Journal of Materials Processing Technology 232 (2016) 184–194

Contents lists available at ScienceDirect

Journal of Materials Processing Technology

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

Microstructures and mechanical properties of polylactic acid prepared by a cold rolling process

Lijun Wang, Jianhui Qiu*, Eiichi Sakai

Department of Machine Intelligence and Systems Engineering, Faculty of System Science and Technology, Akita Prefectural University, 84-4 Tsuchiya Ebinokuchi, Yurihonjo, Akita 015-0055, Japan

ARTICLE INFO

Article history:
Received 15 July 2015
Received in revised form 1 February 2016
Accepted 6 February 2016
Available online 8 February 2016

Keywords:
Polylactic acid
Rolling process
Microstructures
Mechanical properties

ABSTRACT

A cold rolling process was performed with extruded polylactic acid (PLA) as the crystalline polymer at different rolling ratios. The variations of the crystalline morphology, crystallinity, density, molecular orientation, and the microhardness were investigated during the process. Moreover, the dynamic mechanical properties and mechanical properties were evaluated by dynamic mechanical analysis and tensile test, respectively. The results showed that plastic deformation more easily occurred on the surface than on the interior. In addition, with the increase of the rolling ratio, the crystallinity decreased; however, the molecular orientation increased. Dynamic mechanical analysis revealed that the rolled PLA displayed an anisotropy during the process. Moreover, the tensile strength increased from 51.1 MPa to 86.0 MPa, and the fracture strain increased from 5.3% to 103.1%, in the case of a 60% rolling ratio along the rolling direction, indicating that the PLA was homogenized during the rolling process. This certified that an appropriate rolling process (i.e., the 60% rolling ratio) was conducive for improving the comprehensive mechanical properties of PLA in the rolling direction.

1. Introduction

In the field of materials, recycling is one of the most important technologies to conserve resources and to reduce waste. Biological degradation is widely considered as an effective recycling technology. In recent years, many biologically degradable polymers, e.g., polybutylene succinate (PBS), polycaprolactone (PCL) and polylactic acid (PLA) have been developed. Out of these polymers, PLA is considered as one of the most promising biodegradable, compostable, thermoplastic, and crystalline polymers. Additionally, PLA is a sustainable alternative to petrochemical-derived products and can be derived from renewable resources (Jonoobi et al., 2010). PLA has many advantages, such as high-strength, high-modulus (Garlotta, 2001) and good stiffness (Jonoobi et al., 2010). However, because PLA belongs to the group of brittle materials, the fracture strain is very low (approximately 5%) (Garlotta, 2001). Hence, this disadvantage may limit its applications in industry.

To improve the ductility of PLA and extend its industrial applications, many researchers have proposed various methods to increase its ductility while maintaining or reinforcing its original strength. To achieve ideal mechanical properties and to greatly enhance its commercial potential, two common methods have been developed. One is to incorporate fillers into the polymers, such as calcium phosphate (Bleach et al., 2002), carbon nanotube (Kuan et al., 2008), and natural fibers (Oksman et al., 2003). In particular, Bondeson and Oksman (2007) prepared PLA/cellulose nanowhisker (PLA/CNW) nanocomposites, and the results of the tensile property tests showed that only relative small improvements in the tensile properties of the prepared nanocomposites were achieved (the tensile strength was 67.7 MPa, and the elongation at break was approximately 2.4%). Moreover, Jonoobi et al. (2010) reported that the tensile strength of cellulose nanofiber-reinforced PLA composites increased from 58 MPa to 71 MPa, whereas the maximum strain was only 2.7–3.4%.

The other approach is to prepare polymers by plastic processing. Carrasco et al. (2010) reported that extruded/injected PLA showed an increase in the elongation at break (32–35% higher). Rhim et al. (2006) found that PLA films prepared by the thermocompression method were strong and brittle, with maximum tensile strength and maximum elongation at break values of 44.0 ± 2.2 MPa and 3.0 ± 0.1%, respectively. These researchers attempted to improve the mechanical properties of PLA by using plastic processing. Unfortunately, the effect was not as good as expected (Yu et al., 2008).

In general, it is well known that microstructures, including the crystalline structure, molecular orientation, and crystallinity, can influence the mechanical properties of crystalline polymers. Many

* Corresponding author. Tel.: +81 184 27 2134; fax: +81 184 27 2134.
E-mail address: qiu@akita-pu.ac.jp (J. Qiu).

http://dx.doi.org/10.1016/j.jmatprotec.2016.02.006
0924-0136/

researchers have reported that plastic processing, such as die-drawing (Chapleau et al., 2005), roller drawing (Lee et al., 2008), tensile drawing (Bao et al., 2012), equal channel angular extrusion (Qiu et al., 2012a), hydrostatic extrusion (Gibson et al., 1974) and rolling process (Qiu et al., 2012b), can achieve good mechanical properties. In particular, the rolling process can achieve high molecular orientation for polymers while preventing the generation of voids during processing, which has been reported by Nakayama et al. (2001). Therefore, the rolling process has been extensively employed for producing polymers with good properties, such as polyethylene (PE) (Wang et al., 1993), polyoxymethylene (POM) (Mohanraj et al., 2008), polypropylene (PP) (Qiu, 2002), and others. Both Qiu et al. (2000a) and Murata et al. (2013) investigated the changes of morphology and mechanical property in molded polymers. During plastic processing, a multilayer structure will form because of the different cooling processes on the surface as well as in the inner part (Murata et al., 2012). Moreover, the crystallinity is decreased and the molecular orientation is increased by the rolling process as observed with micro Fourier transform infrared (FT-IR) spectroscopy (Qiu et al., 2000b). These researchers obtained the internal structure information in the whole cross section of the polymer and accurately assessed the change of the PP microstructure via the rolling process. To the best of our knowledge, there has been no research conducted on the effect of crystallinity and orientation on microstructures (i.e., crystal morphology, crystallinity, and molecular orientation) and mechanical properties of PLA produced by a cold rolling process. Therefore, it is essential to know whether the rolling process changes the microstructure of PLA, which is key for improving of the mechanical properties of PLA, especially its ductility.

In the present work, a cold rolling process was carried out for extruded PLA as the crystalline polymer under different rolling ratios. The crystal morphology, crystallinity, and molecular orientation were investigated using optical microscopy (OPM), differential scanning calorimetry (DSC), density method, and X-ray diffraction (XRD). Moreover, the microhardness distribution, dynamic mechanical analysis, and tensile properties of PLA at each rolling ratio were measured. Based on the measurement results, the effects of the rolling ratios on the microstructures and mechanical properties were discussed.

2. Experimental

2.1. Materials

Polylactic acid (PLA) was purchased from Nature Works LLC (Ingeo 3001D, America) with a density of 1.24 g/cm^3 (ASTM D792) and a melt flow index of 22 g/(10 min) (ASTM D1238). Its residual moisture content was less than 0.025%, which was recommended to prevent viscosity degradation.

2.2. Specimen preparation and the rolling process

The basic PLA material was vacuum-dried at 50 °C for 8 h. Then, it was manufactured using a twin screw extruder (KZX25TW-60MG-NH (-1200)-AKT, Technovel Co., Ltd., Osaka, Japan) with a screw speed of 100 rpm, and the temperature profile was varied from 150 °C at the feeding zone to 190 °C at the die. The extruded PLA was cooled down in a water bath and pelletized after the first extrusion process. Then, the granular extruded PLA was dried at 50 °C for 8 h again, and PLA plates were produced by the same extruder at the same extrusion conditions. The reason for two extrusions is to compare the PLA and its composites with each other at the same thermal history and to discuss their properties in a later paper.

Thereafter, the extruded PLA plates were used for the rolling process. The rolling process was performed with different rolling ratios (0%, 20%, 40%, 60, and 75%) to evaluate the effect of the rolling ratio on the properties and morphology of PLA. 2000 mm (length) × 100 mm (width) × 1.2 mm (thickness; the maximum thickness was 1.6 mm) extruded plates were machined into specimens with dimensions of 100 mm (length) × 80 mm (width) × 1.2 mm (thickness; the maximum thickness was 1.6 mm). The rolling process was carried out by a rolling machine (TKE-0; Imoto Machinery Co., Ltd., Tokyo, Japan) at room temperature (23 ± 2 °C) with a rotation speed of 3 m/min (Fig. 1). The rolling direction was matched to the extrusion direction and the effective width and diameter of each roller were 150 mm and 100 mm, respectively. The rolling ratio ξ was calculated using the following equations.

$$\xi = \left[\frac{(H_0 - H_1)}{H_0}\right] \times 100\% \quad (1)$$

where H_0 is the initial thickness of the specimen, and H_1 is the thickness of the rolled specimen, which was measured by a micrometer after the rolling process.

Finally, the rolled plates were cut using a dumbbell-shaped mold to obtain specimens with dimensions of 75 mm (length) × 10 mm (width), but with different thicknesses based on the different rolling ratios. The different thicknesses of the rolled plates were achieved by adjusting the distance between the two rollers (Fig. 1). The specimens were used for evaluating the variations of crystallinity and molecular orientation of PLA and its mechanical properties.

2.3. Observation of internal microstructures

The internal microstructures of PLA with different rolling ratios were observed by a polarized optical microscopy (Eclipse model ME600D, NIKON, Tokyo, Japan) to investigate the variation of the crystal structures. To achieve visibility, the middle part of dumbbell-shaped specimens was cut into 10 μm slices in longitudinal sections by a microtome (RM2145, Leica Microsystems, Tokyo, Japan).

2.4. Investigation of crystallization behaviors

2.4.1. Differential scanning calorimetry

Differential scanning calorimetry (DSC) was performed using a DSC instrument (X-DSC7000, SII Nano Technology Inc., Tokyo, Japan). The specimens (approximately 10 mg) for the tests were cut from the middle part of the dumbbell-shaped specimens in the whole cross-sectional direction, and were scanned from 30 to 200 °C at a scan rate of 10 °C/min under a nitrogen flow of 50 mL/min. Only the heating process was carried out to investigate the effect of the rolling ratio on the crystallization behavior of the rolled PLA. The DSC result was obtained from three measurements of each specimen group. Again, the degree of crystallization χ_c of PLA was determined from the DSC heating traces by the following equation.

$$\chi_c = \left[\frac{\Delta H_m - \Delta H_c}{H_m^0}\right] \times 100\% \quad (2)$$

where ΔH_m is the melting enthalpy during the heating process, ΔH_c is the enthalpy of crystallization, $\Delta H_m{}^0$ is the enthalpy for 100% crystallization of PLA, which is approximately 93.6 J/g (Kalb and Pennings, 1980).

2.4.2. Determination of the density

A water displacement method (JIS K7112, method A) was employed to measure the density of the rolled PLA by using an