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Crystallization behaviours of bacterially synthesized poly(hydroxyalkanoate)s in the presence of oxalamide compounds with different configurations

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ABSTRACT

Bacterially synthesized poly(hydroxyalkanoate)s (PHAs) suffers from low crystallization rate which is enhanced by using tailor-made oxalamide compounds as nucleators. The influence of nucleator configurations on the crystallization behaviour of the PHAs was investigated using differential scanning calorimetry (DSC), polarized optical microscopy (POM) and X-ray diffraction (XRD). The oxalamide compounds with ringy terminal structures (cyclohexyl and phenyl), notably the phenyl group, show higher nucleation efficiency and a better compatibility in the PHAs matrix, while the linear terminal structure (*n*-hexane) has poor nucleation effect. The crystallization temperature (T_c) and the crystallinity (X_c) of the PHAs are increased from 58 °C to 71 °C and from 5% to 48%, respectively, after addition of 0.75 wt% of the nucleator (phenyl group) upon cooling from the melt. Meanwhile, the half-life isothermal crystallization time ($t_{0.5}$) of the PHAs at 110 °C is decreased by 70%. The oxalamide compounds increases the nuclei density of the PHAs accompanied with a reduction in spherulitic size. In addition, the crystal form and crystallization mechanism of the PHAs are not altered obviously after addition of the nulceators as confirmed by the POM, XRD and Avrami analysis.

1. Introduction

Biodegradable polyhydroxylalkanoates including polyhydroxybutyrate (PHB) and its copolymers are biocompatible and bacterially yielded polymers [1–4]. PHB is the most widely studied in the family of PHAs. However, it still has some shortages, e.g., (i) very large spherulite size and high crystallinity leading to brittleness; (ii) poor heat resistance because of the narrow temperature window between the melting point and the thermal degradation temperature; (iii) low crystallization rate due to lacking of nucleators. Crystallization of commercial PHAs generally do not occur during melt processing such as injection molding leading to long molding-cycle time, low productivity, high energy consumption in processing, and poor properties of the products. Therefore, the poor crystallizability has limited the widespread use of PHB.

Bacterial copolymerization of PHB with other monomer components such as 3-hydroxylvalerate and 3-hydroxyhexanoate would improve the mechanical performances such as toughness [5–10], while the crystallization rate would be even lower. Therefore, addition of nucleators (NAs) is strongly needed to promote heteronucleation and improve the crystallization rate, leading to short(er) processing-cycle time in industry [11,12].

So far, a number of inorganic fillers have been used as NAs for PHB and its copolymers, such as boron nitride, talcum powder, terbium oxide and metal phosphonate [13–15]. However, the aggregation of inorganic nucleators usually occurs because of their poor miscibility resulting in random shape/size and crystallization promotion effect. In addition, organic additives such as uracil [16], orotic acid (OA) [17,18], poly (vinyl alcohol) particle [19], are applied as nucleators as well for PHAs. Although some reported NAs in literatures showed a certain extent nucleation effect, the nucleation efficiency is still inadequate. Hence, it is necessary to develop high-efficiency NAs for bacterially synthesized PHAs.

The miscibility between the polymer melt matrix and NAs is very important to the crystallization process. For a soluble type of NAs, it could dissolve in the polymer melt and then separate out

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before the crystallization of the polymer matrix which would offer heterogeneous crystal nucleus [20].

In this work, three oxalamide compounds were used as nucleators to improve the crystallization properties of the PHAs. To systemically study the effect of the nucleator structure on the crystallization behaviours of the PHAs, three oxalamide compounds with different terminal groups (i.e., cyclohexyl, phenyl and *n*-hexane) were synthetized [21] and the crystallization kinetics of the PHAs with the oxalamide compounds were investigated. The use of these oxalamide compounds greatly improves the crystallization rate and thus may broaden the applied range of the PHAs materials.

2. Experimental section

2.1. Materials

Poly(hydroxylalkanoate)s (PHAs) powders with a M_w of 750 kDa were provided by Tianan Biopolymer Inc. Ningbo, China. The oxalamide compounds (abbreviated as NA_i), as structured in Scheme 1, were synthesized according to the reported methods [21].

2.2. Sample preparation

The PHAs/NA_i blends were prepared by melt mixing at 170 °C and 50 rpm for 4 min by using a Haake mixer (HAAKE Polylab-OS, Thermo Fisher Scientific, Germany). All materials were dried under vacuum at 60 °C for 24 h before using. The concentration of NA_i was fixed at a constant concentration (0.75 wt%) in the PHAs/NA_i blends which are recorded as PHAs/NA_i where i indicates the type of terminal groups of NA, as shown in Scheme 1. In contrast, neat PHAs were undergone the identical processing conditions.

2.3. Characterization

Differential Scanning Calorimetry (DSC): A DSC analyzer (PE, 8000, USA) was used to study the crystallization behaviours of PHAs and PHAs/NA_i blends under a nitrogen atmosphere. The samples were firstly heated at 190 °C at 10 °C/min for 3 min to eliminate thermal history. For isothermal crystallization, the samples were then quenched to desired crystallization temperatures at 100 °C/min. For non-isothermal crystallization, the samples were then cooled to 0 °C at 50 °C/min and reheated to 190 °C at 10 °C/min.

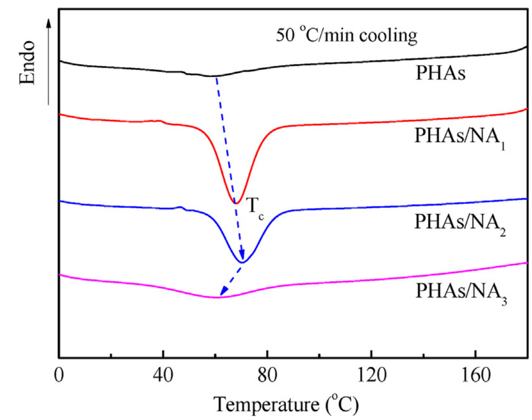


Fig. 1. DSC cooling curves of PHAs and PHAs/NA_i blends at a cooling rate of 50 °C/min.

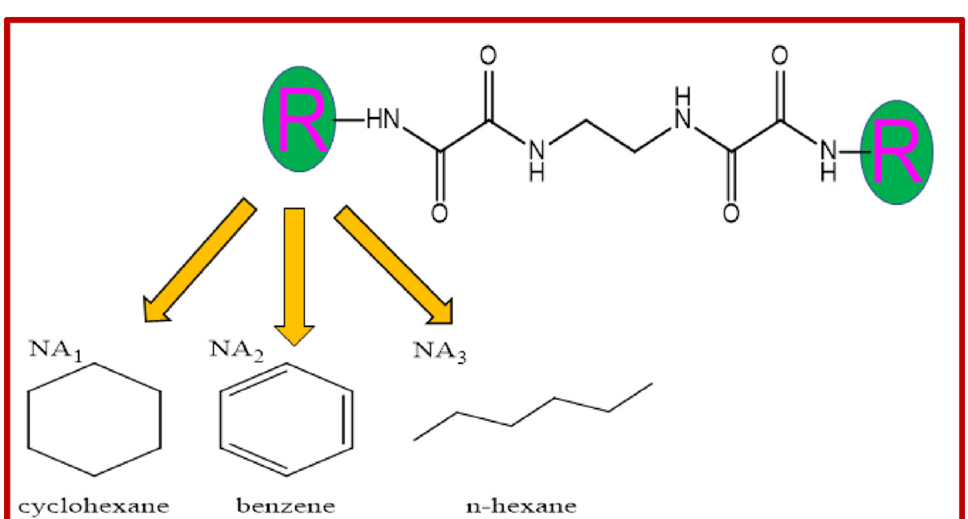
Polarized optical microscopy (POM): The spherulitic morphology of the samples was examined using an Axio Scope 1, Zeiss POM with a hot stage (Linkam, THMS600). The thin samples were quenched from 190 °C (persisted for 3 min) to the desired temperatures at 50 °C/min for isothermal crystallization.

X-ray diffraction (XRD): The crystalline structure was recorded on a Bruker AXS D8 X-ray diffractometer with a Cu Kα radiation source (λ = 0.1542 nm) working at 40 kV and 200 mA. The measurements were operated from 5° to 40°.

3. Results and discussion

3.1. Non-isothermal crystallization behaviour

According to literature, 0.5–1 wt% of organic nucleators such as cyanuric acid and cyclodextrins are suitable for nucleation in semi-crystalline polymers [16,22,23]. Therefore, 0.75 wt% of NA_i was chosen in this work to investigate the effect of end configuration of the nucleators on the nucleation and crystallization of the PHAs. The curves and thermal parameters were displayed in Fig. 1 and Table 1, respectively. Neat PHAs have a wide and weak crystallization peak (T_c = 58 °C) with a crystallization enthalpy ($\triangle H_c$) of 7.6 J/g. This result shows a weak crystallization capability of the PHAs due to the poor regularity of chain configuration and the lacking of effective nucleators [24]. The crystallization exotherms



Scheme 1. Illustration of the chemical structures of the oxalamide compounds with different terminal groups (R).