

Material behaviour

Crystallization kinetics and morphology of biodegradable poly(lactic acid) with a hydrazide nucleating agent



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ABSTRACT

The effect of tetramethylenedicarboxylic dibenzoylhydrazide (designated here as TMC) on the non-isothermal and isothermal crystallization behavior of PLA was investigated by differential scanning calorimetry (DSC), polarized optical microscopy (POM) and wide angle X-ray diffraction (WAXD). TMC shows excellent nucleating effect on PLA. With the addition of 0.05 wt% TMC, the crystallization half-time of PLA decreases from 26.06 to 6.13 min at 130 °C. The isothermal crystallization data were further analyzed by the Avrami model. The values of the Avrami exponent of the blends are comparable to that of neat PLA, indicating that the presence of TMC does not change the crystallization mechanism of the matrix. The observation from POM and WAXD measurements showed that the presence of TMC increases significantly the nuclei density of PLA but has no discernible effect on its crystalline structure.

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1. Introduction

In the past few years, poly(lactic acid) (PLA) has attracted increasing attention due to its excellent biodegradability and biocompatibility [1,2]. PLA can be produced completely from renewable sources and degrade into carbon dioxide and water in soil [3,4], which makes it a suitable alternative to traditional petrochemical-based polymers for films, thermoformed containers and stretch-blown bottles [1,5]. However, due to its intrinsic slow crystallization rate, PLA products are usually amorphous under fast cooling processes such as injection molding and extrusion [5,6]. In its amorphous form, the application of PLA is limited by its low glass transition temperature (around 60 °C) [7]. Moreover, slower crystallization usually causes difficulties in the ejection of parts and results in longer molding cycles. Therefore, to extend PLA into applications such as electrical and automotive parts, where heat resistance is required, increasing the crystallization rate of the materials becomes critical.

Adding nucleating agent is an efficient way to accelerate the crystallization of PLA. Numerous potential nucleating agents have been investigated, including talc [8,9], carbon nanotube [10,11],

graphene nanosheets [12], nanoclay [13,14], zinc phenylphosphonate [15,16], orotic acid [17], poly(D-lactic acid) [18], polyoxymethylene [19], PLA inclusion complex [20], multiamide [21–24] and phthalimide [25]. In addition, some hydrazides are regarded as highly effective nucleating agents. Kawamoto et al. [26,27] synthesized a series of hydrazide compounds having variety of methylene chain numbers and substituents to develop an advanced nucleating agent for PLA. Benzoylhydrazide compounds were found to be more effective in the enhancement of crystallization of PLA [26,27]. Tetramethylenedicarboxylic dibenzoylhydrazide (trade name: TMC-306, abbreviated as TMC in this article) is one of these compounds. To the best of our knowledge, the crystallization behavior and nucleation ability of TMC-nucleated PLA have not been investigated in detail.

In this paper, the crystallization behavior, morphology and crystal structure of PLA nucleated by TMC were investigated by differential scanning calorimetry (DSC), polarized optical microscopy (POM) and wide angle X-ray diffraction (WAXD).

2. Experimental section

2.1. Materials

The PLA, consisting of 98% L-lactic acid and 2% D-lactic acid contents, was obtained from Nature Works. The number- and

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weight-average molecular weights of this resin were 1.11×10^5 and 1.71×10^5 , respectively. The hydrazide compound (TMC-306), i.e., tetramethylenedicarboxylic dibenzoylhydrazide, was kindly supplied by Shanxi Provincial Institute of the Chemical Industry, China. Its chemical structure is shown in Fig. 1.

2.2. Sample preparation

Neat PLA and PLA/TMC blends were prepared via a solution and casting method. Preweighed TMC was added to chloroform and ultrasonically treated for 30 min. PLA was then added to the suspension and stirred rigorously. The mixture was poured into a dish to evaporate the solvent at room temperature. The film obtained was dried at 70 °C under vacuum for 3 days to remove the solvent completely. The PLA was dried at 80 °C for 4 h before mixing while the nucleating agent was used without further treatment. The weight fractions of TMC in PLA blends were 0, 0.05 and 0.5 wt% and these blends were defined as neat PLA, TMC0.05 and TMC0.5.

2.3. Differential scanning calorimetry

A Mettler-Toledo DSC1 Instrument was used to study the crystallization behavior of PLA and the PLA nucleated with TMC. Calibration for the temperature and energy scale was carried out using high-purity indium and zinc standards. Sample weight was about 6 mg. Each sample was used only once and all the runs were carried out in a nitrogen atmosphere. For nonisothermal crystallization, the samples were heated to 200 °C at 20 °C/min and held for 5 min to erase the thermal history, and then the DSC traces were recorded during cooling at a rate of 2 °C/min. For isothermal crystallization, the samples were heated to 200 °C at 20 °C/min and held for 5 min to eliminate prior thermal history, the melt was then cooled rapidly to the designated crystallization temperature (T_c) and, finally, the DSC traces were recorded during the isothermal process.

2.4. Polarized optical microscopy

The spherulitic morphologies of the samples were investigated on an Olympus BX61 polarizing microscope, equipped with a digital camera system and a Linkam THMS 600 hot stage. A thin film of each sample was sandwiched between two glass slides. After melting at 200 °C for 5 min, it was quickly cooled to the designed isothermal crystallization temperature (140 °C) and then the crystallization process was recorded.

2.5. Wide angle X-ray diffraction

The crystalline structures of PLA/TMC blends were detected by an X-ray diffractometer (XRD, D8 Advance, Bruker, Germany), using Cu K α radiation, with the generator working at 40 kV and 40 mA in the range of 5–40° with a scanning rate of 5°/min. The films prepared via a solution and casting method were directly used for investigating the crystalline structure of PLA/TMC blends at room temperature.

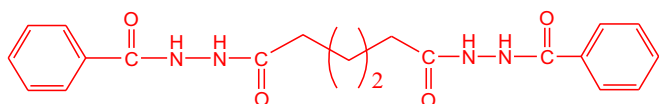


Fig. 1. Chemical structure of TMC-306.

3. Results and discussion

3.1. Nonisothermal crystallization behavior

The effect of TMC on the nonisothermal melt crystallization of PLA was first investigated by DSC, since most polymer processing operations are performed under nonisothermal crystallization conditions. Fig. 2 shows the DSC cooling curves of neat PLA and its two blends at 2 °C/min. As shown in Fig. 2, the crystallization exotherms are more easily observed in the blends than in neat PLA. Neat PLA had a crystallization peak temperature (T_p) of 99.1 °C with a crystallization enthalpy (ΔH_c) of 2.7 J/g. For the TMC0.05 sample, it showed a T_p at 121.5 °C with a ΔH_c of 8.0 J/g. With further increase of the TMC content, TMC0.5 showed a T_p at 128.8 °C with a ΔH_c of 8.4 J/g. The nonisothermal melt crystallization of PLA was enhanced significantly by a very low loading of TMC, indicating that TMC is an efficient nucleating agent for PLA.

3.2. Isothermal crystallization behavior

The effect of TMC on the isothermal crystallization kinetics of PLA was further studied using DSC over a wide crystallization temperature (T_c) range from 120 to 150 °C. Fig. 3 shows the DSC curves for neat PLA and its blends crystallized at various crystallization temperatures. As can be seen, the crystallization peak of neat PLA is very broad. With the incorporation of TMC, the crystallization peak sharpens and the crystallization time shortens.

The relative crystallinity, $X(t)$, can be obtained from the ratio of the area of the exotherm at crystallization time, t , to the total area of the exothermal peak, i.e.

$$X(t) = \frac{\int_0^t (dH/dt)dt}{\int_0^\infty (dH/dt)dt} \quad (1)$$

where dH/dt is the heat flow rate.

The well-known Avrami equation [28,29] was adopted to analyze the overall isothermal crystallization kinetics of polymers, which assumed that the relative crystallinity developed with the crystallization time,

$$1 - X(t) = \exp(-kt^n) \quad (2)$$

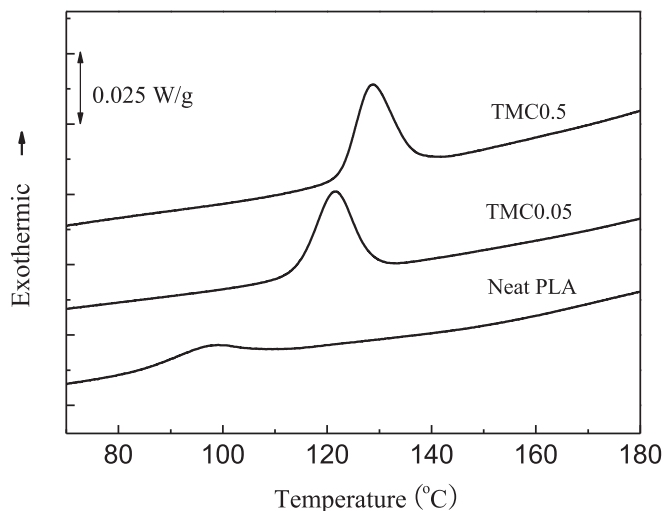


Fig. 2. DSC cooling curves of PLA and its blends at a cooling rate of 2 °C/min.

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