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Enhanced crystallization kinetics of symmetric poly(L-lactide)/poly(D-lactide) stereocomplex in the presence of nanocrystalline cellulose

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ABSTRACT

In this work, poly(L-lactide)/poly(D-lactide)/nanocrystalline cellulose (PLLA/PDLA/NCC) stereocomplex blends were prepared using a solution blending method. The effect of NCC on the crystallization kinetics of symmetric PLLA/PDLA blend was systematically investigated. The incorporation of NCC significantly enhanced the formation of stereocomplex crystal (sc), as indicated by increasing the crystallization peak temperature and crystallinity of sc from approx. 143 °C and 24% to around 160 °C and 40%, respectively, during the non-isothermal crystallizing upon cooling at 10 °C/min. Meanwhile, the addition of NCC caused no influence on the crystal morphology and crystal form of sc in the PLLA/PDLA blend, as evidenced by the POM and WAXD results. The crystallization kinetics of the PLLA/PDLA/NCC blends was studied in detail by using the Dobreva and Gutzow model, the Avrami-Jeziorny equation and the well-known Avrami model. It was found that NCC showed high nucleating activity in the PLLA/PDLA blend. The half-life time of crystallization of the PLLA/PDLA blend was decreased by ca. 78% at 180 °C after the addition of 0.5 wt% NCC. In addition, POM tests showed that the nuclei density in the PLLA/PDLA blend during isothermally crystallizing at 180 °C was largely increased by the addition of NCC.

1. Introduction

Poly(lactide) (PLA) has attracted much attention because it is biocompatible, biodegradable, biomass-derived, and nontoxic to the environment. However, PLA is generally amorphous after conventional extrusion or injection molding due to its slow crystallization rate. Since PLA is a semi-crystalline polymer, controlled crystallization rate and morphology are extremely important in determining its physical and chemical properties [1].

PLA is usually prepared by ring-opening polymerization from lactide which has three enantiomeric forms: L-lactide (LLA), D-lactide (DLA), and racemic-lactide (DLLA), showing various properties [2]. Among the available polymorphs of PLA, stereocomplex crystal (sc) developed by combining the stereoisomers of PLA, i.e., poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA), signifies a promising strategy for optimizing the crystallinity and thermal properties of PLA products. One of the most important property of sc is that its melting temperature (T_m) is 50 °C higher than that of PLA homogeneous crystal (hc) [3,4]. The distinctive melting behavior confers sc the ability to significantly improve the nucleation activity and thermal stability of hc [5], outlining the roadmap for the development of PLA products with high crystallinity and melting point [6,7]. The molecular weight [8], blending ratio [9] and the architecture [10] of PLLA and PDLA chains are main factors that can significantly influence the formation of sc during the melt-crystallization process. It is reported that the ratio of PLLA and PDLA plays a vital role in achieving complete sc, i.e., without any formation of hc. A weight ratio of 50:50 between PLLA and PDLA generally promotes (nearly) full stereocomplexation [11–13], but the processing conditions, processing method, and homopolymer molecular weight have far-reaching implications on the relative amount of PLA stereocomplex (sc-PLA) compared to PLA homocrystallites (hc-PLA) [8,14–16]. There exists a critical molecular weight of about 10^5 g/mol, above which stereocomplexation is significantly suppressed.

Recently, Tsuji et al. [17] found sole sc as crystalline specie was formed in star-shaped 4-armed neat 4-DL, 4-LD, and 4-DL/4-LD (50/50) blend, irrespective of the crystallization temperature (T_c). The overall sc

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crystallization rate of 4-DL/4-LD blend was highly accelerated compared with that of neat 4-DL and 4-LD, which was a result of the largely elevated spherulite nuclei number per unit mass in the blend. Matsuba et al. [18] researched 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 (30 min). The authors attributed the enhanced crystallization of sc to the improved mixing of PLLA and PDLA chain fragments at the molecular level by shear. Ma et al. [19] synthesized 3-armed poly(propylene oxide)-*block*-poly(D-lactic acid)-*block*-poly(L-lactic acid) (PPO-PDLA-PLLA) copolymers with high molecular weight (M_n > 2.0 × 10^5) and equivalent D-LA/L-LA compositions. Those 3-armed PPO-PDLA-PLLA copolymers exhibit exclusive sc crystallization behavior with a T_m of about 207 °C.

Various methods has been explored to promote the formation of sc-PLA in the last decades. However, only limited efforts have been devoted to the fully bio-based sc-PLA composites, and even less attention was paid to the crystallization kinetics of bio-based sc-PLA composites. In this work, poly(L-lactide)/poly(D-lactide)/nanocrystalline cellulose (PLLA/PDLA/NCC) stereocomplex blends were prepared by solution blending. The effects of NCC on crystallization behavior, crystal morphology and crystal structure of the blends were systematically investigated. More importantly, the influence of NCC on the crystallization kinetics of the symmetric PLLA/PDLA blend was evaluated using the Dobreva and Gutzow model [20], the Avrami-Jeziorny equation [21] and the well-known Avrami equation [22,23], which provided a deeper understanding on the high nucleation efficiency of NCC for the sc-PLA.

2. Experimental section

2.1. Materials

PLLA (M_n = 51 kDa, PDI = 1.4) in the form of granules was kindly provided by Zhejiang Hisun Biomaterials Co., Ltd, China. PDLA (M_n = 70 kDa, PDI = 1.8) was synthesized via ring opening polymerization of D-lactide (purity ≥99%, Shenzhen Esun Industrial Co., Ltd, China.). Optical purity of the PLLA and PDLA is approx. 99%. Microcrystalline cellulose (MCC) with a purity of 96% and other chemicals (purity ≥ 99%) were purchased from Sinopharm Group Chemical Reagent Co. Ltd., China.

2.2. Preparation of NCC and the PLLA/PDLA/NCC blends

Nanocrystalline cellulose (NCC) was prepared via acid hydrolysis of microcrystalline cellulose as reported in literature [24,25]. In brief, MCC was acid hydrolyzed in sulfuric acid (64 wt%) at 45 °C for 30 min. The suspension was washed with deionized water until approximate neutral by successively centrifugal (10,000 rpm, 8 min). NCC was finally obtained by freeze-drying of the suspension. The prepared NCC behaved as rod-like nanoparticles with an average aspect ratio (L/d) of 12.5 (Fig. S1a) and displayed the typical cellulose I crystal form (Fig. S1b) [25].

To obtain PLLA/PDLA/NCC blends, PLLA and PDLA resins were first dissolved in chloroform and then NCC was added in. All the operations were proceeded under continuous stirring at 40 °C until a homogeneous mixture formed. Finally the mixture solution was casted, evaporated and dried completely under vacuum condition at 45 °C to obtain the PLLA/PDLA/NCC blends. As reference, the PLLA/PDLA blend was prepared via the same procedure. The weight ratio of PLLA to PDLA was fixed at 1:1 while the NCC contents of 0.5, 1, 2 and 5 wt% were chosen to check the effects of different NCC contents on the stereocomplexation of PLA.

2.3. Characterizations

Differential Scanning Calorimetry (DSC): The crystallization behavior of the PLLA/PDLA/NCC blends was studied using DSC (DSC 8000, Perkin Elmer). For non-isothermal crystallization, the samples were heated to 250 °C at 20 °C/min and kept for 2 min to erase the thermal history and then cooled to room temperature (25 °C) at 5, 10, 20 and 40 °C/min, respectively. The subsequent melting behavior was also monitored by reheating the crystallized samples to 250 °C at 10 °C/min. For isothermal crystallization, fresh samples were quenched (50 °C/min) to desired temperatures after melting at 250 °C for 2 min and kept at the desired temperatures until the crystallization was complete.

Polarized Optical Microscopy (POM): POM Axio Scope 1 (Carl Zeiss MicroImaging GmbH, Germany) equipped with a hot-stage unit (Linkam THMS600, UK) was used to investigate the morphology and crystal growth of sc crystals. For non-isothermal crystallization, the samples were first melted at 250 °C for 2 min and then to 25 °C at 10 °C/min. For isothermal crystallization, the samples were cooled down rapidly (50 °C/min) to the required isothermal crystallization temperature after melting at 250 °C for 2 min.

Wide Angle X-ray Diffraction (WAXD): WAXD measurements for the PLLA/PDLA/NCC blends were carried out using an X-ray diffractometer (Bruker AXS D8, Germany) with a Ni-filtered Cu Kα radiation source with a wavelength of 1.542 Å. The measurements were operated at 40 kV and 40 mA with scan angles from 5° to 35°at a scan rate of 3°/min. The samples were treated by Linkam hot-stage unit (cool from 250 °C to 25 °C at 10 °C/min) before the WAXD measurements.

3. Results and discussion

3.1. Effect of NCC on the crystallization of the symmetric PLLA/PDLA blend

The effect of NCC on the non-isothermal crystallization and melting behavior of the symmetric PLLA/PDLA blend was first studied using DSC. The DSC cooling and subsequent heating curves of the PLLA/PDLA/NCC blends are show in Fig. 1. The corresponding parameters, that is crystallization peak temperature (T_c), crystallization enthalpy (ΔH_c), melting peak temperature (T_m), melting enthalpy (ΔH_m), and crystallinity (X_c) of stereocomplex crystal (sc) and homogeneous crystal (hc) are summarized in Table 1. The crystallinity of sc and hc is calculated as

$$X_{c-sc} = \frac{\Delta H_{m-sc}}{p \times 142\ \mathrm{J/g}} \times 100\% \quad (1)$$

and

$$X_{c-hc} = \frac{\Delta H_{m-hc}}{p \times 93\ \mathrm{J/g}} \times 100\% \quad (2)$$

respectively, where the $\Delta H_{m\text{-}sc}$ and $\Delta H_{m\text{-}hc}$ are the melting enthalpy of sc and hc obtained from the DSC second heating curve, p is the total PLA mass percent (including PLLA and PDLA) in the blends, and the 142 J/g and 93 J/g are the reported melting enthalpy values with 100% crystallinity for sc and hc, respectively [26].

As shown in Fig. 1a, the PLLA/PDLA blend formed an obvious crystallization peak with a T_c of 142.7 °C upon cooling at 10 °C/min, which indicated the formation of sc. The $T_{c\text{-}sc}$ of the PLLA/PDLA blend increased to 155.1 °C after adding only 0.5 wt% NCC, in the meanwhile, the $X_{c\text{-}sc}$ increased to 39.9% from 23.6%, indicating that NCC enhanced the formation of sc. The $T_{c\text{-}sc}$ increased to 165.7 °C with further increasing the NCC content to 5 wt%, but the $X_{c\text{-}sc}$ only increased slightly (Table 1). Compared to the significant enhancement on the crystallization of sc, the effect of NCC on the crystallization of hc was much inappreciable, since the crystallization peak of hc was still very tiny even the NCC content was high as 5 wt% (Fig. 1a). The addition of NCC