Influence of tacticity and molecular weight of poly(vinyl alcohol) on crystallization and biodegradation of poly(3-hydroxybutyric acid)/poly(vinyl alcohol) blend films

Tetsuya Ikejima, Naoko Yoshie, Yoshio Inoue*

Department of Biomolecular Engineering, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-Ku, Yokohama 226-8501, Japan

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Abstract

The crystallinity and the profile of biodegradation by environmental microorganisms in river water were investigated for bacterial poly(3-hydroxybutyric acid) [PHB] blend films with stereoregular poly(vinyl alcohol)s [PVA] and low-molecular weight atactic PVAs. According to the DSC thermal analysis, the crystallization of PHB was found to be not suppressed by blending with highly isotactic PVA. This result is consistent with previous results obtained by using Fourier-transformed infrared spectroscopy, that is, PVA sample with higher syndiotacticity brings about higher suppression of crystallization of PHB. In the PHB/PVA blend system, the formation of small PHB crystals was found by wide angle X-ray scattering, even in the samples for which the melting endotherm of PHB was not detected by DSC. The biodegradation profile of these blend films depends strongly on the water solubility of the PVA component. The PHB blends with low-molecular weight atactic PVA, which shows higher water solubility than atactic PVA with higher molecular weight and stereoregular PVA, exhibited faster degradation compared to the PHB blends with high-molecular weight atactic PVA system. The biodegradability of the PHB blends with stereoregular PVA became extremely low, when the PVA composition in the blends became high. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

Bacterially synthesized poly(3-hydroxybutyric acid) [PHB] has many advantages such as biodegradability, biocompatibility and optical activity [1–3]. PHB is thermoplastic with high degree of crystallinity [2,4-6], thus this has much potential in applications to medical materials, such as drug delivery system, and as biodegradable molded plastics. But, up to now, PHB has not been widely utilized due to its stiffness and brittleness. An approach to overcome these undesirable properties is to make miscible blends of PHB with flexible polymers and/or plasticizer. It is desirable to choose biodegradable blend partners for PHB, when the blends are designed to use as the biodegradable materials. PHB has been reported to be miscible in the melt with a few chemically synthetic polymers, such as, poly(ethylene oxide) [PEO] [7], poly(ethenyl acetate) [PVAc] [8], poly(vinylidene fluoride) [PVdF] [9] and poly(vinyl phenol) [PVPh] [10]. The PHB/PEO blend systems are fully biodegradable, but the PHB/PVAc, PHB/PVdF and PHB/PVPh blends are only partially biodegradable. Blending brings about various modification of properties, such as improvement of handling, change of biodegradation rate and so on [11–13]. The non-degradable components sometimes inhibit the degradation of the degradable components in the blend. For example, on the enzymatic degradation of PHB/PVAc blend films, degradation of PHB in the blends was found to be suppressed by the non-degradable PVAc layer existing in the surface region [14]. Enzymatic degradation rate of PHB/PEO blends is faster than those of PHB [11]. In this system, since PEO in the blend is dissolved into water during the degradation, the accessibility of depolymerase increases.

The authors have chosen fully saponified poly(vinyl alcohol) [PVA] as the partner of the PHB blend. In fact, PVA has biodegradability [15] and excellent...
mechanical properties [16] compared with pure PHB. Since both microbial PHB and chemosynthetic PVA are biodegradable [1,15], PHB/PVA blend is considered as the fully biodegradable polymer blend system.

The PHB/PVA blend system has been found to be partially compatible [17–19]. The decrease in the crystallinity of PHB by blending with PVA was found by using differential scanning calorimetry (DSC) [17] and Fourier transformed infrared spectroscopy (FT–IR) [19]. The influence of tacticity of PVA on the crystallization of PHB and the compatibility between PVA and PHB in the blends have been also investigated [18,19]. According to these reports, PVA with higher syndiotacticity, which has higher ability to form intermolecular hydrogen bond with PHB, has higher compatibility with PHB. The PHB blends with highly isotactic PVA [i-PVA] have been also investigated in the previous report using FT–IR spectroscopy [19].

In this article, the crystallinity of PHB in the PHB/i-PVA blends will be further investigated by using DSC. PHB/i-PVA blends will serve clearer information about the effect of the hydrogen-bond interaction on the crystallization behavior of PHB. The crystallization behavior of PHB in the blends with stereoregular PVAs will also be investigated by using DSC and wide angle X-ray diffractometry (WAXD). The PHB blends with low-molecular weight atactic PVAs [a-PVAs] will also be investigated, as the molecular weight of a component polymer is one important factor affecting mixing states of polymer blend systems.

The composition-dependent change of the solid structure of the PHB/PVA blend system, found in our previous studies [17–19], should affect the biodegradability of the blend system. Moreover, since PHB and PVA are known to be biodegraded by different microorganisms with different pathways [1,15], the biodegradation profile of the PHB/PVA blends is expected to be largely dependent on their composition as well as mixing states. The biodegradation profile of the PHB/a-PVA blend system has already been observed by biochemical oxygen demand (BOD) method [20]. In the PHB/a-PVA blend films, an acceleration of degradation was observed, which reflected the change of the solid-state structure of the blend component.

In this article, the biodegradation profile of PHB blend films with highly stereoregular PVA and low-molecular weight a-PVA under natural environment will also be investigated. The solubility of PVA in water is expected to play an important role in the degradation. The solubility of PVA in water is known to depend on its degree of crystallinity and crystalline morphology, in turn to depend on its stereoregularity [21] and molecular weight [16]. A series of BOD tests will serve the information about the dominant factors determining the biodegradation profile of the PHB/PVA blend system.

2. Experimental

2.1. Sample preparation

PHB (LOT No. 06707KN) purchased from Aldrich Chemical, USA, was used after purification by precipitation in n-hexane from chloroform solution, subsequently precipitated in methanol from chloroform solution. The average molecular weight \( M_w \) and the melting point of purified PHB sample were 380000 and 170.5°C, respectively.

a-PVA was purchased from Nacalai Tesque, Kyoto, Japan. Highly syndiotactic PVA [s-PVA] and highly isotactic PVA [i-PVA] were kindly supplied by Kuraray Co. Ltd., Osaka, Japan. Molecular characteristics, such as average molecular weight, melting temperatures as well as triad tacticities of these PVA samples have already been reported [19]. These PVAs were used without further purification.

Low-molecular weight a-PVA samples, denoted as a-PVA-1, 3 and 5, were also supplied by Kuraray Co. Ltd. Low-molecular weight a-PVA, denoted as a-PVA-5C, was purchased from Nacalai Tesque. All low-molecular weight a-PVA samples were treated with NaOH aqueous solution before use, in order to saponify completely. Characteristics of these low-molecular weight PVAs are shown in Table 1.

All blend samples were prepared by casting from a solution of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), which was kindly donated by Central Glass Co. Ltd., Tokyo, Japan. The films were crystallized at room temperature for 10 days, subsequently dried at 60°C for 5 days to eliminate the solvent. In this study, the blend composition was shown as wt%.

2.2. FT–IR measurement

FT–IR spectra were obtained on a JASCO FT/IR-7000 spectrometer by the transmission method, at room temperature under N\(_2\) purge. A Mettler FP80 thermal controller and a FP82HT hot stage were equipped for measurements at higher temperature up to melting points. All IR spectra were obtained from 4600 to 400

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average molecular weight in ( M_n )</th>
<th>Degree of saponification /%</th>
<th>Melting temperature /°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-PVA-1</td>
<td>4400</td>
<td>&gt; 99(^a)</td>
<td>230.7</td>
</tr>
<tr>
<td>a-PVA-3</td>
<td>13200</td>
<td>&gt; 99(^a)</td>
<td>228.8</td>
</tr>
<tr>
<td>a-PVA-5</td>
<td>22000</td>
<td>&gt; 99(^a)</td>
<td>231.6</td>
</tr>
<tr>
<td>a-PVA-5C</td>
<td>22000</td>
<td>&gt; 99(^b)</td>
<td>231.0</td>
</tr>
</tbody>
</table>

\(^a\) Determined by \(^1\)H-NMR.

\(^b\) Determined by FT–IR.

\(^c\) Determined by DSC.
cm$^{-1}$ at a resolution of 4 cm$^{-1}$. Intensity of absorption was normalized by height.

2.3. Thermal analysis

DSC thermograms were recorded on a SEIKO DSC-20 with SEIKO SSC-580 control system. The dried film as cast was packed in an aluminum pan for DSC measurement. The sample was heated from 50 to 300°C at a rate of 10°C min$^{-1}$. The melting temperature and heat of fusion of PHB were determined by the first scan.

2.4. Wide-angle X-ray diffraction

Wide angle X-ray diffraction patterns were recorded on a Rigaku RU-200 and a Rigaku IP R-AXIS-DS3 data processing system. The nickel-filtered Cu-K$_\alpha$ X-ray beam with a pinhole graphite monochromator was used as the source. The wavelength of the X-ray beam was 0.15418 nm.

Diffraction intensities of the films were measured in a 20 range of 5–40° at a scanning speed 1° min$^{-1}$. The power of the source was tuned to 50 kV/180 mA for the intensity analysis.

Photographic diffraction patterns of the films were measured at the radiation time of 30 min. The power of the source was tuned to 20 kV/35 mA for the photographic analysis.

2.5. BOD analysis

BOD values were determined using a TAITEC 200-F BOD tester from the amount of oxygen consumption based on the method reported by Abe et al. [22]. The BOD biodegradability was defined as follows for polymer samples:

$$\text{biodegradability}\% = \frac{\text{BOD}_{\text{sample}} - \text{BOD}_{\text{blank}}}{\text{ThOD}} \times 100$$

Here, BOD$_{\text{sample}}$ and BOD$_{\text{blank}}$ are experimentally observed values of oxygen demand of sample and blank medium, respectively. ThOD is theoretically expected value of oxygen demand of blend sample, which was obtained by assuming that the film completely degraded into CO$_2$ and H$_2$O. Since the degradation of PHB and PVA in the blend film would proceed independently, the value of ThOD of each film was assumed as the weight average of the values of oxygen demand of both components. The value of biodegradability of each sample was determined as an average of values at least two independent experiments.

Water of the River Tama was taken in November 1998 and used as an environmental medium. The water was collected around the foot of the former Futako bridge (the border region between Kawasaki City and Setagaya-ku, Tokyo). The river water was filtered using 17G glass filter and saturated by oxygen before BOD test. The BOD medium contained 200 ml of the oxygen-saturated river water, 0.2mL of mineral salt stock solution (KH$_2$PO$_4$ 8.5 g L$^{-1}$, K$_2$HPO$_4$ 1.75 g l$^{-1}$, Na$_2$HPO$_4$.H$_2$O 33.3 g l$^{-1}$, NH$_4$Cl 1.7 l$^{-1}$, MgSO$_4$.7H$_2$O 8.55 g l$^{-1}$, CaCl$_2$ 27.5 g l$^{-1}$, FeCl$_3$.6H$_2$O 0.25 g l$^{-1}$). Each of the medium was kept at 25°C through the test. The 7×7 mm blend film (within 10 mg of weight, 100 μm of thickness) was immersed into each medium. Total organic carbon concentration (TOC) of the medium was measured by the combustion method using Shimadzu TOC-5050A.

3. Results and discussion

3.1. Crystallinity of the components in the PHB/stereo-regular PVA blends

3.1.1. Crystallinity of PHB in the i-PVA blends detected by DSC

Thermal properties of PHB in the blends with a-PVA [17] and s-PVA [18] have been investigated. In the blends with a-PVA and s-PVA, melting temperatures [$Tm$] of PHB were clearly observed by DSC. The DSC results for the PHB/i-PVA blends were shown in Table 2. PHB shows much fewer decreases in Tm by blending with i-PVA than that found for the PHB blends with a- and s-PVA. Since the FT–IR spectra of PHB in the blends with i-PVA did not show the crystallinity-sensitive change, the DSC results found have corresponded well to the FT–IR results [19].

In Table 2 are also shown the heat of fusion [$\Delta H$] and degree of crystallinity of PHB in the blends with i-PVA. The degree of crystallinity of PHB in the blends was calculated by assuming that the $\Delta H$ value of 100% crystalline PHB is 146 J g$^{-1}$ [23]. The degree of crystallinity of PHB in the blends with i-PVA is nearly the same as that of pure PHB, while that of PHB in the blends with a-PVA and s-PVA has been found to decrease with decrease in PHB content. The result of DSC experiment indicates that the crystallization of PHB is not suppressed by blending with i-PVA, consistent with the previous FT–IR results [19].

Table 2

<table>
<thead>
<tr>
<th>PHB content /wt%</th>
<th>Melting temperature /°C</th>
<th>Heat of fusion /$\Delta H$/J g$^{-1}$</th>
<th>Crystallinity /%a</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>168.2</td>
<td>18.6</td>
<td>51.0</td>
</tr>
<tr>
<td>50</td>
<td>168.6</td>
<td>40.2</td>
<td>55.1</td>
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<tr>
<td>75</td>
<td>170.2</td>
<td>60.3</td>
<td>55.1</td>
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<tr>
<td>100</td>
<td>170.5</td>
<td>82.1</td>
<td>56.2</td>
</tr>
</tbody>
</table>

*a Calculated from the $\Delta H$ by assuming the $\Delta H$ of 100% crystalline PHB is 146 J g$^{-1}$ (Ref. [23]).
3.1.2. WAXD patterns of PHB/stereoregular PVA blends

Fig. 1 shows the WAXD patterns of the PHB blend films with α-PVA, s-PVA and i-PVA. All blend films, even those containing only 25% PHB, exhibit well-discriminated diffractions arisen from the crystal lattice of PHB. Since DSC data [17,18] indicated that the crystallization of PHB was suppressed by blending with α- and s-PVA, and no PHB melting peak was observed for α- and s-PVA-rich blends by DSC, the WAXD results seem to be contradictory to the DSC results. This contradiction is supposed to be caused by different sensitivity of both methods to the lamellar size of PHB crystal. Since in DSC the change of heat flow is measured, its sensitivity is not enough to detect the small melting peak arisen from the microcrystal. While, X-ray diffraction occurs when the periodic structure exists.

The crystallinity of the PVAs in the blends could not be determined by WAXD, because the diffraction peaks arisen from PVA is overlapped with those from PHB.

The possible factor other than hydrogen-bonding interaction, which lowers the degree of crystallinity of PHB, is the difference in the glass transition temperature \( T_g \) between PHB and PVA. The crystallization temperature (room temperature) is much lower than \( T_g \) of PVA (about 85°C, for conventional PVA [16]), but is higher than that of PHB (about 0°C [5,24]). Hence, PHB molecules in the amorphous phase are probably trapped by the "glassy" PVA environment, as PHB and PVA are compatible in the amorphous phase. Similar behavior has been observed for the blends of PHB/cellulose acetate butyrate [25], both of which are crystallizable and their \( T_g \) values are largely different.

3.2. The effect of molecular weight of PVA on the crystallization of PHB

Since the mixing state of polymer blend system is generally affected by the molecular weight of the components, it is interesting to investigate the effect of the molecular weight of PVA to the crystallinity of PHB in the PHB/PVA blend system. Fig. 2 shows the PHB C=O stretching region of IR spectra of pure PHB and the blends with α-PVA-3 containing 10, 20, 30 and 40% PHB observed at room temperature. The blend-composition-dependent change of the C=O spectral feature is quite similar to that observed for PHB/high-molecular weight α-PVA blends [18]. In Tables 3–5 are shown the thermal properties, such as \( T_m \), \( \Delta H \) and crystallinity of the PHB in the blends with α-PVA-1,3 and 5. The tendency of blend-composition dependence of crystallinity observed for the blends with lower molecular weight α-PVAs were almost the same as those observed for the PHB/high-molecular weight α-PVA blend system [17]. The WAXD patterns of PHB/α-PVA-5C were shown in Fig. 3, which showed almost similar trends to those of PHB/α-PVA system, as shown in Fig. 1(a). This result also suggests that the crystallization state of the PHB in the blend with α-PVA-5C was almost the same as those of the PHB in the blend with α-PVA. Within the molecular weight range of PVA investigated in this study, the crystallization behavior of PHB in the blends was independent.

Fig. 1. Wide angle X-ray diffraction of PHB, stereoregular PVA and PHB/PVA blends: (a) PHB/α-PVA, (b) PHB/s-PVA, (c) PHB/i-PVA.
to the molecular weight of blend partner, PVA. This result suggests that the suppression of crystallization of PHB and PHB/a-PVA partial miscibility in the PHB/a-PVA system is caused by the glassy environment effect of PVA amorphous phase, besides by the formation of intermolecular hydrogen bonds between the PHB carbonyls and PVA hydroxyls. As discussed in the previous paper [19], a rigid environment produced by a-PVA, whose Tg is much higher than that of PHB, suppresses PHB crystallization in the amorphous phase of the miscible blend. If the enthalpic factor, such as intermolecular hydrogen bonding, is only the dominant factor, miscibility of the binary system should be changed by the change of molecular weight of the component, as suggested by the Flory-Huggins equation [26].

3.3. The effect of tacticity of PVA on the biodegradability

Several methods to estimate the biodegradability of polymer have been applied to the investigation of biodegradation of poly(hydroxyalkanoic acid)s. One of the popular methods is observation of weight loss and concentration of water-soluble low-molecular weight compound formed by degradation, during enzymatic degradation using isolated extracellular depolymerase. Here, the BOD experiment under river water was used as the testing method for the biodegradation of PHB/PVA blend system. There are at least two merits for using this method. First, the BOD biodegradation profile

### Table 3

<table>
<thead>
<tr>
<th>PHB content/wt%</th>
<th>PHB/a-PVA-1</th>
<th>PHB/a-PVA-3</th>
<th>PHB/a-PVA-5</th>
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<tbody>
<tr>
<td>10</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
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<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
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<tr>
<td>30</td>
<td>170.0</td>
<td>162.1</td>
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<td>40</td>
<td>171.5</td>
<td>165.8</td>
<td>167.0</td>
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<tr>
<td>50</td>
<td>170.1</td>
<td>162.4</td>
<td>168.2</td>
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<td>175.4</td>
<td>168.9</td>
<td>172.0</td>
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<td>175.1</td>
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<td>100</td>
<td>175.3</td>
<td>175.3</td>
<td>175.3</td>
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</table>

* a n.d. = Not detectable by DSC.

### Table 4

Heat of fusion [ΔH] of PHB in the blends with low-molecular weight a-PVA

<table>
<thead>
<tr>
<th>PHB content/wt%</th>
<th>PHB/a-PVA-1</th>
<th>PHB/a-PVA-3</th>
<th>PHB/a-PVA-5</th>
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<td>80.6</td>
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<td>100</td>
<td>88.4</td>
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* a n.d. = Not detectable by DSC.

### Table 5

Normalized degree of crystallinity of PHB in the blends with low-molecular weight a-PVA

<table>
<thead>
<tr>
<th>PHB content/wt%</th>
<th>PHB/a-PVA-1</th>
<th>PHB/a-PVA-3</th>
<th>PHB/a-PVA-5</th>
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<tr>
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<td>60.5</td>
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</tbody>
</table>

* a Calculated from the ΔH by assuming the ΔH of 100% crystalline PHB is 146 J g⁻¹ (Ref. [23]).

* b n.d. = Not determined.
under an environmental water is expected to reflect
directly the profile of practical environmental degra-
dation. Since PHB and PVA have the different pathways
of biodegradation, it is desirable to conduct the biode-
gradation test under a complex ecosystem. Second, the
BOD test is applicable to a water-soluble material. Since
PVA is soluble in water, biodegradability of PVA under
an aquatic environment can not be estimated by meth-
ods based on the measurements of the weight-loss and
the total organic carbon [TOC] method. According to
Matsumura et al., the isotactic triad sequence of PVA is
preferably degraded by an environmental microbials
isolated from river water [27]. So, PHB/PVA blends are
expected to exhibit different biodegradation behavior
dependent on the stereoregularity of PVAs. Fig. 4 shows
the biodegradation profile of stereoregular PVA and
high- and low-molecular weight a-PVA in river water
taken in November 1998. Aerobic biodegradability of a-
PVA was decreased by about half as that carried out in
July 1997 [20], probably due to the change of the spec-
trum of environmental microbes. As shown in Fig. 4, s-
PVA and i-PVA were not degraded up to 30 days. After
the BOD degradation test, the pure s-PVA and i-PVA
films remaining visible and not swelled, while a-PVA
and a-PVA-5C films were partially degraded and the
remained films were softened by swelling with water.
The solubility in water of both s-PVA and i-PVA is
quite low. The solubility of PVA in water is mainly
controlled by the degree of saponification and tacticity.
Increasing the degree of saponification and syndiotacti-
city causes decrease in solubility in water.

Fig. 5 shows the plots of BOD biodegradability
against elapsed time after the PHB/s-PVA blend films

![Fig. 4. BOD biodegradation profiles of pure PVA films in river water.](image)

![Fig. 5. BOD biodegradation profiles of PHB, s-PVA and PHB/s-PVA
blend films in river water.](image)
were put into the BOD testing medium. The notable feature is that the films of PHB and PHB-rich blend films were degraded, but those of 25% PHB blend as well as pure s-PVA were not.

The biodegradation profile of PHB/i-PVA blend films was also shown in Fig. 6. The PHB-rich blend films show good biodegradability. The PHB/i-PVA blend film containing 25% PHB exhibited a little biodegradability, while the PHB/s-PVA film with the same blend composition showed no biodegradation. This result is well explained by the difference of mixing state, as discussed in our previous papers on thermal properties and crystallinity of PHB/PVA blend system [17–19]. Since PHB can mix more intimately with s-PVA than with a-PVA and i-PVA, PHB is supposed to be trapped tightly in the s-PVA environment. While, i-PVA is immiscible with PHB and it does not have any ability to suppress the PHB crystallization, the PHB domain on the surface region of the film may be exposed to the aqueous medium without shielding by i-PVA. So, the biodegradability of i-PVA blend with 25% PHB should be attributed to that of the PHB on the surface region of the blend film. The degradation of PHB in the deeper region of the blend film should be retarded and inhibited by the slow-degradable i-PVA phase surrounding the PHB phase. The blend films containing 50 and 75% PHB were degraded well and became invisible after the BOD test. This result is comparable to that of PHB/a-PVA blends [20].

3.4. The effect of molecular weight of PVA on the biodegradability

From the result of the previous subsection, solubility of PVA in water is thought to play an important role in the biodegradation of PHB/PVA blends, as found for poly(ethylene oxide) [PEO] in the enzymatic degradation of the PHB/PEO blends [11]. Thus, it is interesting to investigate the biodegradability of the blends of PHB/low-molecular weight PVA. Decreasing molecular weight of PVA improves its water solubility.

Fig. 7 shows the biodegradation profile of PHB/a-PVA-5C blend films. A marked improvement in biodegradability of a-PVA as well as of blends was observed by using low-molecular weight a-PVA. As discussed in the former section, the mixing state and crystallinity of PHB in the blends with low-molecular weight a-PVA exhibited nearly the same trend as those in the PHB/a-PVA blends [20].

Table 6

<table>
<thead>
<tr>
<th>PHB content/ wt%</th>
<th>BOD biodegradability/%</th>
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<tbody>
<tr>
<td></td>
<td>PHB/ a-PVA</td>
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<td>57</td>
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</table>

a The reference; carried out in July 1997 (Ref. [20]).

Fig. 6. BOD biodegradation profiles of PHB, i-PVA and PHB/i-PVA blend films in river water.

Fig. 7. BOD biodegradation profiles of PHB, a-PVA-5C and PHB/a-PVA-5C blend films in river water.
high-molecular weight a-PVA blends. So, the difference of biodegradability between PHB/a-PVA blends and PHB/a-PVA-5C blends should not be due to the mixing state, but to the specific properties of the a-PVA-5C itself, such as better solubility in water. In Fig. 7, the initial degradability of the a-PVA-5C blends containing 50 and 75% PHB was increased compared to that of pure PHB. A similar acceleration has been found for the PHB-rich blends with high-molecular weight a-PVA [20]. In PHB/a-PVA-5C blends, however, the range of blend composition at which the accelerated degradation was observed was wider than that in PHB/a-PVA blends.

At the end of the BOD experiment, the TOC concentration of the medium was ranged from 0 to 2 ppm. No significant difference in TOC concentration was found among all BOD samples such as PHB, s-PVA, i-PVA, a-PVA, a-PVA-5C and PHB-based blends with s-PVA, i-PVA and a-PVA-5C. The temperature of environmental water, kept at 25°C through the BOD degradation test, was not enough to dissolve completely the PVA, even a-PVA-5C, into water. But, the status of swelling with water was clearly different between a-PVA-5C and stereoregular PVA. Though complete dissolution was not achieved, swelling status with water was found to affect the biodegradation rate.

4. Conclusion

The effect of the tacticity and molecular weight of PVA component on the extents of crystallization in the blends of PHB and biodegradation profile of PHB/PVA blend system have been studied. According to DSC measurement, in the blends with highly isotactic PVA, PHB was found to crystallize in the same way as for pure PHB. This result is consistent with the results obtained by FT–IR spectroscopy. Since i-PVA has poor ability to form intermolecular hydrogen bonds, the suppression of PHB crystallization found in the PHB/a- and s-PVA blend systems may be caused by the formation of the intermolecular hydrogen bonding between the PHB carbonyls and the PVA hydroxyls. The other factor leading low crystallinity of PHB in the blends was thought to be arisen from trapping of the amorphous PHB by the PVA amorphous phase.

The degree of crystallinity of PHB decreased by blending with low-molecular weight atactic PVA, when PVA was a major component of the blends. This result is the same as that found for the PHB blends with high-molecular weight a-PVA. The result suggests that the suppression of crystallization of PHB in the PHB/a-PVA system is caused by the glassy environment effect of PVA amorphous phase, besides by the enthalpic interaction such as formation of intermolecular hydrogen bonds.

Solubility of the PVA component in water was found to affect the biodegradability of whole PHB/PVA blend system. The PHB-rich blend films with s-PVA and i-PVA exhibited very low degradability, due to the low water-swellability and/or water-solubility of stereoregular PVA. The PHB/low-molecular weight a-PVA blends with wider blend composition showed faster biodegradation as compared to the PHB/high-molecular weight a-PVA system. The strategic choice of low-molecular weight PVA is effective.

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