



Comparison of anhydrous and monohydrated forms of orotic acid as crystal nucleating agents for poly(3-hydroxybutyrate-co-3-hydroxyvalerate)



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ABSTRACT

A small molecule nucleating agent, orotic acid (OA), was investigated to enhance crystallinity and crystallization kinetics in poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) for the purpose of addressing embrittlement and reducing solidification time after thermal processing. In particular, the effectiveness of monohydrated (OA-m) and anhydrous (OA-a) forms of OA as nucleating agents for isothermal and non-isothermal crystallization of PHBV films was investigated and compared. Both forms of OA were able to increase crystallization temperature of PHBV as well as form more uniform crystal structures, based on differential scanning calorimetry. It was found that OA-a at 1–2 wt% was most effective in PHBV crystal nucleation because of the increase in overall polymer crystallinity and faster crystallization rate. Additionally, the faster crystallization of OA-a led to fibrillar film morphology of the PHBV/OA blends.

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1. Introduction

Though highly attractive as a biodegradable and biorenewable class of polymers, polyhydroxyalkanoates (PHAs) have seen limited application, particularly in foams, due to long term embrittlement [1], poor melt strength and thermal stability [2] and, in some cases, slow crystallization [3]. Embrittlement during storage has been widely measured in poly(hydroxybutyrate) (PHB) [4] and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) [5]; it occurs because the crystallization rate is slow when cooling from the melt state [6]. It is typical for small molecule solids to be used as crystal nucleating agents to raise the crystallization temperature and crystallization rate [7] and thus reduce the time for solidification upon cooling after foam extrusion.

Cell or bubble nucleating agents have regularly been used for the enhancement of foams of linear polymers such as polypropylene (PP) [8] and poly(lactic acid) (PLA) [9], whose melt strengths are poor and comparable to PHBV. For example, talc contents of 1, 5 and 10 wt% were found to consistently increase cell density in PP foams [8]. Nanoclays have also been used for PHBV

blends [10–12], leading to fivefold decrease in cell size and three orders of magnitude increase in cell density [11,12]. Cell nucleation follows homogeneous and heterogeneous mechanisms that are common to crystal nucleation, where either gas molecules or polymer chains associate to form a cell or crystal nuclei of critical radius. Also, crystallized polymer can serve to nucleate bubbles either indirectly by increasing gas concentration nearby or directly through heterogeneous nucleation on its surface [13,14]. Additional factors that contribute to the dominant nucleation mechanism include particle size, shape and distribution, surface interaction between polymer and gas, solubility of gas in the polymer and processing parameters such as temperature and pressure drop rate. Increasing crystallinity can have potentially beneficial foaming effects on solidification and viscosity as well as reduced brittleness of the final material, while increasing cell nucleation leads to higher cell density and smaller cell sizes. Therefore, crystal nucleating agents may also serve as bubble nucleation agents and provide multiple benefits to foaming processes.

Orotic acid, uracil and cyanuric acid have all been shown to be effective nucleating agents for PHBV [15] and poly(hydroxybutyrate-co-hydroxyhexanoate) (PHBHHx) with varying HHx content [7,15–17]. Orotic acid (OA) was found to be an excellent PHB crystal nucleating agent that was even better than boron nitride based on spherulite size [16]. It was proposed that the matching dimension of the OA and PHB crystal lattices and ability to form hydrogen bonds

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allowed for very close interaction [7]. Furthermore, OA was shown to be readily dispersed in PHB, allowing for uniform nucleation [7]. The aforementioned studies only used monohydrated OA without drying, even though PHAs are susceptible to hydrolytic degradation at high temperature, and the presence of bound water may hinder the close interaction of OA and hydrophobic PHA needed for effective nucleation [2]. Thus, anhydrous OA may be an even more effective nucleating agent for PHAs.

Here, we investigated the use of anhydrous OA as a PHBV nucleating agent and compared it to the nucleating ability of monohydrated OA in PHBV solvent-cast films using isothermal and non-isothermal crystallization in order to determine whether OA was a good nucleating agent for PHBV and whether OA-a would be better than OA-m. Additionally, imaging of films was performed for understanding dispersion and film morphology. Ultimately, by using an appropriate nucleating agent, PHBV may be better suited for thermal processes used for producing plastic products.

2. Materials and methods

2.1. Materials

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) with 5 mol% hydroxyvalerate content (PHB5V) was used in a white powder form (trade name ENMAT Y1000) with molecular weight of 607 kg/mol and polydispersity of 4.04. Orotic acid monohydrate (OA-m) of 98% purity (Acros Organics) and anhydrous orotic acid (OA-a) of 98% purity (Acros Organics) were used as nucleating agents in solvent-cast films. The melting temperature of OA is 300 °C.

Hexafluoroisopropanol (HFIP) and chloroform were used as described in Section 2.2 for solvent casting. Activated azodicarbonyl (AZ) (Celogen AZ780) was generously provided by Lion Copolymers and used as the chemical blowing agent during extrusion foaming. AZ780 decomposes between 140 and 150 °C, generating up to 190 cm³ of gas/g solid, according to the manufacturer, and produces primarily nitrogen gas.

2.2. Solvent film casting

0, 1, 2, 5 and 10 wt% OA-a or OA-m (relative to PHBV) were sonicated for 30 min in 10 mL chloroform before adding the appropriate amount of PHBV powder to the solution to achieve 1 w/v%. PHBV/OA solutions were stirred at 55 °C in a water bath for 1 day to ensure complete dissolution. Films for DSC and SEM measurements were produced by pouring 7 mL of PHBV/OA solution into a 50 mm diameter glass petri dish and allowing the solvent to evaporate over 2 h at room temperature. Films were then further dried in a vacuum desiccator at room temperature for two days to ensure complete removal of solvent. To produce thin films for polarized light optical microscopy, 1 mL of solution was pipetted onto a glass slide before undergoing the same drying steps as above.

2.3. Microscopy imaging of films

A Nikon UFC optical microscope (OPTIPHOT-POL) mounted with a Nikon 70S camera was used to take polarized light optical microscopy (PLOM) images of the thin films prepared as described above in order to check dispersion of the OA in the film.

Samples from close to the film centers were sputter-coated with Au60Pd40 alloy using a Gressington 108Auto sputter coater operated at 20 mA for 90 s then imaged using a scanning electron microscope (SEM, FEI XL30 Sirion with FEG source).

2.4. Differential scanning calorimetry

Small samples of films (2.8–3.3 mg) were enclosed in aluminum pans; one sample per composition. A TA Instruments Q100 differential scanning calorimeter (DSC) was used at a nitrogen flow rate of 50 mL/min. The temperature in the DSC was first equilibrated to –40 °C, then heated to 185 °C. The sample was then cooled to –40 °C before heating to 185 °C for films and 200 °C for extruded solids in the second heating cycle. All heating and cooling rates were 10 °C/min.

T_g was taken to be the midpoint of the heat capacity change. The melting temperature, T_m , was measured as the minimum of the endothermic peak(s) from the second heating cycle (C2) to reflect consistent processing conditions and the crystallization temperature, T_{cc} , was taken as the maximum temperature of the exothermic peak upon cooling. The first heating cycle (C1) reveals crystallization occurring during processing such as solvent casting or cooling after extrusion, while C2 reveals crystallization from the melt at a controlled cooling rate in the DSC. Crystallinity, χ , was also calculated using melting enthalpy from C2 where:

$$\chi = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^0} \times 100\% \quad (1)$$

ΔH_m is the experimental melting enthalpy (J/g), ΔH_c is the experimental crystallization enthalpy (J/g) upon heating, and ΔH_m^0 is the melting enthalpy of 100% crystalline PHB, 146 J/g [18]. Since the measured enthalpies are based on overall sample weight (polymer and additive), crystallinity was adjusted based on polymer mass fraction to represent PHA crystallinity since the additive contributes to the overall weight, but does not melt. The full-width half max (FWHM) represents the width of the melting peak at half of the depth and is a measure of the narrowness of that feature.

For isothermal crystallization, 4–6 mg samples of each film were heated at 20 °C/min up to 180 or 185 °C for PHBV and 185 or 190 °C for PHBV/OA blends, depending on the melting endotherm range, and held for 1 min to remove thermal history. Then, samples were cooled at 50 °C/min to the temperature for crystallization (T_c) and held until crystallization was completed. For PHBV, T_c values were 80, 85, 90, 95, 100, 107, 113 and 119 °C. For 2% OA-m, T_c was 80, 90, 100, 105, 110, 117, 125 and 130 °C. For 2% OA-a, T_c values were 105, 115, 120, 125, 130, 135 and 137 °C. For all other PHBV/OA blends, the T_c values were 125, 130 and 135 °C. After each crystallization step, the samples were heated to 180 or 185 °C for PHBV and 185 or 190 °C for PHBV/OA blends at 20 °C/min to melt the formed crystals. The equilibrium melting temperature was determined by extrapolating the observed T_m at a given T_c to the $T_m = T_c$ line according to the Hoffman–Weeks method [19]. It should be noted that only the T_c s that led to crystallization after the T_c was reached were used in the Hoffman–Weeks plot to ensure only isothermal crystallization was captured.

3. Results and discussion

3.1. OA dispersion in PHBV/OA blend films

As mentioned, dispersion of particles is important for film homogeneity. From optical microscope images shown in Fig. 1, the OA particles appear to be uniformly distributed across the thin films produced with chloroform, where the darkest particles are presumed to be OA particles in the left column and the bright particles are OA in the polarized images in the right column. This uniform distribution also provides security that the samples used in DSC measurements are representative of the bulk blends.

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