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Crystallization of equimolar poly(L-lactide)/poly(D-lactide) blend below the melting point of α crystals under shear

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ABSTRACT

The isothermal crystallization behavior of a 1:1 poly(L-lactide)/poly(D-lactide) (PLLA/PDLA) mixture under pulsed shear was investigated by *in-situ* polarized light optical microscopy (POM) and wide angle X-ray scattering (WAXS). The effects of shear rate and temperature were studied. The results showed that application of shear flow increased the nucleation density, crystallization rate and degree of orientation for both stereocomplex crystals (SC) and α crystals. Interestingly, when the crystallization temperature was below the melting temperature of α crystals, the phase content of SC increased with shear rate, while the α content displayed a bell-shaped curve with regard to shear rate. The structure formation in this system was closely related to the shear-induced nucleation, phase mixing and chain mobility.

1. Introduction

Poly(L-lactic acid) (PLLA) is derived from renewable resources and has been considered as one of the most promising alternatives to substitute the traditional petro-polymers due to the biodegradability, renewability and the attractive mechanical properties [1,2]. Poly(L-lactic acid) (PLLA) and its enantiomer, poly(D-lactic acid) (PDLA), can form racemic, stereocomplex crystals (SC) [3]. Compared with other crystal modifications of PLA, i.e. α′ [4,5], α [4–6], β [7,8], and γ [9], SC exhibit a melting temperature (~230 °C) nearly 50 °C higher. PLA materials containing SC exhibit better Young's modulus, tensile strength, fracture strain [10,11] and in particular thermal properties [12]. On the molecular scale, equimolar amounts of PLLA chains and PDLA chains arrange compactly in a trigonal unit cell, adopting a 3_1 helical conformation [7,13].

A vast number of investigations were conducted on the crystallization behavior of PLLA/PDLA mixtures with different blend ratios, which have been summarized in several reviews [2,14–16]. Most of them focused on the PLLA-rich blends with a minor fraction of PDLA, in which SC acted as nucleating agents [17–22] or as physical constrains [23–26] for PLLA. A small amount of SC can act as the most efficient nucleating agent for homo-crystals (α′ or α) [21]. On the other hand, the spherulitic growth rate of homo-crystals and the overall degree of crystallization of PLLA either remained unchanged [27] or depressed [17,22]. One general explanation is the reduced molecular mobility of PLLA chain segments, which is restricted

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by the physical network constructed by the inter-connected SC crystallites [27]. Another straightforward explanation is that a fraction of the PLLA is involved in SC with PDLA, so they cannot at the same time contribute to homo-crystals. Normally, as a result of slow molecular motion in the melt, blends with average molecular weight higher than 100 kg/mol [28] will only form a low fraction of SC under crystallization conditions, accompanied by a large amount of homo-crystals, which is unfavorable for high performance applications. Therefore, several effective methods have been developed, chemical or physical, to increase the SC content in PLLA/PDLA blends. For example, the synthesis of stereoblock copolymers of PLLA-*block*-PDLA [29,30], the introduction of a trace loading (0.1–0.5%) of cross-linker [31], nucleating agents (e.g. zinc phenylphosphonate) [32], or the compatibilizers (e.g. poly(ethylene glycol) [33] or poly(methyl methacrylate) [34]), and the application of intense shear forces onto the PLLA/PDLA (50/50) blend during non-isothermal crystallization processes [35].

Shear flow, a key factor in polymer melt processing, influences significantly the crystallization behavior of semi-crystalline polymers [36]. The crystallization rate can be greatly enhanced [37–39] due to the entropy depression caused by the locally ordered structure. Oriented morphologies including shish-kebab or row-like crystals [40–43] have been observed under shear. Furthermore, the phase content in polymorphic polymers can also be influenced by shear [44–46]. Several studies have been conducted on the shear-induced crystallization of PLLA [37–39,43,47–50]. It was observed that PLLA with a small amount of SC is more sensitive to the shear flow [51]. Recently, Matsuba et al. [52] studied shear-induced crystallization of an equimolar PLLA/PDLA blend at 200 °C which is higher than the melting point of α crystals ($T_{m,\alpha}$, 175 °C). Apart from the enhanced SC nucleation density and the shorter induction time, the crystallinity of SC increased from 1.7% under quiescent conditions to 22% under shear condition after the same crystallization time (1800 s). The authors attributed the enhanced crystallization of SC to the improved mixing of PLLA and PDLA chain fragments at the molecular level by shear in the PLLA/PDLA blend. However, since the crystallization temperature was higher than the melting temperature of homo-crystals, the effect of shear flow on the competition of SC and homo-crystals was still not clear.

In this study, a short-time shear flow was utilized to manipulate the crystallization kinetics of an equimolar PLLA/PDLA blend. The evolution of crystalline structures and phase contents of SC and α crystals was traced by in-situ X-ray scattering and optical microscopy. The effects of shear rate and temperature were investigated systematically with an emphasis on the complicated interplay between SC and α crystals when both of them could form. It was shown here that the crystallization kinetics of both SC and homo-crystals and the phase content of SC were enhanced under low or mediate shear, while their mutual competition still existed.

2. Experimental section

2.1. Materials and sample preparation

PLLA (M_n = 96 kg/mol, M_w = 155 kg/mol, polydispersity, DPI = 1.62) and PDLA (M_n = 90 kg/mol, M_w = 135 kg/mol, polydispersity, DPI = 1.50) were provided by Corbion Purac Biochem B.V. Equal weight of PLLA and PDLA were well dissolved and stirred in dichloromethane with a concentration of 20 mg/ml. The solution was then poured into a flat disk and allowed to evaporate the solvent at room temperature. Afterwards, the obtained film was dried at 80 °C in a vacuum oven for 24 h. The melting points of the PLLA α crystals and SC ($T_{m,SC}$) obtained from these isotactic PLLA and PDLA ingredients are 175 °C and 223 °C, respectively, as determined by the TA Q2000 apparatus (data not shown here).

2.2. Polarized light optical microscopy (POM)

The spherulitic morphologies under quiescent or shear condition were observed by an Olympus (Tokyo, Japan) polarization microscope (BX53) equipped with a high-temperature optical shearing stage (Linkam CSS-450, UK). The PLLA/PDLA blend film was positioned between two quartz plates (Kapton film for in-situ WAXS). The gap between the plates was set to 150 μm. Driven by a micro-stepped stepper motor, the bottom plate could rotate in three modes: steady, step and oscillatory. The circular observation window had a diameter of 2.8 mm, locating at a radius of 7.5 mm to the center of rotation axis. The isothermal crystallization of dried PLLA/PDLA films under both quiescent and shear conditions was performed as indicated in Fig. 1: (a) heat the sample to 260 °C at 30 °C/min and hold there for 3 min, (b) cool down to the crystallization temperature (T_c) at 30 °C/min, (c) and isotherm at T_c for a period during which the crystallization morphology was captured simultaneously. The supercooled melt with a thickness of 150 μm was imposed by shear for 5 s as soon as the temperature reached T_c.

2.3. In-situ WAXS

The in-situ WAXS experiments were conducted at the beamline BL16B1 at Shanghai Synchrotron Radiation Facility (SSRF). The photon energy was 10 KeV, corresponding to a wavelength of 1.24 Å. Scattering patterns were recorded by a MAR CCD (MAR-USA) detector with a resolution of $2048 * 2048$ pixels (pixel size: $79 * 79$ μm^2). The sample thickness was ~300 μm. The temperature/shear procedure was the same as that of POM experiment, as shown in Fig. 1. The 2D WAXS patterns were converted into 1D intensity profiles by Fit2D software. The phase contents and the overall crystallinity were calculated as follows [53]: