretching around T_g. It was found that a network structure consisting of cohesional entanglements was formed during the usual compression molding process, leading to the brittleness of PLLA, and the destruction of the network structure due to disentanglement after pre-stretching, leading to the toughness of PLLA. The network structure could not be destroyed when pre-stretching ratio (PSR) was in the elastic deformation region I and strain softening region II (PSR < 0.2). However, when PSR got into the strain hardening region III (PSR $= 0.2$), the network structure was destroyed resulting from the disentanglement, leading to the brittle to ductile transition. With PSR increasing from 0.2 to 0.4, the orientation was formed in pre-stretched PLLA, leading to further increase of the elongation at break. And then the degree of orientation increased along with the occurrence of the mesophase (PSR ≥ 0.5), therefore, the modulus and strength increased, while the elongation at break decreased. However, the elongation at break was still larger than that of undrawn PLLA.

1. Introduction

Poly(L-lactic acid) (PLLA) is one of the most popular bio-based plastics with excellent biocompatibility and biodegradability. PLLA has high tensile strength and modulus, and can also be processed variously as sheets, films, bottles, fibres and textiles with a broad market potential in biomedical and commodity fields. Therefore, PLLA is expected to be a sustainable alternative to conventional petroleum-based polymers [1]. However, the inherent brittleness has significantly impeded its wide applications. To overcome this drawback, a good deal of approaches have been used to improve the toughness of PLLA, such as plasticization [2–6], copolymerization [7–9], and melt blending [10–15]. Among them, blending PLLA with flexible polymers has proven to be an effective and economic method, unfortunately, the increase in toughness is accompanied by an obvious decrease in strength and modulus [16].

It is known that stretching is a green and effective modification method without any additives. Numerous investigations have been focused on the development of orientation and the strain-induced crystallization when drawing PLLA in the rubbery state [17–22]. Mulligan et al. [22] reported the occurrence of a nematic-like order upon drawing amorphous PLLA in the rubbery temperature ranges using *X*-ray scattering and birefringence measurements. Stoclet et al. [18] discussed the strain-induced structural changes in amorphous PLLA upon uniaxial stretching at 70–100 °C. The mesophase was found at no higher than 70 °C by stretching amorphous PLLA, and a crystalline phase named α' crystal form was generated when the drawing temperature was above 70 °C. In addition, Hu et al. [19] identified the existence of the mesophase with a characteristic band at 918 cm^{-1} in PLLA samples drawn at 65 °C by the WAXD and polarized FTIR techniques.

Although abundant works have been done on strain-induced structural changes of amorphous or crystalline PLLA, the mechanical response of drawn PLLA, especially the improvement of toughness, remained poorly addressed. Wu et al. [23] reported that the biaxial-stretched PLLA films showed the increased tensile stress but decreased tensile strain when the biaxial stretching ratio (the ratio of the length after biaxial stretching to the original length of the sample) exceeded 2 × 2. Velazquez-Infante et al. [24] found that the tensile properties of drawn PLLA films including modulus, stress and strain at break increased compared with the amorphous films. However, the mechanism of enhanced mechanical properties

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* Corresponding author.
** Corresponding author.
E-mail addresses: ljhan@ciac.ac.cn (L. Han), dongls@ciac.ac.cn (L. Dong).

https://doi.org/10.1016/j.polymer.2018.02.032
0032-3861/© 2018 Published by Elsevier Ltd.

produced by pre-stretching process was not reported in detail. Recently, Jariyasakoolroj et al. [25] clarified that isotropically small crystalline lamellae induced by biaxial-stretching was the key microstructure to obtain super-tough PLLA which tensile strength reached 180 MPa and elongation at break was close to 80%. However, the toughness of the drawn PLLA was still small, and the stretching rate (75 mm/s) and draw ratio (5 × 5) were so high that could not be achieved easily in the actual production.

In the present work, the PLLA was uniaxially pre-stretched at the rubbery state for the purpose of improving the mechanical properties of it. The mechanical properties, thermal behavior, crystallization behavior and microstructure of undrawn PLLA and ps-PLLA were determined to establish a relationship between the microstructure and the mechanical properties, and then the toughening mechanism of pre-stretching was obtained. These results will help us to obtain the PLLA with as-desired mechanical properties by simply controlling the processing conditions and so extend the application of PLLA.

2. Experimental section

2.1. Material and sample preparation

The PLLA used in this work is the 4032D grade material from Natureworks LLC (USA) consisting of 98% L-lactic acid and 2% D-lactic acid. It exhibited a weight-average molecular weight of 207 000 g/mol and dispersity of 1.74 (gel permeation chromatographic analysis, GPC). The glass transition temperature (T_g) and melting temperature (T_m) of PLLA were 60.6 °C and 169.9 °C, respectively (DSC analysis). Before procession, PLLA was dried in a vacuum oven at 80 °C for 12 h. The pellets were melted by using a torque rheometer (XSS-300, ShanghaiKechuang Rubber Plastic Mechanical Equipment Co., Ltd., China) with a screw speed of 40 rpm for a total mixing time of 5 min at 175 °C, and then the samples were cut into small pieces for compression molding. After melting process, samples were prepared using a hot-press with a wide dumbbell shaped die at 180 °C for 3 min followed by cold-press at room temperature to form PLLA sheets with necks of 25.0 mm long and cross-sectional areas of 22.0 mm × 1.0 mm, which were used for uniaxial-stretching in the next step. Besides, some of hot-pressed samples were quenched by liquid nitrogen after melting at 180 °C for 3 min, and then the quenched samples were used for corresponding characterization immediately.

2.2. Pre-stretching experiments

In order to obtain stretched PLLA sheet, the pre-stretching experiments for PLLA were carried out on a tensile-testing machine (Instron-1121, USA) equipped with a high-low temperature environmental chamber at a stretching rate of 5 mm/min. Parallel ink marks like the gauge were printed along the sample so as to determine the local plastic strain, *i.e.* pre-stretching ratio (PSR) according to the following equation:

$$PSR = L/Lo - 1 \tag{1}$$

where L and L_o were the gauge length of the sample after and prior to deformation, respectively. Before pre-stretching, the specimens were heated to the pre-stretching temperature (T_{ps}) and equilibrated at it with 3 min. Here, 60 °C, closed to the T_g of PLLA, was chosen as the T_{ps}. In order to select appropriate PSR, the deformation behaviors of PLLA at 60 °C were traced. The result is showed in Fig. 1. It was found that there was a strain softening zone in the engineering stress-stretching ratio curve, indicating the formation of neck. Therefore, it would be more meaningful to give the correlation of true internal stress (engineering stress × (L/L_o)) with stretching ratio. The true internal stress-stretching ratio curve included three distinct regions: elastic deformation region I, strain softening region II, and strain hardening region III. It displayed an elastic deformation with a high Young's modulus within the low strain range of about 0.02, and an obvious strain softening with a decrease in true internal stress occurred after the yield point. The strain hardening behavior could be observed with the true internal stress increasing after strain softening [20,26]. Therefore, according to the true internal stress-stretching ratio curves, various PSRs in above-mentioned three distinct regions were performed for PLLA as marked in Fig. 1. Thus, various stretched PLLA sheets were acquired. After pre-stretching, samples were cooled to room temperature by air before they were removed from the collet.

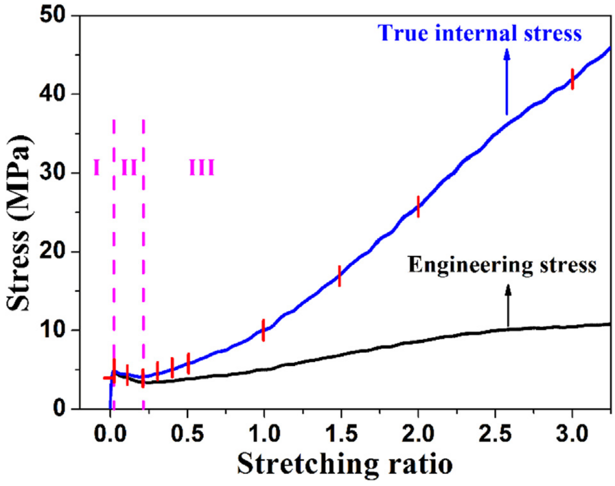

Fig. 1. Stress-stretching ratio curves of PLLA sheets with the division of regions I, II, and III during pre-stretching process at 60 °C. (The stretching ratio marked from left to right represents 0.01, 0.02, 0.1, 0.2, 0.3, 0.4, 0.5, 1.0, 1.5, 2.0, 3.0, respectively.)

2.3. Tensile measurements

The static mechanical properties of quenched PLLA, undrawn PLLA and pre-stretched PLLA (ps-PLLA) were measured by a tensile-testing machine (Instron-1121, USA) according to ISO 527–1:1993. The ps-PLLA samples were cut from the pre-stretched PLLA sheets along the pre-stretching direction into dumbbell-shaped specimens with necks of 20.0 mm long and 4.0 mm wide, of particular note, the thickness of the ps-PLLA varied with the PSR from 1.00 mm to 0.50 mm. Meanwhile, the quenched and undrawn PLLA samples, cut from the previous compression molding sheets, were also tested for comparison. The test was carried out with a crosshead speed of 5 mm/min at room temperature in the tensile mode. At least five specimens were tested for each sample to get an average value.

2.4. DSC measurements

Thermal analysis was performed using a TA Instruments differential scanning calorimeter (DSC) Q20 with a Universal Analysis 2000. Sample weights were in the range of 5–8 mg. The heat enthalpy and temperature of the DSC were calibrated with standard indium. All the specimens were heated from 0 °C to 190 °C at a heating rate of 10 °C/min under nitrogen atmosphere.