The Effect of Methylated Cyclodextrins on the Morphological Change of Poly(3-hydroxybutyrate) with and without the Formation of Inclusion Complex

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Introduction

Bacterial poly(3-hydroxybutyrate) [P(3HB)] is accumulated as the intracellular energy reserve by a variety of microorganisms in the environment. It can be degraded into water and carbon dioxide under environmental conditions by a variety of bacteria and has the potential for applications of biodegradable plastics. However, the inherent brittleness impedes the bacterial P(3HB) from being an engineering plastic. It is known that the brittleness of P(3HB) is due to the quite large size of the spherulites and secondary crystallization.[1] To inhibit the brittleness and to improve the processing efficiency, nucleating agents, such as boron nitride or talc, must be added during the production of P(3HB) materials. However, to produce a more environmentally friendly product, it is important to seek an alternative nucleating agent. The nucleation of the P(3HB) segment was found to be enhanced and the crystallization to be accelerated upon partial complexation with cyclodextrin. Moreover, our recent investigation showed that the direct addition of cyclodextrin powder into P(3HB) can enhance the nucleation and promote the crystallization of P(3HB), although there can be the difference in the extent of effect between a direct addition and inclusion complexation.[2,3]

From this view point, we investigate the possibility of inclusion complex (IC) formation between various CDs and P(3HB), the subsequent effect of CDs on the crystallization of P(3HB), and the possible interactions between CDs and P(3HB) chain which can be varied with the degree of substitution of CDs.

Experimental

The blend samples of methylated CDs with P(3HB) were prepared in the chloroform solution. In the case of unmodified natural CD/P(3HB) blend, the blend sample was prepared in the suspension state of chloroform since natural CD cannot be dissolved in chloroform. pure P(3HB) sample and respective CDs were added together in chloroform under vigorous stirring. After stirred at 60°C for 3 hours, the mixture was cooled to the room temperature and stirred for further 1 day. The solvent was evaporated at room temperature for 2 days, and then the products were dried in vacuum at room temperature for 2 days.

The effects of methylated CDs on the crystallization behavior of P(3HB) have been investigated by employing differential scanning calorimetry (DSC), polarized optical microscopy (POM), wide-angle X-ray diffraction (WAXD), and Fourier transform infrared (FT-IR) spectra.

Results and discussion

As shown in Figure 1, it was found that the types of interaction between CDs and P(3HB) was quite dependent on the degree of methyl-substitution of cyclodextrin. The nucleation of the P(3HB) was found to be enhanced and the crystallization to be accelerated upon the immiscible blend with unmodified natural cyclodextrin, while the crystallization of P(3HB) was restricted by the introduction of methylated cyclodextrin via the formation of miscible blend with di-O-methyl cyclodextrin, and via the formation of IC with tri-O-methyl cyclodextrin.

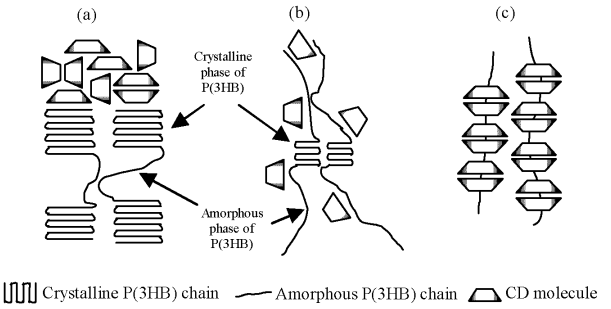

Figure 1. Proposed phase structure of (a) β-CD/P(3HB) blend, (b) β-DMCD/P(3HB) blend, (c) β-TMCD/P(3HB) blend.

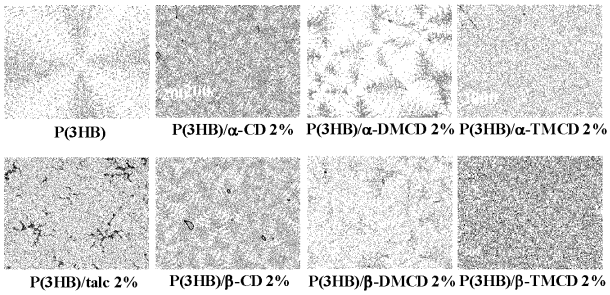

Figure 2. POM photographs of P(3HB), P(3HB)/talc blend, and P(3HB)/CD blends.

As shown in Figure 2, the crystallization behavior and the nucleation density of P(3HB) were improved by the introduction of various CDs, although the nucleating effects of CDs did not come up to that of talc.

P(3HB)/β-TMCD blend, which was proved to be an inclusion complex in the previous investigation, showed the highest crystallization rate among all P(3HB)/CD blends, indicating that the possibility of IC formation can affect the nucleating effect of CD on the crystallization of P(3HB).

The crystallization of P(3HB) was enhanced by the incorporation of methylated CDs in an appropriate range of prescription and restricted by a negative effect of miscible blend when the amount of addition exceeds the optimum value for the maximum nucleating effect.

Conclusions

The hydrophobicity of cyclodextrin could be varied with the methyl substitution of host CD, and the possibility of IC formation and the types of interaction between respective CDs and polyesters were subsequently changed. Further, the effect of cyclodextrins on the morphological change of biodegradable polymer was shown to depend on the degree of IC formation between cyclodextrin and biodegradable polymer as well as on the type of interaction between respective CDs and polyesters. That is, the enhancement and/or the restriction of the crystallization of P(3HB) were observed by the incorporation of various kind of cyclodextrins with different cavity size and hydrophobicity.

References

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