

## Material behaviour

## Effect of phthalimide as an efficient nucleating agent on the crystallization kinetics of poly(lactic acid)



Dongran He, Yaming Wang\*, Chunguang Shao, Guoqiang Zheng, Qian Li, Changyu Shen

National Engineering Research Center for Advanced Polymer Processing Technology, Key Laboratory of Advanced Materials Processing & Mold, Ministry of Education, Zhengzhou University, 97 Wenhua Road, Zhengzhou 450002, China

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## ABSTRACT

The effect of phthalimide compound on the nonisothermal and isothermal crystallization behavior of poly(lactic acid) (PLA) was investigated by differential scanning calorimetry (DSC) and polarized optical microscopy. It was found that the incorporation of a small amount of phthalimide promoted the crystallization of PLA significantly. The Avrami model was applied to analyze the isothermal crystallization kinetics. It was found that the Avrami exponent was higher for PLA/phthalimide blends than for neat PLA, indicating a heterogeneous nucleation mechanism. These results indicate that phthalimide may act as an efficient nucleating agent to improve the crystallization of PLA and expand its applications.

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## 1. Introduction

Eco-friendly poly(lactic acid) (PLA) has drawn increasing interest in recent decades for replacement of petroleum-based polymers in the fields of films, thermoformed containers and stretched-blown bottles [1,2]. However, due to its relatively slow crystallization rate, the application of PLA has been restricted in many other fields where heat resistance is required, for instance, electrical appliances and automotive parts [2]. In spite of the fact that PLA is a semicrystalline polymer, almost no crystallization occurs during fast cooling such as in injection molding and extrusion [2–4]. In its amorphous form, the application of PLA is limited by its low glass transition temperature  $T_g$  (around 60 °C) [5], while only the crystalline form can confer useful mechanical properties at temperature greater than its  $T_g$ . Poor processability, such as difficulties in the

ejection of parts, is also ascribed to its slow crystallization rate.

Adding nucleating agent is an efficient way to promote the crystallization of PLA. Nucleating agents can induce higher crystallization temperature and degree of crystallinity, and hence can improve mechanical properties, optical properties, heat resistance and processability of the materials. Large numbers of potential nucleating agents have been investigated, including talc [6,7], poly(D-lactic acid) [8], zinc phenylphosphonate [9], carbon nanotubes [10,11], PLA inclusion complex [12], natural fiber [13], and so on.

Some low-molecular-weight organic compounds have also been found to be efficient nucleating agents. Pan et al. [14] studied the effect of nucleobases on PLA and found that uracil could accelerate the crystallization of PLA most effectively. Qiu et al. [15] used otrotic acid as nucleating agent and found that it apparently enhanced the crystallization rate of PLA. Kawamoto et al. [16] synthesized a series of hydrazide compounds and proved its effectiveness for the nucleation of PLA. Several research groups have reported that low-molecular weight aliphatic amides are efficient

\* Corresponding author. Tel.: +86 37163887567; fax: +86 37163887570.

E-mail address: [wangyaming@zzu.edu.cn](mailto:wangyaming@zzu.edu.cn) (Y. Wang).

nucleating agents for PLA crystallization [17–19]. Kimura et al. [20] found that 1,3,5-benzenetricarboxylamide derivatives could enhance the crystallization of PLA effectively, and *N,N,N'*-tricyclohexyl-1,3,5 benzenetricarboxylamide was the most effective in terms of increase in crystallization rate. Recently, Ren et al. [21] investigated the crystallization behavior and morphology of PLA/*N*-aminophthalimide blends and found that *N*-aminophthalimide accelerated the crystallization of PLA effectively. However, no work has addressed the effect of phthalimide as a nucleating agent on the crystallization of PLA, although the chemical structure of phthalimide is similar to that of *N*-aminophthalimide.

In the present study, the enhanced crystallization of PLA in the presence of phthalimide was investigated by differential scanning calorimetry (DSC) and polarized optical microscopy.

## 2. Experimental section

### 2.1. Materials

The PLA, consisting of 98% *L*-lactic acid and 2% *D*-lactic acid contents, was purchased from Nature Works. The number- and weight-average molecular weights of the material were  $1.11 \times 10^5$  and  $1.71 \times 10^5$ , respectively. Phthalimide with a melt temperature of about 238 °C was purchased from Shanghai Dibai Chemical Company (China). Fig. 1 shows the chemical structure of phthalimide.

### 2.2. Sample preparation

Neat PLA and PLA/phthalimide blends were prepared by directly mixing in a Haake mixing chamber by premixing at 190 °C 30 rpm for 3 min, and then mixing at 190 °C 60 rpm for 6 min. PLA was dried at 80 °C for 4 h before mixing. The contents of phthalimide in PLA were 0.1, 0.3, 0.5, 1 and 2 wt% of PLA.

### 2.3. DSC measurements

A DSC 2920 (TA Instruments) was used to study the crystallization behavior of neat PLA and PLA/phthalimide blends. Calibration for the temperature and energy scales was carried out using a pure indium standard. Sample weight was about 7 mg. For the nonisothermal melt crystallization, the samples were rapidly heated to 200 °C and held for 5 min to erase any thermal history, then the melt was cooled to crystallize at a rate of 5 °C/min. Isothermal melt crystallization kinetics of neat PLA and PLA/phthalimide blends was also studied. The samples were rapidly heated to 200 °C, held for 5 min to erase any thermal

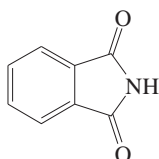


Fig. 1. Chemical structure of phthalimide.

history, quenched to the desired crystallization temperature ( $T_c$ ) and held for a period of time until the isothermal crystallization was complete. The exothermal traces were recorded for subsequent data analysis. Each sample was used only once and all the runs were carried out in a nitrogen atmosphere.

### 2.4. Polarized optical microscopy (POM)

POM observation was performed on an Olympus BX61 polarizing microscope, equipped with a digital camera system and a Linkam THMS 600 hot stage. All the samples were first inserted between two microscope cover slips and squeezed at 200 °C to obtain a thin slice. Subsequently, the as-prepared slice was transferred to the hot stage and held at 200 °C for 5 min to achieve thermal equilibrium. This was followed by rapid cooling to the selected crystallization temperature of 136 °C. The polarized optical micrographs during isothermal crystallization were recorded.

## 3. Results and discussion

### 3.1. Nonisothermal melt crystallization

The effect of phthalimide on the nonisothermal melt crystallization of PLA was first studied with DSC. Fig. 2 presents the DSC cooling traces of neat PLA and PLA/phthalimide blends at a cooling rate of 5 °C/min. Clearly, the crystallization exotherm shifts to higher temperature with the incorporation of phthalimide. Moreover, the enthalpy of the exotherm increases when the phthalimide content increases from 0 to 0.3 wt%, while it decreases with further increase of the amount of phthalimide. It is also observed that the exothermic curves of PLA/phthalimide blends are rather blunt with shoulders, which can be ascribed to a sudden acceleration of the growth of PLA spherulites, as demonstrated by Di Lorenzo [22]. Similar observation has been reported for PLA nucleated by carbon black [23].

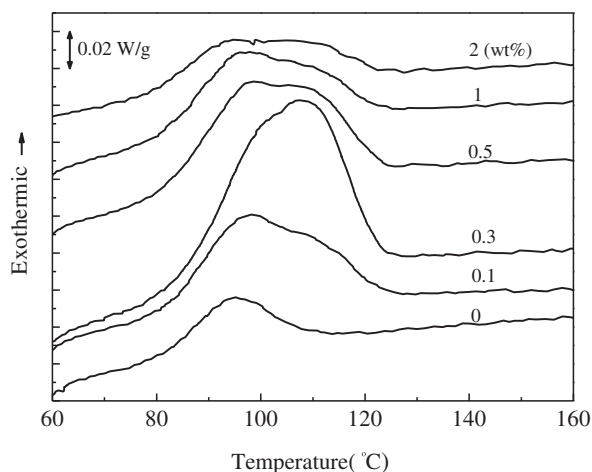


Fig. 2. DSC traces recorded in nonisothermal melt crystallization at a cooling rate of 5 °C/min for neat PLA and PLAs containing different contents of phthalimide.

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