



Non-isothermal crystallization kinetics and spherulitic morphology of nucleated poly(lactic acid): Effect of dilithium hexahydrophthalate as a novel nucleating agent



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ABSTRACT

The effect of dilithium hexahydrophthalate (HHPA-Li) as a novel and efficient nucleating agent on the non-isothermal crystallization behaviors and spherulitic morphology of poly(lactic acid) (PLA) was studied. Jeziorny's, Ozawa's and Mo's models were employed to describe the non-isothermal crystallization kinetics of the nucleated PLA samples. The activation energies (ΔE) of non-isothermal crystallization were calculated by Friedman formula. The results showed that Jeziorny's and Mo's methods well described the non-isothermal crystallization kinetics of the nucleated PLA samples, while Ozawa's model failed. The crystallization rate of PLA/0.5 wt% HHPA-Li sample was faster than that of PLA/0.2 wt% HHPA-Li sample, while ΔE of the former was lower than that of the latter. It was also found that the presence of HHPA-Li significantly increased the number and decreased the size of spherulites.

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1. Introduction

Due to the diminishing resources and the increasing environmental problems, biodegradable polymers have attracted more and more interests. Biodegradable polymers are good alternatives to petroleum-based polymers, which can be derived from renewable agricultural resources, and easily composted into water and carbon dioxide [1]. For these reasons, biodegradable polymers are expected to reduce the impact on the environment caused by the production and utilization of petroleum-based polymers [2].

Among biodegradable polymers, poly(lactic acid) (PLA) plays a special role for its several advantages, i.e., good mechanical properties, thermoplasticity, biocompatibility, and easy forming process. PLA is a linear aliphatic thermoplastic polyester which can be obtained from renewable resources such as corn, potato and sugar beet [3,4]. PLA is widely used in extensive application including surgical sutures, textiles, containers and engineering materials, as well as food packages [5–7]. However, PLA still has some disadvantages such as slow crystallization rate, slow degradation rate and poor heat resistance.

The degree of crystallinity and crystallization rate of PLA strongly affects both the processability and productivity of mold processing. Thus, it is necessary to improve the crystallization rate

of PLA to adapt for various applications. In general, blending with a nucleating agent is the most effective method to increase the crystallization rate. The nucleation activation energy is decreased and the crystallization is initiated at higher temperature upon cooling by a nucleating agent [8].

Previous studies had shown that some inorganic compounds were effective to increase the overall crystallization rate of PLA. Su et al. [9] found the crystallization rate of PLA was increased when 3 wt% carbon black was added. Li et al. [10] found the nucleation density of PLA increased and the crystallization half-time reduced with the addition of talc. Xiao et al. [11] also reported the incorporation of talc increased the crystallization rate and decreased the crystallization half-time of PLA. Nam et al. [12] studied the crystallization behavior of PLA/montmorillonite (MMT) nanocomposites and found that MMT particles accelerated the overall crystallization rate and decreased the spherulitic size of PLA. Kim et al. [13] and Xu et al. [14] reported that multi-walled carbon nanotube reduced the crystallization half-time and increased nucleation density of PLA. Zhou et al. [15] found that carbonated hydroxyapatite increased the crystallization rate and crystallinity of PLA under the non-isothermal condition.

The stereocomplex was regarded as a potential nucleating agent for PLA [16]. Tsuji and Tezuka [17] found that the overall crystallization rate of poly(L-lactic acid) (PLLA)/poly(D-lactide) (PDLA) (1:1) stereocomplexes was higher than that of pure PLLA or PDLA. Schmidt and Hillmyer [18] investigated the isothermal and nonisothermal crystallization behaviors of PLLA blended with

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PDLA or talc. They found that the nucleation efficiency with addition of 6 wt% stereocomplex was almost twice as much as that of talc. Yamane and Sasai [19] also found the crystallization rate of PLLA increased with the addition of high molecular weight PDLA.

Recently much attention was focused on some organic compounds. Nam et al. [20] and Tang et al. [21] found the crystallization rate and crystallinity significantly increased with the addition of *N,N*-ethylenebis(12-hydroxystearamide) (EBH). Harris and Lee [22] suggested that ethylenebisstearamide (EBS) improved the isothermal and non-isothermal crystallization rates of PLA as well as the crystallinity. Kawamoto et al. [23,24] synthesized a series of hydrazide compounds and found that octamethylenedicarboxylic dibenzoylhydrazide (OMBH) was the most effective to accelerate the crystallization of PLA under higher cooling rate. Li and Dou [25] confirmed that OMBH is an effective nucleating agent for PLA and they found that the spherulitic size of the nucleated PLA decreased and the crystallinity increased. Chen and Dou [26] investigated the crystallization behavior of PLA with the addition of a commercial nucleating agent (NT-C). Their results showed that the crystallization temperature and crystallinity increased and the spherulitic size decreased for the nucleated PLA. He et al. [27] reported that the incorporation of phthalimide significantly enhanced both the non-isothermal and isothermal crystallization of PLA even at very low content. Pan et al. [28] and Wang et al. [29] reported that layered metal phosphonates accelerated the crystallization rate of PLA.

In this study, dilithium hexahydrophthalate (HHPA-Li) was evaluated as a novel nucleating agent for PLA. PLA/HHPA-Li samples were prepared by melt blending. Our study was mainly focused on the non-isothermal crystallization kinetics and spherulitic morphology of the nucleated PLA samples.

2. Experimental

2.1. Materials

PLA (4032D) was a commercial product of Nature Works, USA. Dilithium hexahydrophthalate (HHPA-Li) was synthesized as follows: *cis*-hexahydrophthalic anhydride (HHPA) (analytical grade, 0.062 mol, 9.56 g), lithium hydroxide (analytical grade, 0.124 mol, 2.98 g) and water (300 ml) were heated to 75 °C and lasted for 50 min under stirring. Then the solution was evaporated to give a white powder. The Fourier transform infrared spectroscopy (FTIR) spectra of HHPA and HHPA-Li are shown in Fig. 1.

2.2. Preparation of the nucleated PLA samples

PLA (40 g)/HHPA-Li (0.08 g, 0.2 wt%) and PLA (40 g)/HHPA-Li (0.2 g, 0.5 wt%) mixtures were dried under vacuum at 85 °C for 8 h

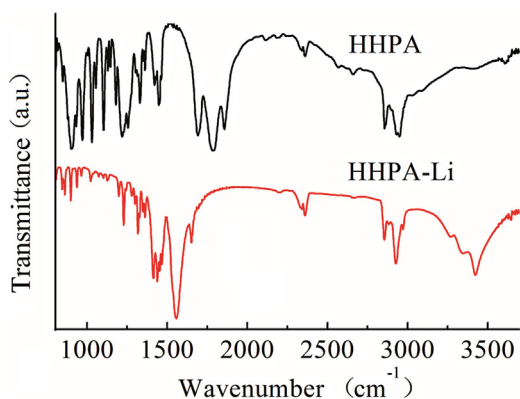


Fig. 1. FTIR spectra of HHPA and HHPA-Li.

before use. Then they were intensely mixed in an internal mixer (HL200, Jilin University Science & Technology Equipment Factory, Changchun, China) at 185 °C and 40 rpm for 6 min. The melt was cooled and cut into small pieces.

A small piece was placed between two glass slides on a hot stage kept at 200 °C for 5 min to make the sample melt completely and remove thermal history. It was squeezed on the top slide to form a film, and then was quickly transferred onto a hot stage kept at 110 °C for 60 min. Finally, the film was quenched to room temperature. The isothermally crystallized samples were used for differential scanning calorimetry (DSC) measurement and polarized light microscopy (PLM) observation.

2.3. DSC measurement

The melting and crystallization behaviors of the isothermally crystallized samples were performed on a differential scanning calorimeter (ZF-DSC-D2, Shanghai Zufa Industry Co., Ltd., Shanghai, China) under a dry nitrogen atmosphere. The temperature and heat flow was calibrated with indium, tin and zinc, respectively. All the samples were heated from room temperature to 200 °C at a rate of 10 °C/min, and held at 200 °C for 5 min to eliminate the thermal history. Then, the melted samples were cooled down to 30 °C at the rate of 5 °C/min and held at 30 °C for 5 min, finally reheated to 200 °C at the rate of 10 °C/min.

The melting and cooling curves were recorded. The cold crystallization temperatures (T_{cc}), melting temperatures (T_m), and enthalpies of cold crystallization (ΔH_{cc}) and melting (ΔH_m) were determined from the melting curves. The peak crystallization temperatures (T_{cp}) and enthalpies of crystallization (ΔH_c) were determined from the cooling curves. The total percent crystallinity (X_c) of the samples was calculated using Eq. (1).

$$X_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^0 w_{PLA}} \times 100\% \quad (1)$$

where w_{PLA} is the wt% of PLA in the blend, $\Delta H_m^0 = 93.6$ J/g for 100% crystalline PLA [30].

During the non-isothermal crystallization kinetic measurements, about 6 mg of each sample was sealed into an aluminum crucible, heated from 30 °C to 200 °C at 10 °C/min, and held at 200 °C for 5 min to remove the thermal history, then cooled to 30 °C at the constant cooling rate of 3, 6, 9 and 12 °C/min, respectively. The onset (T_c^{on}) and the peak (T_c^p) crystallization temperatures were determined from the cooling curves.

2.4. PLM observation

Spherulitic morphologies of the isothermally crystallized samples were observed on a polarized light microscope (LW-200-4JS, Shanghai LW Scientific Co., Ltd., Shanghai, China) equipped with cross polarizers and a CCD camera. Pictures were captured and stored in a computer.

3. Results and discussion

3.1. DSC measurement

Fig. 2 shows the DSC melting and cooling curves of the isothermally crystallized samples, and the relevant data are listed in Table 1. There were double melting peaks in the first melting curves for the pure PLA and PLA/0.2 wt% HHPA-Li samples (Fig. 2a). The peak at lower temperature should be associated with the fusion of some amount of the original crystals grown by normal primary crystallization, whereas the peak at higher temperature is attributed to the melting of the perfect crystals formed through a

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