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Structure and biocompatibility of highly oriented poly(lactic acid) film produced by biaxial solid hot stretching

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ABSTRACT

Highly oriented long-chain-branched poly(lactic acid) (LCB-PLA) film was fabricated through biaxial hot stretching in solid state. Compared with neat PLA, more homogeneous film with higher draw ratio can be obtained for LCB-PLA. With increasing draw ratio, the long period, lamellae thickness and grain size of LCB-PLA decreased, while the crystallinity increased. For LCB-PLA with draw ratio of 6*6, the tensile strength and elongation at break can reach up to 208 ± 6 MPa and 85% respectively. After drawing, the increasing content of —CH3 and C=O group on the surface of LCB-PLA film was beneficial for cell adhesion and growth on it.

Introduction

Poly(lactic acid) (PLA, –[CH(CH_3)COO]$_n$–) is a linear aliphatic thermoplastic polyester which is produced from lactic acid by converting sugar or starch obtained from renewable sources (e.g., corn, wheat, or rice) [1–3]. PLA has been considered to be a good candidate for biomedical materials due to its biodegradable and biocompatible nature, and approved by the Food and Drug Administration (FDA) for numerous clinical applications, such as sutures, bone plates, abdominal mesh, and extended-release pharmaceuticals [4–6]. However, some problems still exist for PLA when it acts as implanted biomaterials and bio-devices: the mechanical strength of PLA is still not sufficient for weight-bearing implant fixation; the relatively poor biocompatibility of PLA may cause immunological rejection and lead to the formation of an intolerable inflammatory reaction when it is implanted in the body.

Polymer sheets or films can be oriented by biaxial stretching (BO), as a consequence, the changes of microstructure give the drastic change in mechanical properties as well as other performances such as high-gloss, transparency, excellent gas barrier, etc [5–7]. In industrial film processing, simultaneous biaxial stretching modes are widely used [8–10]. In this case, deformation of a sheet or film occurs in both machine and transverse directions, and produces nearly equivalent mechanical properties in both directions. Yu et al. [11] reported that stretching of a melt PLA film induced crystallization and chain relaxation, and thus resulted in an increase of film mechanical properties (3.5 ± 0.2 GPa in modulus and 142.8 ± 4.9 MPa in tensile strength). Tsai et al. [12] successfully prepared transparent biaxial oriented PLA (BOPLA) films with improved mechanical properties and dimensional stability by controlling the crystallization of PLA and stretching in 4*4 at 80 °C. Jariyasakoolroj et al. [13] fabricated super tough BOPLA film (180 MPa in tensile strength and 80% in elongation at break) by stretching in 5*5 through biaxial stretching processing at quite high stretching rate. Nevertheless, it can be concluded that, the mechanical strength of these biaxial oriented PLA materials is still not sufficient for weight-bearing implant fixation due to their low biaxial draw ratio, because the tensile strength higher than 200 MPa must be required for the fixation. Moreover, no literature on the effect of orientation on the biocompatibility of PLA can be available.

The great difficulty in ultra-drawing (especially two-dimensional drawing) of PLA was mainly due to its low viscosity and poor melt strength [14–17]. In our previous studies, in order to enhance the melt strength and thus obtain high orientation degree, long chain branched PLA (LCB-PLA) was prepared by reactive processing [18]. It was found that the molecular weight of PLA increased and topological structures with star-like chain and tree-like chain formed, and consequently the draw ratio as high as 1200% can be achieved during the subsequent hot stretching. The successful formation of long chain branched structure for LCB-PLA and the

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achievement of high draw ratio for LCB-PLA during uniaxial solid hot drawing processing encouraged us to perform biaxial orientation processing study.

In this work, the rheological behavior of LCB-PLA was first investigated in terms of dynamic rheology and uniaxial extensional viscosity by comparison with PLA, from which the processing stability and stretch-ability of the materials can be readily examined. Then, the biaxial oriented films of PLA and LCB-PLA were prepared through simultaneous biaxial drawing technology. The structure evolution during biaxial orientation and mechanical properties of the resultant oriented samples were studied, and the mechanism of biocompatibility improvement was tried to be explored.

Experimental

Materials

Poly(lactic acid) (PLA) (NatureWorks® PLA Polymer 3052D) was supplied by Nature Works in pellet form, and the molecular weight (M_w) was about 1×10^5. Pyromellitic dianhydride (PMDA) (AR) was obtained from Sinopharm Chemical Reagent Co., Ltd, China. Pentaerythritol polyglycidyl ether (PGE) (AR) was obtained from Energy Chemical Co. Ltd., China.

Preparation of biaxially stretched PLA films

Long chain branched PLA (LCB-PLA)

After dried at 70 °C for 5 h in a vacuum oven, PLA pellets were added in a Haake internal melt mixer (Rheocord 90, Germany). After they were totally melted, PMDA (3 wt% of PLA) was added to react with PLA for several minutes, and then PGE (3 wt% of PLA) was added into the mixture. When the reaction was completed, the product was cut into small granules.

Biaxially stretched PLA film

The PLA and LCB-PLA pellets were pressed into sheets ($50 \times 50 \times 1\ mm^3$) and then biaxially stretched in two perpendicular directions (machine direction (MD) and transverse direction (TD)) at the same rate and ratio by using a biaxial stretching machine. After the desired draw ratio was obtained, the sample was cooled down to room temperature, and then the load was released.

Measurements

Dynamic rheological analysis

The dynamic rheological properties of PLA samples were studied with a stress-controlled rheometer (AR 2000ex, TA Instruments, New Castle, DE) equipped with parallel-plate geometry (diameter of 25 mm). The gap was fixed at 1200 μm. Firstly the strain sweep was carried out with a strain range of 0.01–1000% and a frequency of 1 Hz to determine the linear viscoelastic (LVE) zone for PLA and LCB-PLA. The frequency sweep was conducted with a frequency range from 0.01 to 100 Hz and the applied strain was 1% (in the linear viscoelastic region of the melts). Dynamic time sweep tests were conducted with a frequency of 2 Hz and the applied strain was 1%. All rheological experiments were conducted in a nitrogen atmosphere at 170 °C.

Extensional rheology analysis

The sheets of PLA samples were cut into pieces with width of 10 mm and length of 17 mm for the uniaxial extensional viscosity measurements, which were carried out with ARES rheometer (TA instrument, New Castle, DE) under constant strain rates of 0.1, 0.5, 1 s^{-1} at 160 °C. A pre-elongation for 3 s was performed before the measurements to make sure no slipping between the sample and the fixtures.

Non-isothermal DSC analysis

The non-isothermal crystallization of PLA samples was performed with a Netzsch 204 differential scanning calorimetry (DSC) (Phoenix Co, Germany). The temperature scale of DSC was calibrated with indium. Granulated samples of about 10 mg were heated from ambient temperature to 200 °C at a constant rate of 10 K/min under nitrogen atmosphere. X_c can be calculated with the following equation [19]:

$$X_c = (\Delta H_m / \Delta H_0)^* 100\% \quad (1)$$

where ΔH_m is the melting enthalpy of the samples and ΔH_0 is the balance melting enthalpy, i.e., the melting enthalpy of 100% crystallizing polymer.

Two-dimensional X-ray diffraction analysis

Two-dimensional small-angle X-ray scattering (2D-SAXS) and two-dimensional wide-angle X-ray diffraction (2D-WAXD) analysis of PLA samples were carried out on the BL16B beamline in Shanghai Synchrotron Radiation Facility (SSRF), Shanghai, China. The wavelength used was 0.124 nm. 2D-SAXS and 2D-WAXD patterns were collected by a MAR CCD X-ray detector (MAR-USA) with an acquisition time of 20 s for data frame. The sample-to-detector distance was 2835 mm for 2D-SAXS, and 166 mm for 2D-WAXD. All X-ray images were corrected for background scattering, air scattering, and beam fluctuations.

Mechanical properties

The mechanical properties of PLA samples were measured with a 4302 material testing machine (Instron Co, USA) according to ISO527/1-1993 (E). The test speed was 50 mm/min, and the sample length between benchmarks was 25 mm.

Contact angle measurement

The hydrophilicity of the surface of PLA samples was characterized on the basis of contact angle measurement with an OCA20 contact angle goniometer (Dataphysics, Germany) equipped with video capture at ambient temperature. For the static contact angle measurements, a total of 2 μl double distilled water and ethylene glycol (AR) was dropped on the air-side surface of the samples at room temperature, and the contact angle was measured after 10 s. At least five measurements were averaged to get a reliable value.

Attenuated total reflection Fourier transform spectroscopy (ATR-FTIR)

The chemical groups on PLA and LCB-PLA surface before and after orientation were analyzed with attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR, Magna IR 560, Nicolet, USA). The scanning range was in the range of 400–2000 cm^{-1}.

Three-dimensional digital microscope

The surface morphology of PLA samples was observed with a VHX-1000C digital microscope (Keyence, Japan) by three-dimensional (3D) profile measurement mode.

Protein adsorption

Protein adsorption measurement was carried out with bovine serum albumin (BSA) and fibronectin (Fn) solutions under the static condition. Firstly, the samples with an area of $1 \times 1\ cm^2$ were immersed in a phosphate buffer solution (PBS), containing BSA or Fn with the concentration of 50 μg/ml, and incubated at 37 °C for 1 h. Then the samples were rinsed slightly with PBS solution and

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