Effect of Nucleating Agents on Crystallization of Poly(3-hydroxybutyrate) and Its Copolymer

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Abstract: Crystallization and nucleation behavior of microbial poly(3-hydroxybutyrate) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) were investigated by differential scanning calorimetry. The polymers mixed with talc as a nucleating agent showed promotion of crystallization of the polymers, while the addition of saccharin hardly promoted crystallization. However, melting points and long periods of these polymers crystallized isothermally after mixing with talc and saccharin, decreased considerably. The depression in melting points and long periods of the polymers mixed with saccharin was larger than that mixed with talc, implying that saccharin was included more easily within the polymer crystal playing the role of diluent. The concentration of around 4% is most appropriate to reveal typical effect of nucleating agents without severe deterioration of mechanical properties. Large spherulites were formed in plain polymers and those mixed with saccharin, whilst extremely small spherulites were formed in the polymers mixed with talc.

1. Introduction

Poly(3-hydroxybutyrate)(PHB) and its copolymer poly(3-hydroxybutyrate-co-3-hydroxyvalerate) \( P(\text{HB-co-HV}) \) can be isolated from the cells of many types of bacteria by solvent extraction \( \{1,2\} \). These products are thermoplastic, biodegradable and biocompatible materials \( \{3,4\} \). The polymers are highly pure because of microbial origin without catalysts so that they are very convenient materials to study crystallization kinetics and the effect of nucleating agents. Crystallization and morphology of PHB and \( P(\text{HB-co-HV}) \) have been reported by a few authors \( \{5,6\} \). These polymers slow extremely slow crystallization rate \( \{7,8\} \), which is disadvantageous to the manufacturing process of fibers or films for practical use. Nucleation behavior of nucleating agents (1% of talc and saccharin) for PHB has been reported by polarized optical microscopic observation \( \{9\} \), however, there is no further investigation on the nucleation behavior of these polymers.

In this study, crystallization and melting behavior of PHB and \( P(\text{HB-co-HV}) \) mixed with higher content of nucleating agents have been investigated by differential scanning calorimetry (DSC). From the comparison with kinetic rate constants evaluated from crystallization isotherms, the effect of nucleating agents was discussed. Melting points and structural change of the polymers crystallized isothermally after mixed with talc and saccharin were evaluated.

2. Experimental

The microbial PHB and \( P(\text{HB-co-9 mol}\% \text{HV}) \), which show relatively speedy crystallization processes, were purchased from Aldrich Chemical Co., Inc. As the nucleating agents, talc and saccharin were used. The content of nucleating agents was mainly selected to 4 wt%. However, contents of 1 and 10 wt% were adequately used for comparison. The polymer and the nucleating agent were well mixed and ground in a small grinding bowl so as to control a diameter of agent less than 5 \( \mu \text{m} \), then hot-pressed at 185 °C for 2 min to form a film. The minimum melt temperature and time should be chosen because the polymers easily decompose if heated up at temperatures above 180°C \( \{10,11\} \). The films lapped with aluminum foil were crystallized isothermally for 24 h in silicone oil after melting at 185 °C for 2 min.

Heating and cooling curves of these polymer films (3 mg) were studied in a Perkin Elmer Model DSC-7 dif-
Differential scanning calorimeter (DSC) at a heating rate of 5 °C/min under nitrogen flow. In order to obtain the crystallization isotherms, the samples were melted at 185 °C for 2 min in DSC, then rapidly cooled to the desired temperature (within 15 sec). Temperature and calorimetric scales were calibrated with indium (156.6 °C and 28.4 J/g) and benzoic acid (122.4 °C and 8.13 J/g), respectively. Long periods of the polymers were obtained from small-angle X-ray scattering (SAXS) patterns recorded using nickel-filtered CuKα X-ray beams with a pinhole collimator from a Rigaku-Denki Rotaunit RU-200.

3. Results and Discussion

Typical DSC heating and cooling cyclic curves of PHB and P(HB-co-9 mol% HV) mixed with 4 and 10% talc and saccharin are shown in Fig.1. The film sample was heated up to 185 °C, and successively cooled down with a rate of 5 °C/min. The peak temperatures of melting and crystallization of PHB were 175 and 124 °C, respectively. The melting point of PHB remained almost unchanged and the peak of crystallization shifted to the higher temperature to ca. 2 °C irrespective of the talc content. Whereas, the peaks of melting and crystallization for PHB mixed with 4% saccharin shifted to lower temperatures of 3 and 12 °C, and those mixed with 10% saccharin to 9 and 26 °C, respectively, reflecting typical diluent effects. The copolymer P(HB-co-9 mol% HV) also shows the effect of nucleating agents very similar to PHB, though the effect becomes somewhat indistinguishable.

Fig. 1 DSC heating (---) and cooling (-----) cyclic curves for PHB and P(HB-co-9 mol% HV) mixed with talc and saccharin.

Crystallinity of PHB estimated from melting peak area was ca. 75%, which remained almost unchanged after mixed with 4% talc but slightly decreased (ca. 5%) after mixed with 4% saccharin. Crystallinity of the copolymer was ca. 65% very close to that reported previously [12], and showed similar variation to those of PHB.

Fig. 2 shows typical DSC exothermic curves obtained during isothermal crystallization for PHB mixed with 4% talc and saccharin. Crystallization temperatures were indicated.

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Fig. 2 shows typical DSC exothermic curves obtained during isothermal crystallization for PHB mixed with 4% talc or saccharin. Crystallization of PHB accelerated and delayed with the addition of talc and saccharin, respectively. P(HB-co-9 mol% HV) also showed similar variation of DSC curves. Crystallization isotherms were obtained
Table 1 Values of Avrami Index (n) and the Kinetic Rate Constant (k) as a Function of Tc for Polymers Plain and Mixed with 4% Talc and Saccharin

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tc/°C</th>
<th>n</th>
<th>k/min^n</th>
<th>t1/2/min</th>
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<tbody>
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<td></td>
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<td></td>
<td></td>
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<td>110</td>
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<td>1.90×10^{-4}</td>
<td>12.0</td>
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<tr>
<td></td>
<td>100</td>
<td>2.5</td>
<td>8.91</td>
<td>0.35</td>
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<td>P(HB-co-9 mol% HV)</td>
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<td>90</td>
<td>2.4</td>
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<tr>
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<td>90</td>
<td>2.4</td>
<td>3.09×10^{-1}</td>
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</table>

by plotting Xt (weight fraction of crystallinity at time t to the final one) against the crystallization time t, from which the crystallization time t1/2 at a half fraction of crystallinity (Xt=1/2) was evaluated as the same procedure to the other literature (13).

Table 1 lists Avrami index n, kinetic rate constant k and t1/2 of PHB and P(HB-co-9 mol% HV) against the crystallization temperature Tc obtained from the crystallization isotherms using the following equation (14):

\[ 1-X_t = \exp (4t^n) \]  

The index n was the slope obtained from plot of log [\( \ln(1-X_t) \)] against log t. The rate constant k was calculated from t1/2 using the following equation:

\[ k = \ln 2 / (t_{1/2})^n \]  

Comparing k values, it can be said that crystallization of both polymers accelerates with addition of talc, while it rather delays with the addition of saccharin. The n for PHB changed from 2.4 to 3.3, being almost independent or slightly decreasing as the Tc decreased in a similar manner to other literatures (13,15). Barham [9] has deduced that plain PHB melts undergo homogeneous nucleation, that the nucleating effect of talc is due to the reduction in entropy of partially adsorbed molecules, and that the nucleating effect of saccharin is due to adsorption of molecules onto the surface in what is close to their crystallographic form (i.e., epitaxial growth). Under the present conditions, talc shows considerable promotion of crystallization, while saccharin does not contribute to any promotion of crystallization.

Fig. 3 shows melting points of PHB and P(HB-co-9 mol % HV) film samples mixed with 4% of talc or saccharin isothermally crystallized for 24 h after melted at 185 °C. Both samples crystallized at temperatures below 130 °C showed doublet melting peaks; the lower temperature peak corresponds to real melting peak, while the higher one corresponds to the peak of crystals caused by re-crystallization (16). The real melting points of plain PHB are ca. 5 °C higher than those of PHB mixed with saccharin. While, the real ones for PHB mixed with talc showed less dependence on Tc and showed intermediate variation at Tc above 105 °C, where an intersection of both curves for plain PHB and those mixed with talc was observed. The copolymer P(HB-co-9 mol% HV) showed similar doublet melting peak. The real melting points of the plain copolymer are ca. 3 °C higher than those mixed with saccharin at Tc below 130 °C. Above 130 °C, the copolymer of plain and mixed with saccharin showed lower melting point series because of typical partial melting though that mixed with talc showed single curve of real melting points due to the promotion of crystallization.

Fig. 4 shows long periods of these PHB samples. Long periods increased hyperbolically as Tc increased. Long periods of plain PHB are highest and those mixed with saccharin are lowest. The intermediate effect was observed for talc. The effects of these nucleating agents were closely parallel to those on melting points. Whereas, the long periods of P(HB-co-9 mol% HV) does not show so large depression with addition of talc or saccharin. The copolymer P(HB-co-15 mol% HV) hardly showed any depression in long periods and melting points with addition of 4% talc or saccharin. The effect of nucleating agents for PHB is more prominent than that for P(HB-co-9 mol% HV) as seen in Figs. 3 and 4. Thus,
the effects of nucleating agents for copolymers became indistinguishable as the HV composition increased. This is considered that the foreign monomer units (HV component) randomly included between HB monomer units play the role of nucleating or diluent agents during crystallization of the HB units.

On contrast to SAXS study, there was no change in lattice indices obtained by wide-angle X-ray scattering between plain polymers and those mixed with talc or saccharin. PHB and P(HB-co-9 mol% HV) mixed with 1% talc or saccharin hardly showed any promotion of crystallization and depression in melting points and long periods.

Typical polarized micrographs of P(HB-co-9 mol% HV) mixed with talc and saccharin isothermally crystallized at 120 °C for 24 h are shown in Fig.5. The large spherulites of the copolymer, which is very similar to those of PHB [5,9], are observed for the plain copolymer (a) and that mixed with saccharin (c). The diameter of them is frequently evaluated to a few millimeters. The disorder or irregular regions must be included in spherulites of the copolymer mixed with saccharin because melting points or long periods decreased significantly, though
spherulites apparently seem very similar to those of the plain PHB. Contrast to this, the copolymer mixed with talc (b) shows extremely fine spherulites, whose diameter is evaluated less than 10 μm. More drastic change of nucleating or diluent effect was observed for the plain PHB rather than for the copolymer, reflecting that the effect was predominant.

The nucleating effect similar to talc was observed by using BF₂, SrF₂, Al₂O₃ and etc., whereas the diluent effect similar to saccharin was found by using SnCl₂, ε-aminocaproic acid, hydroquinone and etc., resulting in considerable decrease in molecular weights of the polymers.

The brittle properties of plain polymers [12] were somewhat improved (ca. 50% increase in tensile strain) by mixing with 4% talc because the spherulites became finer. Moreover, the polymers mixed with 4% saccharin became flexible because of the diluent effect (ca. twofold increase in tensile strain) accompanied with slight decrease (ca. 10%) in strength. The properties of the polymers were hardly improved with addition of 1% nucleating agents, while those became rather brittle and deteriorated with addition of 10% agents.

**References**

14. M. Avrami, *J. Chem. Phys.*, 7, 1103 (1939); 8, 211 (1940); 9, 177 (1941).