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Compatibilizing capability of poly(*β*-hydroxybutyrate-*co*-*ε*-caprolactone) in the blend of poly(*β*-hydroxybutyrate) and poly(*ε*-caprolactone)

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Abstract

In order to increase the miscibility in the blend of poly(β-hydroxybutyrate) [PHB] and poly(ε-caprolactone) [PCL], PHB/PCL copolyesters were used as compatibilizers. These PHB/PCL copolyesters were synthesized by transesterification in solution phase. The melting point [T_m] depression, which was not observed in PHB/PCL blend without compatibilizer, was observed when PHB/PCL copolyesters as compatibilizers were added to the PHB/PCL blend system. As the amount of compatibilizer added to the blend increased, the crystallization temperature [T_c] of PCL in the blend increased and T_c of PHB in the blend decreased. The difference in T_c between PHB and PCL was gradually reduced. When the sequence length of PHB block and PCL block in the PHB/PCL copolyester increased, the miscibility of the blend increased. This is evidenced by the depression in the T_m of PHB and PCL in the blend and by the decrease in the difference of Tc between PHB and PCL. From the polarizing optical micrographs, the phase separation in PHB/PCL blend was observed. However, in the presence of PHB/PCL copolyester, the spherulite of PHB grows in equilibrium with one phase melt.

Introduction

The biodegradable polymers developed until now are expensive and their physical properties and processibility are often inferior to non-biodegradable synthetic polymers. In order to improve the mechanical and processing properties of biodegradable polymers, the combination of biodegradability and desired physical properties was tried by blending or copolymerizing the corresponding polymers[1-4]. Bacterial PHB is completely biodegradable. However, the high crystallinity of PHB makes PHB to be very brittle. One of attractive solutions to decrease the brittleness of the PHB homopolymer is blending with a second polymer. Indeed PHB has been shown to be miscible with poly(ethylene oxide) and poly(vinyl acetate)[5,6]. It was reported that immiscible blends of PHB and PCL were obtained regardless of the blending method[7].

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In this study, PHB/PCL copolyesters synthesized by transesterification were used as compatibilizers in the PHB/PCL blends. The miscibility of PHB/PCL blends after adding compatibilizers was studied by Differential Scanning Calorimetry [DSC] and polarizing optical microscope. One of the advantages in making PHB/PCL blends to be miscible by adding PHB/PCL copolyesters is that all the components are biodegradable.

Experimental

Copolymerization

PHB, PCL, dibutyl tin oxide and magnetic bar were put into the flask with three necks. After purging reactor with dry N_2, the reactor was immersed into silicon oil bath set to the reaction temperature. Then, nitrobenzene was added to the reactor. Nitrobenzene can dissolve PHB, PCL and dibutyl tin oxide at the reaction temperature. The reactor was kept under dry N_2 during reaction.

Blend

PHB, PCL and PHB/PCL copolyester were dissolved in the solution consisted of chloroform and trifluoroacetic acid (chloroform/trifluoroacetic acid = 90/10 v/v). This solution was mixed for 12 hr and was dropped into the methanol that was stirred vigorously. After polymer solution was precipitated and filtered, the obtained polymer was dried under vacuum for 1 day.

DSC and Polarizing Optical Microscope

The shape of PHB spherulites in the blends was observed with polarizing optical microscope (PLM, A Leitz, Model Laborlux 12 Pols). The sample was heated to 200 °C and kept at this temperature for 1 min. The temperature was then lowered to the desired temperature (80 °C) and PHB was allowed to be crystallized isothermally. DSC curves were obtained using a Dupont TA 2010 thermal analyzer equipped with a 95 DSC cell. The temperature scan was performed at a heating rate of 20 °C/min under nitrogen purge.

Results and Discussion

It is difficult to synthesize the PHB/PCL copolyesters in melt phase because PHB was seriously degraded above its melting temperature. The copolyesters of PHB and PCL were synthesized by transesterification in nitrobenzene solvent at 160 °C. Dibutyltin oxide was used as catalyst. Obtained copolyesters were characterized by ^{13}C-NMR. The composition of PHB and PCL in the obtained copolyesters is about (1/1 wt./wt.) which is calculated from ^{13}C-NMR.

Table 1 shows the effect of the randomness of copolyester calculated from the intensity of peaks of ^{13}C-NMR on the miscibility of the blends. The larger the randomness of copolyester is, the shorter the average sequence lengths of two polymers in copolyester are. The decrease in the T_m's of two polymers in Blend-1 is more than that in the T_m's of two polymers in Blend-3. The change in $T_{c,PHB}$ and $T_{c,PCL}$, of Blend-1 is larger than that of Blend-3. This result indicates that the difference between the T_c of PHB and PCL in the blend is reduced gradually, when randomness of copolyester is small. And, the change in $T_{g,PHB}$ and $T_{g,PCL}$ is the same result as that in $T_{c,PHB}$ and $T_{c,PCL.}$ In other words, in

Table 1 The effect of randomness of copolyesters on the miscibility for blend of PHB and PCL.

Sample	randomness	L_{PCL}	L_{PHB}	$T_{c,PHB}$	$T_{c,PCL}$	$T_{m,PHB}$	$T_{m,PCL}$	$T_{g,PHB}$	$T_{g,PCL}$
Blend-1 [a)]	0.083	25.64	22.73	29.06	-39.18	151.59	51.24	-4.11	-58.19
Blend-2 [a)]	0.169	10.00	14.49	33.41	-44.85	156.74	52.95	0.84	-62.24
Blend-3 [a)]	0.338	4.48	8.69	36.31	-47.08	157.63	56.04	1.57	-63.92
Blend-4 [b)]	-	-	-	41.28	-55.04	169.36	56.51	1.83	-66.39
PHB		-	-	39.11	-	176.48	-	1.97	-
PCL		-	-	-	-55.37	-	58.91	-	-66.75

L : Average sequence length of PHB and PCL in copolyester.

a) PHB / PCL / copolyester = 1 / 1 / 0.5 (wt. Basis)

b) PHB / PCL / copolyester = 1 / 1 / 0 (wt. Basis)

the blending of PHB and PCL, the copolyester of low randomness is effective for increasing the miscibility of blend. In the case of Blend-4 in the absence of PHB/PCL copolyester, the thermal properties of two polymers in the blend are not nearly changed indicating that PHB and PCL are immiscible.

Figure 1 shows the T_m of PHB and PCL in the PHB/PCL blend. The T_m for PCL was nearly constant regardless of the composition of PCL in the blend. The T_m of homo PHB decreased from 176 °C to 168 °C after blending with 20 wt% of PCL. However, T_m of PHB in the blend was almost constant in spite of adding PCL. This result shows that PHB and PCL are immiscible so that the PHB crystallinity is not affected by PCL[8]. The change in T_m of PHB and PCL by adding a compatibilizing copolyester to the PHB/PCL blend is shown in Figure 2. T_m of PHB is more dependent on the composition of copolyester than that of PCL[5, 8, 9]. The chains in PHB/PCL copolyester act as a bridge between the PCL and PHB phase in the PHB/PCL blend.

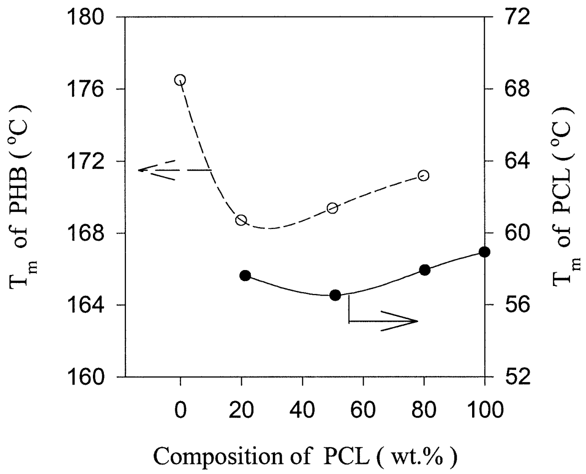

Figure 1
Melting temperature of PHB and PCL in PHB/PCL blend without copolyester as a function of composition of PCL.
[Composition of PCL(wt. %) =PCL/(PHB+PCL) x100].

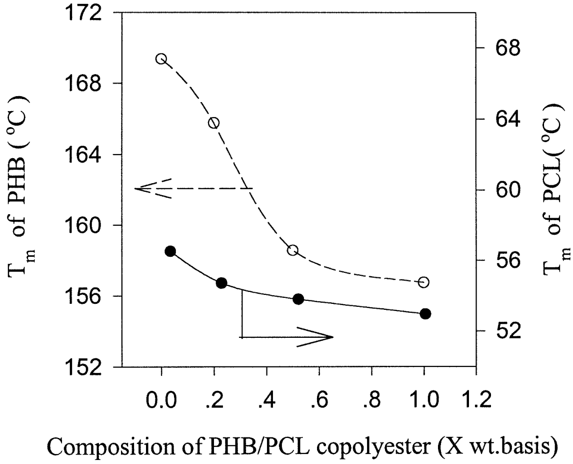

Figure 2
Melting temperature of PHB and PCL in PHB/PCL/copolyester blend (1/1/X wt. basis) as a function of composition of PHB/PCL copolyester.

Figure 3 shows the DSC curve of PHB/PCL/copolyester blends as a function of the composition of copolyester. PHB/PCL copolyester compatibilizes immiscible PHB/PCL blend to form a homogeneous phase as shown in Figure 3. In PHB/PCL blend without copolyester, two melting peaks appear in the region of T_m of PHB. The lower melting point of PHB is arising from the new crystalline structure of PHB affected by PCL at the interface of PHB and PCL. As the composition of copolyester increases, the higher melting point of PHB moves toward the lower melting point of PHB and coalesces into one peak. The reason for this is that PHB/PCL copolyesters compatibilizes the phase of PHB and PCL to form a homogeneous phase and the amount of crystalline structure of PHB affected by PCL at the interface of PHB and PCL increases. The DSC curves for PHB/PCL blends during non-isothermal crystallization show two exothermic peaks corresponding to the crystallization of PHB and PCL. As shown in Figure 4, both T_c's are dependent on the composition of PHB/PCL copolyester. The T_c of the two polymers

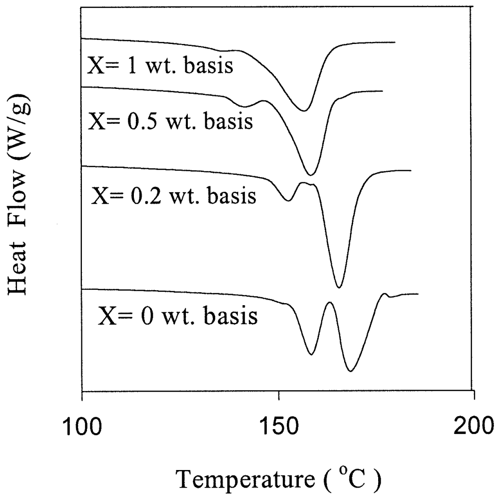

Figure 3
DSC curves of PHB/PCL/copolyester blend (1/1/X wt. basis) as a function of composition of PHB/PCL copolyester.

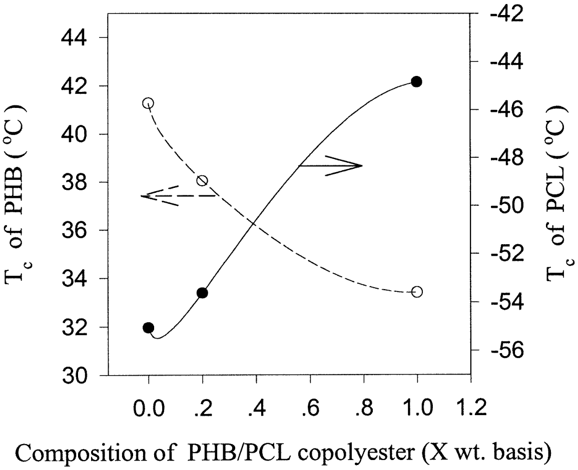

Figure 4
Crystallization temperature of PHB and PCL in PHB/PCL/copolyester blend (1/1/X wt. basis) as a function of composition of PHB/PCL copolyester.

is shifted toward each other as the composition of PHB/PCL copolyester increases. Similar results were found by Martuscelli *et al.* in the case of PEO/ PMMA blends[5]. The decrease in T_c of PHB is related to the depression of spherulite growth rate due to the mutual dilution effect of the PCL and copolyester.

The polarizing optical micrographs of PHB/PCL/copolyester blends in Figure 5 shows that PHB spherulites grow under isothermal conditions. The texture of spherulites is influenced by the amount of copolyester. As shown by Figure 5(b), the spherulite of PHB grows in the presence of two-phase melt in the case PHB/PCL blend. Melt phase of PCL is observed in the spherulite of PHB. For PHB/PCL/copolyester blends, the spherulite of PHB grows in equilibrium with one-phase melt. The molecules of PCL and copolyester might be easily incorporated into interlamellar regions of PHB where they form a homogeneous phase. No apparent evidence of phase separation is observed. Figure 5(c) and Figure 5(d) show the less obvious textures of spherulite when the composition of copolyester is increased from 10 wt% to 50 wt% based on two homopolymers.

Conclusion

Adding the PHB/PCL copolyester increased the miscibility of PHB and PCL in blend. The changes of T_m and T_c in PHB/PCL/copolyester blend suggest that copolyester can improve the miscibility of PHB/PCL blend. The partial miscible PHB/PCL blend was obtained by adding PHB/PCL copolyester of small randomness. In other words, copolyester with blocky structure improves the miscibility between PHB and PCL. The spherulite of PHB grows in equilibrium with one-phase melt in PHB/PCL/copolyester blends in contrast to the PHB/PCL blend.

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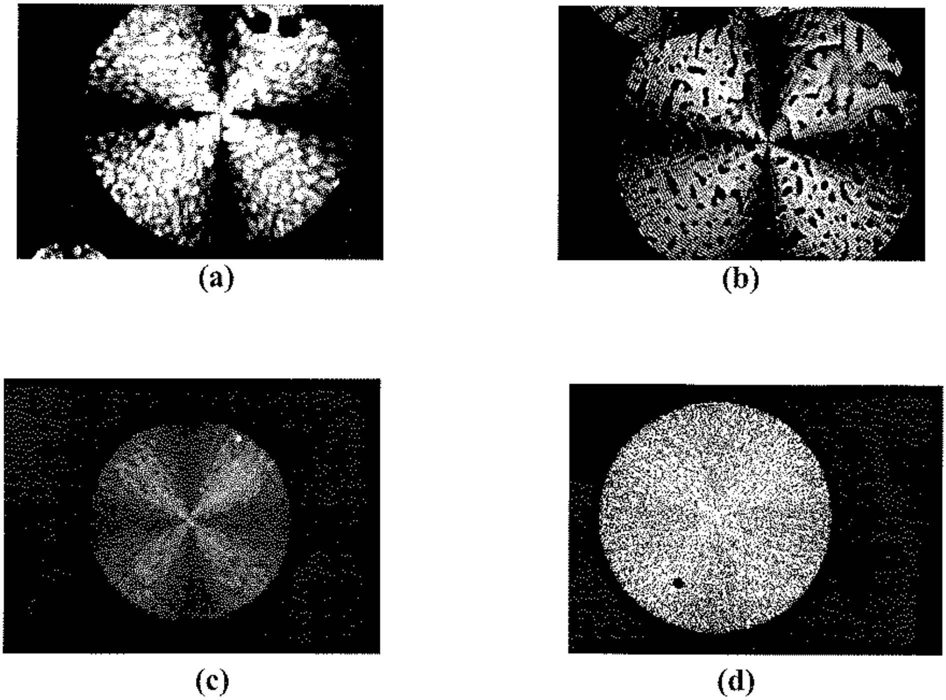

(a) (b) (c) (d)

Figure 5 Polarizing optical micrographs of PHB spherulites PHB/PCL/copolyester blends. a) 1 / 0 / 0, b) 1 / 1 / 0, c) 1 / 1 / 0.2, d) 1 / 1 / 1 (weight basis).

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