

SHORT COMMUNICATION

Inducing Rapid Crystallization of Slowly-crystallizable Copolyester by *in situ* Generation of Crystalline Nuclei in Melt of CopolyesterBy Koichiro TAJIMA,¹ Tungalag DONG,¹ Kenichi HIROSE,¹ Taizo AOYAMA,² and Yoshio INOUE^{1,*}

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Recently bacterial poly(3-hydroxybutyrate) (P(3HB)) has attracted much attention due to its inherent biodegradability. However, its brittleness and narrow processing temperature window limit its application. To overcome the inferior properties of P(3HB), a variety of P(3HB) copolymers such as, poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (P(3HB-co-3HV)) and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (P(3HB-co-3HH)), have been bacterially synthesized.¹ Especially, P(3HB-co-3HH)s with 3HH unit content of about 10–20 mol% have good mechanical properties.² But the crystallization rate of P(3HB-co-3HH) compared with that of P(3HB) is too slow to use as molded products.

In general, the addition of nucleating agents may be an effective method for acceleration of the crystallization of crystallizable polymers and the increase of the nucleation density, resulting in the reduction of the spherulite size. Boron nitride (BN) was found to be effective as the nucleating agent for the crystallization of P(3HB) and P(3HB-co-3HV).^{3,4} But, it is found to be ineffective for P(3HB-co-3HH)s with relatively high 3HH unit content, as mentioned later in this article. Thus, it is in need of development of novel nucleating method effective for the crystallization of P(3HB-co-3HH)s.

It is known that P(3HB-co-3HH) with 3HH composition higher than about 20 mol% is partially miscible with P(3HB) in the amorphous phase.⁵ As bacterially synthesized P(3HB) is a completely isotactic stereoregular polyester, it has higher tendency to crystallize than the 3HB-containing copolyesters.⁶ Bacterial P(3HB-co-3HH)s with high 3HB unit content form P(3HB) homopolymer type crystal, although the crystallization is very slow.⁷ In this study, we studied rapid crystallization of P(3HB-co-3HH) induced by *in situ* generated crystalline nuclei.

EXPERIMENTAL

Bacterial P(3HB-co-3HH) with 3HH unit content 18 mol% [P(3HB-co-18 mol%3HH)] was kindly supplied by Kaneka Corporation, Osaka, Japan.⁸ Because the comonomer-unit compositional distribution of bacterial P(3HB-co-18 mol%3HH) is very wide, as-produced P(3HB-co-18 mol%3HH) was fractionated with a chloroform(solvent)/*n*-heptane-(nonsolvent) mixed solvent systems at ambient temperature.⁸ In this study, one of fractions with narrow comonomer-unit compositional distribution, that is, P(3HB-co-21 mol%3HH) ($M_n = 1.15 \times 10^5$, $M_w/M_n = 1.42$) was used. Bacterial P(3HB) sample ($M_n = 1.55 \times 10^5$, $M_w/M_n = 2.56$) provided by PHB Industrial S/A (Brazil) was used after purification. The BN fine powder was purchased from Nacal Tesque, Inc (Kyoto, Japan). BN is known as nucleating agent for P(3HB).⁹ The films of P(3HB-co-21 mol%3HH), P(3HB-co-21 mol%3HH)/P(3HB) (90 wt%/10 wt%) blend, P(3HB-co-21 mol%3HH)/BN (98 wt%/2 wt%) blend, P(3HB-co-21 mol%3HH)/P(3HB)/BN (88 wt%/10 wt%/2 wt%) blend (ternary blend), P(3HB) and P(3HB)/BN (98 wt%/2 wt%) blend were prepared by solution casting from chloroform solutions. Then, these cast films were dried at room temperature in vacuum for 1 week to remove the residual

solvent. The nonisothermal crystallization studies were performed on a differential scanning calorimeter (DSC:Pyris Diamond, Perkin-Elmer, Japan) with nitrogen as the purge gas. The samples were first melted at 190 °C for 3 min to erase the thermal history, and then the sample was cooled from 190 to –40 °C (cooling scan) at a scanning rate of 2.5 °C/min to observe the crystallization behavior. After cooling, the sample was held at –40 °C for 3 min. Finally the sample was heated from –40 to 200 °C (heating scan) at a scanning rate of 10 °C/min in order to observe the cold crystallization and melting behavior.

RESULTS AND DISCUSSION

Figure 1 shows the DSC cooling curves. The peak crystallization temperature and the temperature range of crystallization of P(3HB)/BN blend are, respectively, higher and narrower than those of pure P(3HB). Thus, it is confirmed that BN is a good nucleating agent for P(3HB).⁹ As expected, P(3HB-co-21 mol%3HH) did not crystallize during DSC cooling scan. Interestingly, P(3HB-co-21 mol%3HH) did not show any detectable exothermic peaks, even in the presence of BN, indicating that BN is not the effective nucleating agent for P(3HB-co-21 mol%3HH). Further, P(3HB) in P(3HB-co-21 mol%3HH)/P(3HB) blend can not crystallize during cooling scan. This may be due to that P(3HB-co-21 mol%3HH) and P(3HB) are partially immiscible in the amorphous phase. It is noticeable that one exothermic peak and two exothermic shoulders were observed for ternary blend, but one of the exothermic shoulders (at 80–10 °C) was very small and broad. The crystallization enthalpy estimated from these DSC peaks for this ternary blend was 30.7[J/g]. Even if the crystallinity of P(3HB) component is 100% in this blend sample, the crystallization enthalpy of P(3HB) component is only 14.6[J/g],¹⁰ as the weight percent of P(3HB) is 10 wt% in the blend. Thus, the contribution of the P(3HB-co-21 mol%3HH) component to the observed enthalpy is at least 16.1[J/g] in the ternary blend. The ternary blend shows the crystallization peak at 115.4 °C and the crystallization shoulders at 105–80 °C and 80–10 °C. The peak temperature of 115.4 °C observed for the ternary blend is very close to that of pure P(3HB)(= 113.6 °C) and lower than that of P(3HB)(= 128.7 °C) in the P(3HB)/BN blend, indicating that this peak corresponds to crystallization of P(3HB) in the ternary blend and P(3HB-co-21 mol%3HH) acts as a diluent that delays the beginning of the crystallization of P(3HB) in the ternary blend.

Figure 2 shows the DSC heating curves. There are several melting peaks in the ternary blend. The highest peak melting point observed at about 169.4 °C for this ternary blend is the melting peak of P(3HB) component, as this peak appeared at almost corresponding peak melting points of pure P(3HB)(= 170.9 °C) and P(3HB)(= 172.7 °C) in the P(3HB)/BN blend. Thus, the broad endothermic peak at 70–110 °C is the melting of P(3HB-co-21 mol%3HH) crystal.⁸

P(3HB-co-21 mol%3HH) showed no detectable exothermic (cold crystallization) peaks, even in the presence of BN. P(3HB-co-21

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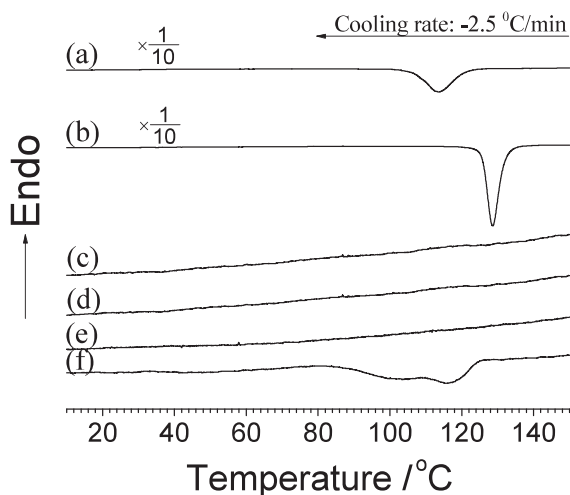


Figure 1. The cooling curves of P(3HB) and P(3HB-co-21 mol%3HH) samples: (a) P(3HB), (b) P(3HB)/BN (98 wt%/2 wt%), (c) P(3HB-co-21 mol%3HH), (d) P(3HB-co-21 mol%3HH)/BN (98 wt%/2 wt%), (e) P(3HB-co-21 mol%3HH)/PHB (90 wt%/10 wt%), (f) P(3HB-co-21 mol%3HH)/P(3HB)/BN (88 wt%/10 wt%/2 wt%).

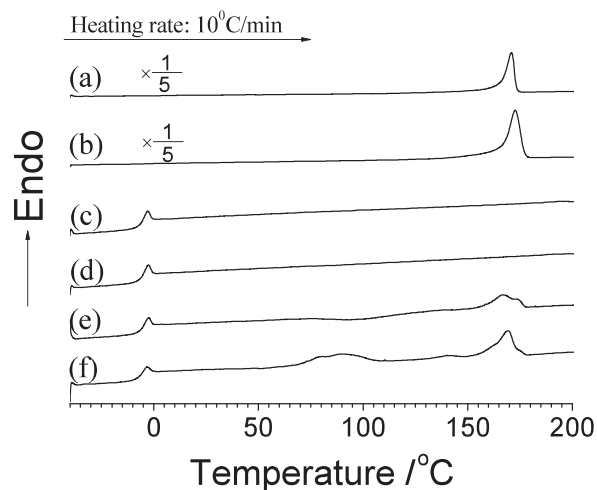


Figure 2. The heating curves of P(3HB) and P(3HB-co-21 mol%3HH) samples: (a) P(3HB), (b) P(3HB)/BN (98 wt%/2 wt%), (c) P(3HB-co-21 mol%3HH), (d) P(3HB-co-21 mol%3HH)/BN (98 wt%/2 wt%), (e) P(3HB-co-21 mol%3HH)/PHB (90 wt%/10 wt%), (f) P(3HB-co-21 mol%3HH)/P(3HB)/BN (88 wt%/10 wt%/2 wt%).

mol%3HH)/P(3HB) blend showed the exothermic (cold crystallization) peak at about 60–140 °C and the endothermic (melting) peaks at about 170 °C. The absolute value of exothermic enthalpy is almost the same as that of endothermic one during heating scan, indicating that only the P(3HB) component in this binary blend overwhelmingly crystallized during heating scan, but not during cooling scan. The P(3HB) and P(3HB)/BN blend did not show any detectable exothermic (cold crystallization) peak during heating scan, indicating that almost all crystallization has finished during cooling scans. The ternary blend shows small exothermic (cold crystallization) peak during heating scan and the cold crystallization enthalpy is 2.0[J/g], indicating that the major parts of the crystallization process have finished during cooling scans. The sum of the exothermic enthalpy of the crystallization at 80–10 °C during cooling scan and the exothermic enthalpy of the cold crystallization at 10–60 °C during heating scan is 5.0[J/g] and the fusion enthalpy of melting peak at 60–110 °C is 12.0[J/g], indicating that the fusion enthalpy of melting peak at 60–110 °C includes not only the contribution from the crystallization enthalpy at 80–10 °C during cooling scan and the cold crystallization enthalpy at 10–60 °C during heating scan but also that from the crystallization observed at 105–80 °C during cooling scan. The spherulites of ternary blend were found to contain the BN particle at the central parts of spherulites by using polarized light microscope. In conclusion, BN is the selective nucleating agent for P(3HB) but not for P(3HB-co-21 mol%3HH). In the ternary blend, during cooling process, the BN particles were found to induce the accelerated crystallization of P(3HB), and then *in situ* produced P(3HB) crystalline

particles induce the rapid crystallization of P(3HB-co-21 mol%3HH). The detailed studies are in progress.

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