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Transition of spherulite morphology in a crystalline/crystalline binary blend of biodegradable microbial polyesters

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ABSTRACT

Crystalline/crystalline binary blend films of microbial polyesters composed of poly[(*R*)-3-hydroxybutyrate-*co*-(*R*)-3hydroxyhexanoate] (P(3HB-*co*-3HH)) and poly[(*R*)-3-hydroxybutyrate] (P(3HB)) that exhibit a morphological change are prepared by solvent casting. Differential scanning calorimetry measurements indicate that P(3HB-*co*-3HH) and P(3HB) are miscible for all blend ratios because a single glass transition temperature is observed. Polarization optical microscopy is used to investigate the transition of spherulite morphology and measure the radial growth rate of spherulites in the blend films. P(3HB-*co*-3HH) and P(3HB) contain positive spherulites, whereas in the binary blends, spherulite morphology changes from positive to negative. This change is related to the different growth rates of P(3HB-*co*-3HH) and P(3HB) lamellar crystals. Partial enzymatic degradation of the film surfaces reveals that the lamellar crystals of negative spherulites are oriented both perpendicular and parallel to the radial direction of spherulites. A new growth mechanism for spherulites in crystalline/crystalline blends is constructed from the results obtained for the blend films.

1. Introduction

Poly[(*R*)-3-hydroxybutyrate] (P(3HB)) is produced from renewable resources such as sugar and plant oil by microbial organisms [1]. P(3HB) is a crystalline thermoplastic, and is biodegradable in natural environments [2]. Until recently, P(3HB) was thought impractical because of its weak, brittle mechanical properties [3,4]. However, the mechanical properties of P(3HB) films and fibers have recently been improved by increasing its molecular weight [5–8], developing new drawing methods [9–12], biosynthesis of P(3HB) copolymers [13–19] and blending P(3HB) with other polymers [20].

The brittleness of P(3HB) has been decreased by copolymerization with a second monomer, such as 3-hydroxyvalyrate [21], 3-hydroxyhexanoate [16,18], and 4-hydroxybutyrate [14]. The second monomer decreases the crystallinity of P(3HB) and increases its flexibility. Poly[(*R*)-3-hydroxybutyrate-*co*-(*R*)-3-hydroxyhexanoate] (P(3HB-*co*-3HH)) is a copolymer of P(3HB) that is biosynthesized from palm oil [22]. The mechanical properties of P(3HB-*co*-3HH) were improved as the 3HH ratio was increased from 0% to 25%; for example, elongation at break increased from 5% to 850% [18]. Polymer blending is another method to improve the material properties of P(3HB). Blends of P(3HB) with other polymers such as poly(epichlorohydrin) [23], poly(*p*-vinylphenol) [24], cellulose ester [25,26], poly(vinyl acetate) [27], atactic poly(3-hydroxybutyrate) [28], poly(lactic acid) [29,30] and poly(ethylene oxide) [31,32] have been reported. Investigation of the spherulitic morphology and highly-ordered structure of polymer blends is also important from the viewpoints of both fundamental science and industry. Feng et al. reported the melting temperature (T_m) and glass transition temperature (T_g) of P(3HB-*co*-3HH)/P(3HB) blends [33], but the crystalline and spherulitic morphologies, growth rate of spherulites and higher-order structures of P(3HB-*co*-3HH)/P(3HB) blends have not been investigated.

In this study, we found that P(3HB-*co*-3HH)/P(3HB) blends exhibit an interesting spherulitic morphology with a negative or

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positive transition depending on blend ratio. We reveal the cause of this transition of spherulitic morphology by differential scanning calorimetry (DSC), polarization optical microscopy (POM), and wide- and small-angle X-ray measurements (WAXD and SAXS) of the blends. Furthermore, partial enzymatic degradation was used to visualize the orientation of lamellar crystals in negative and positive spherulites of blend films by scanning electron microscopy (SEM).

2. Experimental section

2.1. Materials

Poly[(*R*)-3-hydroxybutyrate-*co*-9.6 mol%-(*R*)-3-hydroxyhexanoate] (P(3HB-*co*-3HH)) [weight-average molecular weight (M_w) = 2.6 × 10^5, number-average molecular weight (M_n) = 1.5 × 10^5 and polydispersity (PDI) = 1.7] was supplied by Kaneka Co.. P(3HB) was supplied by ICI Co. [M_w = 5.2 × 10^5, M_n = 3.3 × 10^5 and PDI = 1.6]. P(3HB-*co*-3HH) and P(3HB) were purified by reprecipitation from chloroform solution using *n*-hexane and then dried under vacuum at 30 °C for 3 days.

2.2. Preparation of binary blend films

Blend films were prepared by solvent-casting in chloroform using various blend ratios from 100/0 to 0/100 of P(3HB-*co*-3HH)/P(3HB). The two polymers were mixed in chloroform and then cast onto a Petri dish. The Petri dish was covered with aluminum foil containing air holes, and stored at room temperature for 3 days. Each film was completely dried after drying under vacuum for 3 days.

2.3. Thermal properties of blend films

The cold crystallization temperature (T_{cc}), T_g and T_m of the blend films were measured by DSC (Perkin–Elmer, Inc., DSC-8500, USA). Temperature calibration of the instrument was performed using indium. DSC properties of all samples were measured under a nitrogen atmosphere. The first heating cycle involved heating at a rate of 20 °C/min from −40 °C to 200 °C, maintaining at 200 °C for 1 min, and then quenching to −40 °C at a rate of −200 °C/min. T_g, T_{cc} and T_m were determined from DSC curves obtained for the second heating cycle at a heating rate of 20 °C/min. The thermal properties of the blends after isothermal crystallization at 90 °C were measured by DSC to reveal their higher-order structure.

2.4. POM observation

Samples for morphological observation were prepared by melting blend films between two cover glasses in a washer with a thickness of 20 μm. *In situ* observation of growing spherulites was carried out by POM (Nikon, Eclipse E600 POL, Japan) equipped with a temperature jump stage (two hot-stages) (Japan High Tech Co., LK-300B, Japan). The polarizer and depolarizer were kept at right angles. The first hot-stage was set at 200 °C, and other was set at the desired crystallization temperature. Each sample was melted at 200 °C for 30 s on the first hot-stage, and then the molten sample was transferred to the second hot-stage. Observation was continued until the field was completely covered with spherulites. The radial growth rate of spherulites was calculated from the slope of spherulite radius against observation time. Samples with blend ratios of 100/0, 90/10, 85/15, 75/25, 70/30, 60/40, 50/50, 40/60, 25/75 and 0/100, all of which were annealed at a temperature at 90 °C, were investigated.

2.5. WAXD and SAXS measurements

To investigate the higher-order structure of the blend films, WAXD and SAXS measurements were performed using synchrotron radiation X-rays at BL-45XU and BL-47XU of SPring-8, Harima, Japan. The wavelength, camera length, exposure time and detector used were 0.09 nm, 145 mm (WAXD) or 2400 mm (SAXS), 22 ms (WAXD) or 1058 ms (SAXS) and CCD camera, respectively.

2.6. Enzymatic etching and surface observation of annealed blend films

The amorphous regions on the surfaces of the annealed samples were etched by enzymatic degradation with extracellular PHB depolymerase from *Ralstonia pickettii* T1 (200 μg/mL) and potassium phosphate buffer (pH 7.4, 1 mL). After deposition of a Pt coating, film surfaces were observed by SEM (Hitachi, FE-SEM S-4000, Japan).

3. Results and discussion

3.1. Thermal properties

DSC thermograms of neat P(3HB-*co*-3HH), neat P(3HB) and blend films with various blend ratios of P(3HB-*co*-3HH) to P(3HB) are shown in Fig. 1. T_g, T_{cc}, and T_m of each sample are listed in Table 1. Neat P(3HB-*co*-3HH) and P(3HB) exhibited T_g at −1.5 and 2.1 °C, respectively. For the blend samples, T_g decreased slightly

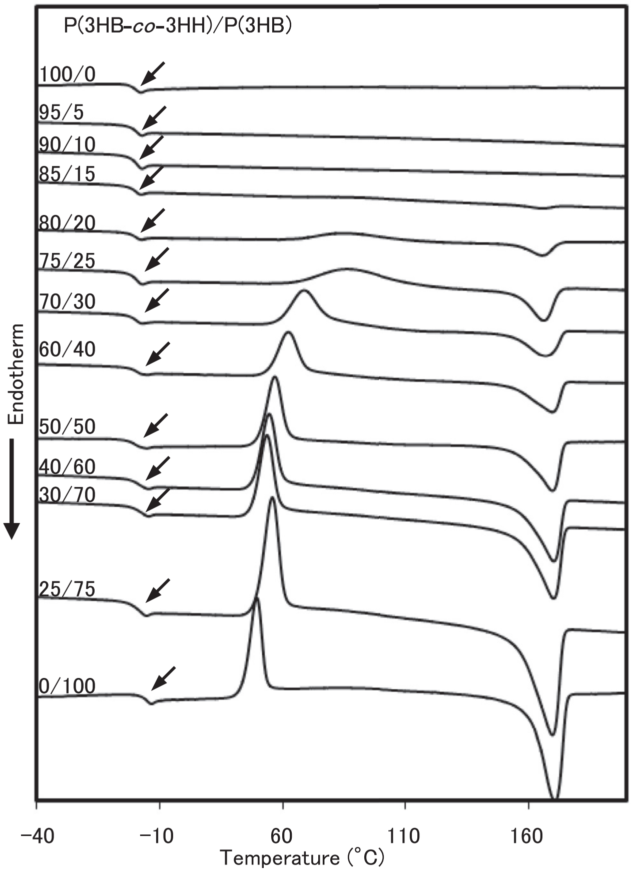

Fig. 1. DSC thermograms of P(3HB-*co*-3HHx)/P(3HB) blends with various blend ratios from the second heating run. The arrows indicate glass transition points.