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Thermal properties of poly(hydroxybutyrate-co-hydroxyvalerate) and poly(ϵ-caprolactone) blends

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Abstract

Crystallization behavior of blends of poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) and poly(ϵ-caprolactone) (PCL) prepared by solution casting has been investigated by differential scanning calorimetry (DSC). In the study of PHBV/PCL blends by DSC, crystallization temperature of PHBV in the blends decreased about 8–12°. From the results of the Avrami analysis of PHBV in the PHBV/PCL blends, crystallization rate constant of PHBV in the PHBV/PCL blends decreased compared to that of the pure PHBV. From the above results, it is suggested that nucleation of PHBV in the blends is suppressed by the addition of PCL. From the measured crystallization half time and degree of supercooling, interfacial free energy for the formation of heterogeneous nuclei of PHBV in the PHBV/PCL blends was calculated and found to be 2360 $(\mathrm{mN/m})^3$ for the pure PHBV and 3090–3160 $(\mathrm{mN/m})^3$ for the blends. This increase in the interfacial free energy of PHBV indicates that the heterogeneity of PHBV in the PHBV/PCL blends is deactivated by the PCL. This result is consistent with the result of crystallization rate constant of PHBV in the blends. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Blends; Biodegradable polymers; Crystallization behavior

1. Introduction

Poly(hydroxybutyrate) (PHB), an aliphatic polyester synthesized by bacterial fermentation, is known to degrade fully in the environment without forming any toxic products [1]. This biodegradable nature of the PHB is very important from the point of view of reducing plastic wastes. However, there are several shortcomings to the commercial use of the PHB. Because of being produced from microorganisms, it is relatively expensive compared to other biodegradable polymers. Also, it is rather brittle for use below the glass transition temperature and can be easily degraded thermally above melting point. To reduce its brittle character, various copolymers which have different types of aliphatic polyester units, for example poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) have been biosynthesized [1–5].

Poly(ϵ-caprolactone) (PCL), an aliphatic polyester made from ring opening polymerization of ϵ-caprolactone, is also known to a biodegradable polymer. Recently, in order to obtain less expensive degradable polymers, blends of PCL and commodity polymers such as polyethylene and polypropylene have been investigated [6–8]. There are many studies about the crystallization behavior for miscible and immiscible polymer blends. However, the crystallization behavior of PHBV/PCL blends has not been reported yet. Also, the studies on the interfacial free energy for the formation of heterogeneous nuclei of a crystalline polymer in polymer blends are very limited.

We report here on the relationship between crystallization kinetics and interfacial free energy for the formation of heterogeneous nuclei of PHBV in the PHBV/PCL blends. The blends have been characterized using differential scanning calorimetry (DSC). The crystallization kinetics of the PHBV/PCL blends was analyzed by the Avrami equation [9]. The interfacial free energy for the formation of heterogeneous nuclei of PHBV in the blends was calculated from the nucleation theory [10].

2. Experimental

2.1. Polymers

The polymers used in this study were obtained from commercial sources. The characteristics and sources of the polymer samples used in this study are shown in Table 1. PHBV was manufactured by Zeneca Bioproducts under the trade name of Biopol (7 mol% HV content). PCL (Tone-787) was supplied by Union Carbide Co.

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Table 1
Characteristics of polymer samples used in the PHBV/PCL blends

	$\overline{M}_w$	$\overline{M}_n$	T_g (°C)[a]	T_m (°C)[a]	T_c (°C)[a]
PHBV[b]	470 000[c]	127 000[c]	5.2	151.2	97.0
PCL[d]	163 300[e]	56 400[e]	− 61.0	64.0	22.2

[a] Measured in our laboratory by DSC.
[b] Supplied by Zeneca Bioproducts Co.
[c] Data from Ref. [2].
[d] Supplied by Union Carbide Chemicals and Plastics Co.
[e] Measured in our laboratory by GPC.

2.2. Blend preparations

Blends of the two polymers were prepared by solution casting. For solution casting, a total of 0.6 g of the PHBV/PCL mixture was dissolved in 20 ml of chloroform at room temperature [3.0%(w/v) solution] for at least 1 day. Blends were cast on glass plates, and all film samples were dried under vacuum for 7 days at room temperature.

2.3. Differential scanning calorimetry (DSC)

The thermal properties of all samples were analyzed by using a Perkin–Elmer DSC, Model DSC-7. Temperature calibration was performed using indium ($T_m = 156.6$°C, $\Delta H_f = 28.5$ J/g). In order to measure the melting temperature and crystallization temperature of the PHBV/PCL blends, blend samples of 5–15 mg were heated in a nitrogen atmosphere from −40 to 175°C at a heating rate of 20 K/min and then cooled to −40°C at a rate of 20 K/min.

Isothermal crystallization experiments of the PHBV in the blends were carried out on DSC. For the isothermal crystallization of the blends, samples were melted at 175°C for 3 min, and then rapidly cooled to the isothermal crystallization temperature.

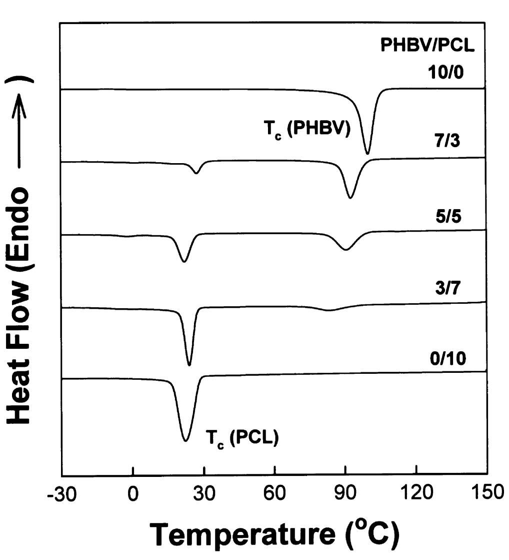

Fig. 1. DSC cooling thermograms of the PHBV/PCL blends.

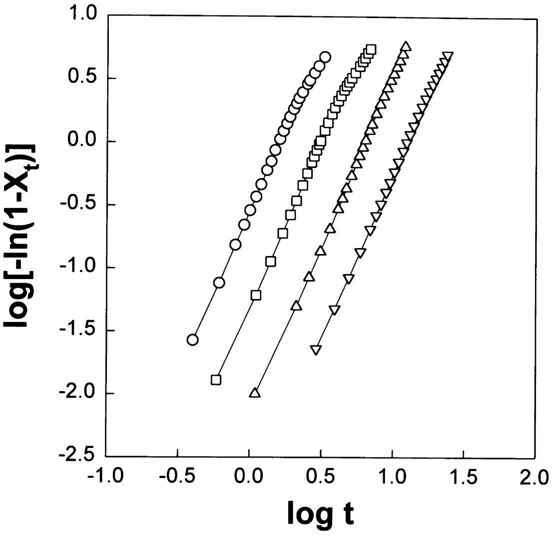

Fig. 2. The Avrami analysis for the 7/3 PHBV/PCL blends at various isothermal crystallization temperature: 105 (○); 110 (□); 115 (△); 120°C (▽).

3. Results and discussion

3.1. Thermal behavior of PHBV/PCL blends

In the thermal analysis of PHBV/PCL blends by DSC, melting temperatures (T_m) of two polymers in the blends are shown to be almost unchanged compared to that of pure polymers. From the measured heat of fusion of the T_m (PHBV), the degree of crystallinity (X_c) was calculated and found to be 0.51, 0.51, 0.51, 0.51, 0.49 and 0.46 for the 10/0, 9/1, 8/2, 7/3, 6/4 and 5/5 PHBV/PCL blends. The X_c of PHBV in the PHBV/PCL blends does not change significantly with composition.

For the PHBV/PCL blends, equilibrium melting temperature (T_m^0) of the PHBV was determined from the Hoffman–Weeks plots. The values of T_m^0 (PHBV) of the pure PHBV and other blend compositions were found to range from 178 to 182°C. There was no significant difference in T_m^0 (PHBV) of the PHBV/PCL blends compared to that of the pure PHBV. This result leads to the conclusion that the blends of PHBV and PCL are immiscible. The miscibility of binary blend is generally evaluated from the glass transition temperature (T_g) of the blend. From DSC measurement, values of the ΔC_p of pure PHBV and pure PCL were found to be 0.20 and 0.09 J/g°C, respectively. However, the ΔC_ps of the PHBV and PCL in the PHBV/PCL blends were too small to detect clearly since the magnitude of transition was so low. Therefore, the T_gs of the PHBV and PCL in the PHBV/PCL blends could not be measured by DSC. From the results of T_m, X_c, and T_m° of the PHBV/PCL blends, it is suggested that the PCL does not affect the melting process of PHBV in the blends.

The DSC cooling thermograms of 1.0, 0.7, 0.5, 0.3 and 0.0 weight fraction PHBV in the PHBV/PCL blends are

Table 2
Crystallization rate constant *(K_n)* and Avrami index (n) of PHBV in the PHBV/PCL blends at different crystallization temperatures

T_c (°C) [a]	PHBV		PHBV/PCL (9/1)		PHBV/PCL (7/3)		PHBV/PCL (5/5)	
	K_n [b]	n [c]	K_n [b]	n [c]	K_n [b]	n [c]	K_n [b]	n [c]
105	1.02×10^{-5}	3.11	9.53×10^{-6}	2.67	6.29×10^{-6}	2.63	1.71×10^{-6}	2.71
110	3.94×10^{-6}	2.96	9.91×10^{-7}	2.75	7.48×10^{-7}	2.71	7.68×10^{-7}	2.53
115	1.62×10^{-6}	2.80	3.43×10^{-7}	2.60	1.09×10^{-7}	2.70	3.54×10^{-7}	2.40
120	2.20×10^{-7}	2.80	4.30×10^{-8}	2.64	2.80×10^{-8}	2.63	1.00×10^{-8}	2.66

[a] Isothermal crystallization temperature.
[b] Overall crystallization constant (s^{-n}).
[c] Avrami index.

shown in Fig. 1. In Fig. 1, the T_c of PHBV in the blends decreased about 8–12° than the T_c of the pure PHBV. The decrease in T_c (PHBV) of the PHBV/PCL blends suggests that the PCL affects the crystallization behavior of PHBV in the PHBV/PCL blends. The effect of PCL on the crystallization behavior of the PHBV is discussed in Section 3.2.

3.2. Isothermal crystallization of PHBV/PCL blends

The crystallization kinetics of the PHBV/PCL blends was analyzed by the Avrami equation [9]. The Avrami plots of PHBV in the 7/3 PHBV/PCL blends are shown in Fig. 2. From the Avrami plots of PHBV in the PHBV/PCL blends, the Avrami exponent (n) and the overall crystallization rate constant (K_n) were obtained and shown in Table 2. The Avrami exponent of pure PHBV is about three that indicates three-dimensional (3D) spherulitic growth from instantaneous nuclei.

In Table 2, we can see that the K_n of PHBV in the PHBV/PCL blends has lower value than that of the pure PHBV. The decrease in crystallization rate constant of the PHBV/PCL blends indicates that the nucleation of the PHBV in the blends is suppressed by the addition of PCL. Such results can be explained by the negative effect of the PCL on the primary nucleation of PHBV.

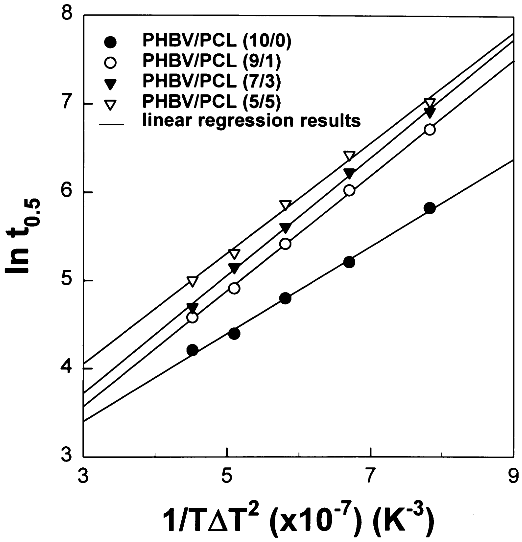

Fig. 3. Effect of degree of supercooling on the crystallization halftime ($t_{0.5}$) for the PHBV/PCL blends. Lines represent the linear regression results.

It is known that the presence of a second component in polymer blends has a great effect on the primary nucleation of the crystallizing component [11]. For the immiscible blends, the deactivation of heterogeneity was reported by Martuscelli et al. [12] and Galeski et al. [13]. For blends of polypropylene (PP) and low-density polyethylene (LDPE), they have reported that the number of heterogeneous primary nuclei of PP decreases with increasing concentration of LDPE in the blends. They have explained that this result is due to the migration of heterogeneity from PP toward LDPE. The driving force for such migration of the heterogeneity would be the difference in interfacial free energies of the impurities in both components. Therefore, in this study, while the PHBV is immiscible with the PCL, the deactivation of heterogeneity in PHBV in the PHBV/PCL blends can be explained by the migration of the heterogeneity from the PHBV to the PCL.

The crystallization behavior of immiscible binary blends depends strongly on the phase state just before crystallization. That is, if the system segregates completely (or makes a macroscopic two-phase state) the crystallization of PHBV will not be influenced so much by PCL. When the degree of segregation is not large, PCL will affect the crystallization behavior of PHBV. From the results of spherulitic morphology of the PHBV/PCL blends, it was observed that phase separation between the two phases was not large at the melted state. Therefore, the crystallization behavior of PHBV in the PHBV/PCL blends is closely related with the phase state of the blends just before crystallization.

3.3. Nucleation of PHBV in PHBV/PCL blends

In primary nucleation processes, heterogeneous nucleation takes place if performed nuclei or foreign surfaces are present. From the nucleation theory [10], the relationship between the free energy for formation of a nucleus from the melt (ΔG^*) and the crystallization half time ($t_{0.5}$) is given by Eq. (1)

$$\ln t_{0.5} = A + \Delta G^*/3kT \qquad (1)$$

where k is the Boltzmann constant, A is the temperature independent constant. From Eq. (1), the interfacial free energy for the formation of heterogeneous nucleus of PHBV in the PHBV/PCL blends can be calculated. The values of PHBV of $T_m^0 = 450$ K, $\Delta H_f = 132$ J/g, and $\rho_c = 1.25$ g/cm^3 were used for calculation [2]. The plots of ln $t_{0.5}$ versus $1/T\Delta T^2$ are shown in Fig. 3. From the slopes of the plots of ln $t_{0.5}$ versus $1/T\Delta T^2$, the values of $\Delta\gamma\gamma\gamma_e$ were found to be 2360, 3120, 3160 and 3090 (mN/m)^3 for 10/0, 9/1, 7/3 and 5/5 PHBV/PCL blends, respectively. Organ and Barham [2] studied nucleation, growth and morphology of PHB and its copolymers, PHBV. From the growth and nucleation rate measurements by optical microscopy, they reported that the surface free energy for homogeneous nucleation of PHBV (7 mol% HV content) is 3115 (mN/m)^3. It is known that heterogeneous nucleation path makes use of foreign pre-existing surfaces to reduce the free energy for nucleation opposing primary nucleation [10]. Therefore, for the heterogeneous nucleation, a lower overall free energy for nucleation is needed than the homogeneous nucleation.

From the above results, the increase in interfacial free energy for PHBV in the PHBV/PCL blends compared to that of the pure PHBV suggests that the heterogeneity of the PHBV in the PHBV/PCL blends is deactivated by PCL. Therefore, the formation of heterogeneous nucleus of PHBV in the PHBV/PCL blends would be more difficult than the pure PHBV. This result is consistent with the result of crystallization behavior of PHBV in the PHBV/PCL blends by DSC. From the above results, it is suggested that crystallization of PHBV in the PHBV/PCL blends is suppressed by the presence of PCL.

4. Conclusions

In the thermal analysis of PHBV/PCL blends by DSC, T_m of PHBV in the PHBV/PCL blends is almost unchanged compared to that of the pure PHBV. T_c of PHBV in the PHBV/PCL blends decreased about 8–12° than the T_c of the pure PHBV. From the isothermal crystallization studies of PHBV in the PHBV/PCL blends, crystallization rate constant of PHBV in the PHBV/PCL blends decreased compared to that of the pure PHBV. From these results, it is concluded that the nucleation of PHBV in the blends is suppressed by the addition of PCL.

From the measured crystallization halftime and degree of supercooling of PHBV in the blends, interfacial free energy for the formation of heterogeneous nuclei of PHBV in the PHBV/PCL blends was calculated and found to be 2360 (mN/m)^3 for the pure PHBV and 3090–3160 (mN/m)^3 for the blends. This increase in the interfacial free energy of PHBV indicates that the heterogeneity of PHBV in the PHBV/PCL blends is deactivated by PCL. This result is consistent with the result of crystallization rate constant of PHBV in the blends.

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