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Nucleation and Crystallization Behavior of Poly(butylene succinate) Induced by Its α-Cyclodextrin Inclusion Complex: Effect of Stoichiometry

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Introduction

In recent years, biodegradable polymers have attracted much attention as environment-friendly materials. However, compared with the traditional engineering polymers, they are inferior with respect to physical properties and processability. To improve these weak points of biodegradable polymers, polymer blending and copolymerization have been investigated by many researchers.[1−5]

An addition of nucleating agent is known to enhance the crystallization rate and the overall crystallinity of crystalline polymers. Cyclodextrins (CDs) are considered to be ideal candidates as a green nucleating agent for biodegradable polymers[5] because they do not elicit immune responses and have low toxicities in animals and humans.[6] In our previous work,[7] we have investigated the effect of α-CD inclusion complexes (α-CD ICs) with several linear threading polymers on the crystallization of biodegradable polymers. It was found that the addition of α-CD−polymer IC more effectively enhances the nucleation of the polymer when the guest polymer of the IC was the same one as the polymer matrix. In this Note, the effect of the stoichiometry between the host α-CD and the guest polymer in the α-CD IC on the enhancement of the polymer nucleation is investigated because the stoichiometry is also expected to affect the extent of the nucleating effect. The nucleation and crystallization behavior of poly(butylene succinate) (PBS) blended with the α-CD−PBS IC with different stoichiometries are investigated by differential scanning calorimetry (DSC) and polarized optical microscopy (POM).

Experimental Section

Materials. PBS ($M_n = 2.2 \times 10^4$; $M_w/M_n = 1.8$) was purchased from Showa Highpolymer Co., Ltd., Japan. α-CD was kindly supplied by Nihon Shokuhin Kako Co., Ltd., Japan. The solvents dimethyl sulfoxide (DMSO), chloroform, and ethanol (Nacalai Tesque, Inc., Kyoto, Japan) were used as received. Before use, PBS was purified by precipitation into ethanol from chloroform solution.

The channel-structured α-CD (α-CD$_{CN}$) used in the present work was prepared according to the method reported in the literature.[8] The methods for the preparation and purification of α-CD−PBS IC (PBS-IC) are similar to those in our previous work.[7] α-CD (4.0 g) and PBS (0.25 g) were dissolved respectively in 8 and 2 mL of DMSO at 80 °C to get clear solutions, and then they were mixed together. The mixed solution was stirred at 60 °C for 3 h, then quenched to 30 °C, and continuously stirred for the desired time. The samples PBS-IC3, PBS-IC2, and PBS-IC1 were obtained after stirring for 1, 2, and 7 days, respectively. The host−guest stoichiometry of each IC was estimated on the basis of ^{1}H NMR analysis. The molar ratio of the PBS monomeric repeat unit to α-CD is about 0.8:1, 1.6:1, and 2.1:1 for PBS-IC1, -2 and -3, respectively.

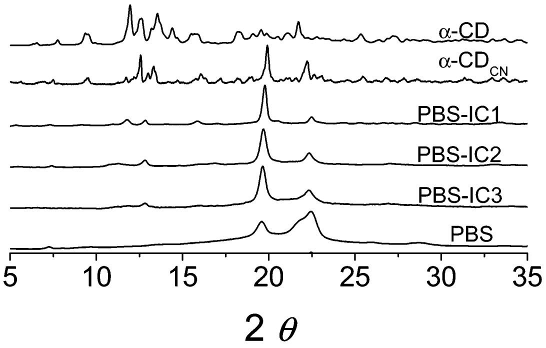

Figure 1. WAXD patterns of α-CD, α-CD$_{CN}$, PBS, and PBS-ICs.

Measurements. Differential scanning calorimetry (DSC) thermograms of the samples presealed into aluminum pans were recorded on a Pyris Diamond DSC (Perkin-Elmer Co., Japan). The sample was heated to 140 °C, melted for 5 min, and then cooled to 0 °C at 10 °C min^{-1}.

Polarized optical microscopic observation was performed on a BX90 polarizing optical microscope (POM) (Olympus Co., Japan) equipped with a digital camera. The samples were first heated to 140 °C, kept at this temperature for 5 min, and then quenched to 90 °C directly.

Results and Discussion

Channel Structure of α-CD and Its PBS-IC. The formation of the α-CD$_{CN}$ was confirmed by wide-angle X-ray diffraction (WAXD) (Figure 1). A prominent peak can be observed at about 20° for the α-CD$_{CN}$, which is well-known to be the characteristic of α-CD-based IC crystals adopting the channel structure.[9] This result strongly suggests that the α-CD$_{CN}$ with the channel structure was mainly obtained, despite the presence of small amount of cage structured α-CDs in the α-CD$_{CN}$ powder. As shown in Figure 1, the prominent peak at about 20° is also observed for each PBS-IC, and the peak corresponding to the cage structure at about 12.5° almost disappeared, indicating that the PBS-ICs adopt the channel structure.

Figure 2 shows the DSC thermograms of α-CD, α-CD$_{CN}$, PBS, and PBS-ICs. α-CD and α-CD$_{CN}$ do not show any detectable thermal transition in the cooling scan. The crystallization temperature (T_c) of pure PBS is observed at about 76.0 °C. Upon IC formation, the crystallization peak of PBS disappeared in the cooling scan of PBS-IC1, indicating that the crystallization of the guest PBS was suppressed in the PBS-IC1. However, the small crystallization peaks of PBS are apparent in the temperature range higher than the T_c of pure PBS, indicating the presence of the PBS chains crystallizable outside the α-CD cavity. This result may be attributable to the limited mobility of uncovered part of the PBS segments constrained by its included part resided in the α-CD cavity, leading to the acceleration of PBS crystallization.

Nonisothermal Crystallization Behavior of PBS. To estimate the nucleation effects of α-CD, α-CD$_{CN}$, and PBS-ICs on the melt crystallization of PBS, nonisothermal crystallization behavior was observed during DSC cooling scan as shown in Figure 3. Upon the addition of PBS-IC1, -2, and -3, the T_c value of PBS increased from 76.0 °C to 79.6, 84.6, and 89.7 °C, respectively. These T_c values clearly show that the nucleating

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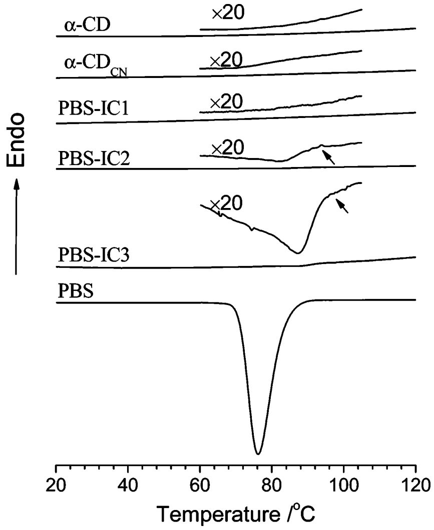

Figure 2. DSC thermograms of cooling scans of α-CD, α-CD$_{CN}$, PBS, and PBS-ICs. The sort curves are the corresponding enlarged DSC curves (×20). The arrows indicate onset temperature of PBS-IC crystallization.

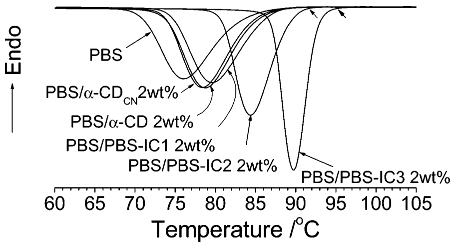

Figure 3. DSC nonisothermal crystallization curves. The short arrows indicate the onset temperature of PBS crystallization.

effect of the PBS-IC increased with the decrease in the number of α-CD molecules threaded on the PBS chain, indicating that the extent of the nucleating effect of α-CD−polymer ICs could be affected not only by the kind of included polymer[7] but also by the stoichiometry of IC.

The PBS/α-CD$_{CN}$ 2 wt % shows the T_c at 78.4 °C, which is almost the same as that of the PBS/α-CD 2 wt %. This result indicates that α-CD is less effective to enhance the crystallization of PBS, regardless of its crystalline structure, and the epitaxial crystallization of PBS on the surface of α-CD is not the main factor for the enhancement of crystallization of bulk PBS containing PBS-ICs. It is thought that the main factor for nucleation of the bulk PBS might be attributed to the crystallization of uncovered PBS segments in PBS-ICs. The uncovered parts of PBS in the PBS-IC2 and -3 with a small amount of α-CD are still crystallizable, and their crystallizations are detected as very broad peaks (Figure 2), suggesting that the α-CD restricts the folding of the uncovered PBS segment and makes it slow. However, the onset crystallization temperatures of PBS-IC2 and -3 are detected at about 92 and 96 °C, close to those of the PBS/PBS-IC2 2 wt % and PBS/PBS-IC3 2 wt % blends, respectively (Figure 3). Therefore, it is thought that the crystallization of bulk PBS starts as the ordering of the uncovered PBS segments on the surface of PBS-IC particles, accompanied by the ordering of the adjacent bulk PBS segments.

Spherulitic Morphology. POM was used to monitor the growth and size of the spherulites. In the isothermal growth at 90 °C, the diameter of pure PBS spherulites reached 400 μm before they impinged on each other. With the addition of PBS-IC1, the average diameter of PBS spherulites decreased to about 150 μm, which is almost the same as those of the PBS/α-CD 2 wt % and PBS/α-CD$_{CN}$ 2 wt %. For the PBS/PBS-IC2 2 wt % sample, the average diameter is about 30 μm. In the case of PBS/PBS-IC3 2 wt %, the improved density of nuclei further increased, and the average diameter drastically drops to about 10 μm. It is clear that the density of nuclei increases as the uncovered parts of the PBS chain in the PBS-ICs increase. These observations agree with those of the DSC analysis.

Conclusion

The DSC and POM results demonstrated that α-CD alone cannot effectively enhance crystallization of PBS, regardless of its crystalline structure. However, the PBS-IC with a small amount of α-CD can greatly accelerate the crystallization of PBS, and its nucleation capability remarkably increases with the decreasing number of threaded α-CD molecules, indicating that the stoichiometry of the PBS-IC can affect the enhancement of the PBS crystallization. Therefore, it is thought that not the α-CD itself, but the PBS segments not covered by α-CD induce the enhanced crystallization of PBS.

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