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Intermolecular interactions and crystallization behaviors of biodegradable polymer blends between poly (3-hydroxybutyrate) and cellulose acetate butyrate studied by DSC, FT-IR, and WAXD

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ABSTRACT

Relationships between composition- and temperature-dependent intermolecular interactions and cold crystallization behaviors of poly(3-hydroxybutyrate) (PHB)/ cellulose acetate butyrate (CAB) blends have been investigated mainly by infrared (IR) spectroscopy, together with differential scanning calorimetry, and wide-angle X-ray diffraction (WAXD). Weak intermolecular hydrogen bondings between OH groups in CAB and C═O groups in amorphous part of PHB define as *inter* were detected in OH stretching bands of the blends. These interactions occur in the blends with high CAB content (w_{CAB}) and highly depend on temperature. For all the blends having $0.2 \leq w_{CAB} \leq 0.7$, when temperature is raised (e.g., above 90 °C for the blend with $w_{CAB} = 0.5$) the cold crystallization of PHB was discerned, as evidenced by an increase of the absorbance of the band due to C═O stretching in the crystal field. The crystallization was found to involve the dissociation of *inter* and transformation of *inter* into intramolecular hydrogen bondings within PHB and within CAB as summarized in Table 2 in this text, which promotes the crystallization and enhances stabilization of the crystals. Consequently, the crystallization of the PHB is influenced by exchanges of the hydrogen bondings as described above with raising temperatures. X-ray diffraction from PHB crystals in the blends show a remarkable decrease of crystallinity with w_{CAB} and eventually disappear when $w_{CAB} \geq 0.8$.

1. Introduction

Recently, the vast wastes of plastic products have become a serious environmental problem, because the majority of them are made from synthetic polymers that cannot be degraded in environments. Biodegradable polymers are one of the most promising alternative substances for solving this serious problem, because of their superior biodegradable properties compared to those of synthetic polymers [1–3]. Besides being degradable, they can be produced also as renewable sources that are environment friendly. As a biosynthesized aliphatic polyester and biodegradable thermoplastic, poly(3-hydroxybutyrate) (PHB) (Fig. 1(a)) has been attracting a considerable practical attention for the biodegradability, biocompatibility, and possibility of the synthesis from glycerol [4]. For these advantages, their crystal structure and thermal or crystallization behaviors have been extensively studied by using various techniques from the academic viewpoint as well as from the viewpoint of practical applications.

However, as a biologically produced stereo-regular macromolecule, PHB is highly crystalline and, hence, rigid and brittle [5], which also acts as a kind of defect for some practical applications. It has a high melting temperature relative to its thermally stable temperature range, which also acts as a defect for its melt processability. From the industrial viewpoint, these defects are really serious for the wide-scale practical applications. Thus, PHB copolymers were synthesized such as Poly(hydroxybutyrate-*ran*-hydroxyvalerate) (PHB-*co*-PHV) [6–8] and graft copolymer of atactic PHB/Poly(methyl methacrylate) (PHB-*g*-PMMA) [9]. In addition, several polymers such as poly(ethylene glycol) (PEG) [10], poly(ethylene oxide) (PEO) [11], poly(vinyl acetate) (PVAc) [12,13], poly(4-vinylphenol) (PVPh) [14,15], poly(vinyl alcohol) (PVA) [16], polylactide (PLLA) [17], and cellulose esters (CE) [2,18–22] have been selected to be blended for lowering the melting temperature and enhancing the processability.

In view of actual applications, blending between PHB and CE, especially for amorphous cellulose acetate butyrate (CAB) hold very promising features such as the elongation at break and toughness [2]. Miscibility analysis of PHB/CAB blends was investigated by Scandola et al. using dynamic-mechanical thermal analysis (DMTA)

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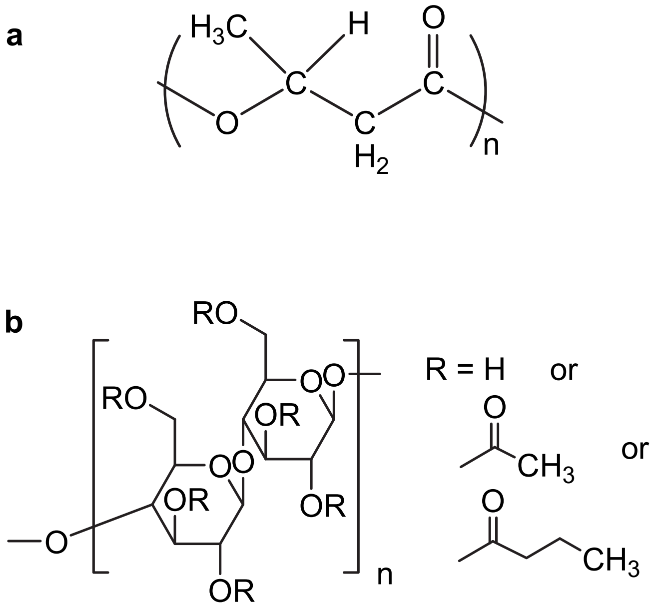

Fig. 1. Chemical structures of (a) poly(3-hydroxybutyrate) (PHB) and (b) cellulose acetate butyrate (CAB).

measurements [18]. They reported that the blends of PHB/CAB are miscible in the amorphous state. The result was in agreement with that by Ceccorulli et al. who further investigated effects of low molecular weight plasticizer on the miscibility of PHB/CAB blends [19]. Pizzole et al. [20], who explored miscibility between PHB and two kinds of CAB in the melt, reported that no interspherulitic segregation was observed, when the blends were crystallized under the given crystallization conditions. Recently, El-Shafee et al.[21] confirmed the miscible blend in melts, showing the effect of the equilibrium melting point depression of PHB crystals upon the addition of CAB. Moreover, it was found that, after crystallization of the PHB component in the blends, CAB exists in the interlamellar amorphous regions and becomes a major component there, as detected by small-angle X-ray scattering (SAXS) [21]. In the drawing process of blend, Park et al. indicated that the orientation behavior of PHB crystals in the blends changes from *c*-axis orientation to *a*-axis orientation with an increase in the CAB content [22]. However, in all of the previous studies described above, intermolecular interactions and their effects on crystallization in PHB/CAB blends have not been fully explored yet.

The purpose of the present study is to investigate the intermolecular interactions and their effects on crystallization behaviors of PHB/CAB blends, primarily with infrared (IR) spectroscopy, together with differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD) as supporting experimental methods, as a function of the blend composition and temperature. The IR results obtained suggest the existence of weak intermolecular interactions between the C=O groups of PHB and the O–H groups of CAB (designated hereafter as *inter*). Moreover, the estimated crystallinity from WAXD patterns of the blends suggests that the crystallinity of PHB in the blends is influenced by the intermolecular interactions.

2. Experimental section

2.1. Materials and sample preparation

The bacterial PHB (number-average molecular weight, M_n, is 2.9×10^5) and CAB (number-average molecular weight, M_n, is 6.5×10^4) were purchased from Aldrich Chemical Co., Ltd., and were used as received. Chemical structures of both samples are given in Fig. 1. As shown in Fig. 1(b), the CAB polymer consists of hydroxyl groups, acetyl groups, and butyryl groups. The weight fraction of each group with respect to the total weight of CAB is 0.0089, 0.293, and 0.18, respectively. Thus, the number of each group per single CAB chain is $6.5 \times 10^4 \times 0.89 \times 10^{-2}/17.0 = 34.0$ for hydroxyl groups, $6.5 \times 10^4 \times 0.293/43.04 = 442$ for acetyl groups, and $6.5 \times 10^4 \times 0.18/71.1 = 165$ for butyryl groups.

Table 1
Thermal properties of the PHB/CAB blend in the second heating process.

PHB/CAB (%wt./wt.)	T_g (°C)	T_{cc} (°C)	T_m (°C)	ΔH_m (J g^{-1})	X_c
100/0	−1.72	–	166.65	93.56	0.64
80/20	−4.86	43.01	166.47	70.71	0.48
60/40	−7.21	43.21	161.95	52.19	0.36
50/50	−7.05	46.25	160.34	40.81	0.28
40/60	−8.13	49.29	156.19	28.67	0.20
30/70	−7.71	50.99	154.83	8.42	0.06
20/80	−2.02	n.d.	n.d.	–	–
10/90	117.94	n.d.	n.d.	–	–
5/95	127.52	n.d.	n.d.	–	–
0/100	145.08	n.d.	n.d.	–	–

n.d.: Not detected.

Samples of PHB/CAB blends were prepared by mixing the prescribed amount of powders and then dissolving them in chloroform. The as-prepared solutions were cast into films of about 5 mg in weight in an aluminum pan for DSC measurements. For WAXD analysis, the solutions were cast on copper plates to form thin films with the thickness of around 200 μm. For IR spectral measurements, thin film specimens of the thickness of around 10 μm were prepared by casting the solutions on CaF_2 substrates. All the prepared films were allowed to evaporate solvent at room temperature for forming thin films. Then, the films were put in a vacuum oven at 60 °C for 16 h to completely remove the residual solvent and then naturally cooled down to room temperature for the measurements. The films thus prepared are designated hereafter as “as-prepared films” and used for DSC, WAXD, and IR measurements.

2.2. DSC

Thermal analyses of the blends were performed with a Perkin–Elmer Pyris 6 by sealing the as-prepared films in an aluminum pan, and a pure indium was used as a standard material for temperature calibration of the calorimeter. For a standard thermal characterization of the blends with DSC, the blends were firstly melted at 190 °C for 1 min to erase the previous thermal history. Then, the DSC thermograms were obtained in the first cooling run from 190 °C to−40 °C at a rate of 20 °C/min and in the second heating run from −40 °C to 190 °C at a rate of 20 °C/min. The thermal properties of blends such as the glass transition temperature (T_g), cold crystallization temperature (T_{cc}), melting temperature (T_m), and enthalpy of fusion (ΔH_m) were determined from the thermograms of the second heating run (see Table 1). Moreover, the net cystallinity (X_c) of each blend as a whole, including amorphous CAB, was also determined using the following equation (see also Table 1):

$$X_c = \frac{\Delta H_m}{\Delta H^0_{PHB}} \qquad (1)$$

where ΔH^0_{PHB} is the enthalpy of melting of pure PHB crystals, i.e., neat PHB having 100% crystallinity, (146 J/g) [23,24]; ΔH_m is the measured enthalpy of fusion in each blend.

We tried directly to compare the cold crystallization behavior of the blends as observed by IR spectroscopy with that as observed by