

Miscibility of Block Copolymers of Poly(ϵ -caprolactone) and Poly(ethylene glycol) with Poly(3-hydroxybutyrate) as Well as the Compatibilizing Effect of These Copolymers in Blends of Poly(ϵ -caprolactone) and Poly(3-hydroxybutyrate)

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ABSTRACT: Atactic poly(3-hydroxybutyrate) (a-PHB) and block copolymers of poly(ethylene glycol) (PEG) with poly(ϵ -caprolactone) (PCL-*b*-PEG) were synthesized through anionic polymerization and coordination polymerization, respectively. As demonstrated by differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) measurements, both chemosynthesized a-PHB and biosynthesized isotactic PHB (i-PHB) are miscible with the PEG segment phase of PCL-*b*-PEGs. However, there is no evidence showing miscibility between both PHBs and the PCL segment phase of the copolymer even though PCL has been block-copolymerized with PEG. Based on these results, PCL-*b*-PEG was added, as a compatibilizer, to both the PCL/a-PHB blends and the PCL i-PHB blends. The blend films were obtained through the evaporation of chloroform solutions of mixed components. Excitingly, the improvement in mechanical properties of PCL/PHB blends was achieved as anticipated initially upon the addition of PCL-*b*-PEG. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2600–2608, 2001

Key words: biodegradable blends; miscibility; compatibilizer; poly(ϵ -caprolactone); poly(ethylene glycol); poly(3-hydroxybutyric acid)

INTRODUCTION

The increasing research interest in biodegradable polymers over the past two decades has led to the availability of a large variety of novel polymers with claims of biodegradability.^{1–3} Current commercial biodegradable polymers are predominantly limited in aliphatic polyesters, polyether,

poly(vinyl alcohol), and native polysaccharides.^{1–5} Among these, the most important biodegradable polymers are aliphatic polyesters, typically including polylactide (PLA), poly(glycolide), poly(ϵ -caprolactone) (PCL), poly(3-hydroxybutyrate) (PHB), and poly(butylene succinate). Until now, much work has been carried out on the properties and applications of these polyesters; however, many properties of these polymers are found to fall short of the required properties for many practical applications.⁶

The properties of these polymers might be improved through several approaches including blending^{7–10} and copolymerization.^{11–13} Blending is a relatively simple and fast way in comparison

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with the copolymer synthesis. However, the miscibility of the components in blends should be of much concern because it is usually a key factor of determining the properties of the blends. On the one hand, the high interfacial energy between two immiscible phases is always one cause for bad mechanical properties of the polymer blends.¹⁴ On the other hand, it has been demonstrated that, for both completely⁸ and partially¹⁵ degradable blends, the biodegradation behavior of the blend is affected by not only the biodegradability of each component but also by the miscibility of the blend components as well. Taking the biodegradation and miscibility into account jointly, it is of very great importance to develop some miscible and, meanwhile, completely biodegradable polymer blends that possess the optimized comprehensive properties compared to the individual polymer.

PCL and PHB are two well-known biodegradable polyesters. They have thermoplasticity, good biocompatibility, and biodegradability. However, the biosynthesized isotactic PHB (i-PHB) has low elongation at break due to the brittleness that results from the high crystallinity. The processing window of i-PHB is very narrow because it is apt to undergo thermal degradation near its melting point.^{16–19} In addition to the biosynthesis via bacterial fermentation, PHB can be synthesized also by anionic polymerization of β -butyrolactone^{11,20}; however, the obtained product is usually the completely amorphous atactic PHB (a-PHB) without film-forming properties even at very high molecular weights. In contrast, PCL has high flexibility while its strength is relatively low and its melting point at 60°C is too low for many applications.⁶ Thus, it is quite reasonable to imagine that the blending of i-PHB with PCL may bring about either improved flexibility or increased strength in comparison with each component, i-PHB or PCL. Disappointingly, due to the immiscibility independent of the composition,^{21,22} the blends of these two polymers could not show the desired properties.

A method to improve the phase adhesion in immiscible blends has long been the subject of considerable research activities. This process of stabilizing polymer blends is commonly called *compatibilization*, and an often-adopted compatibilization strategy is the addition of a premade block/graft copolymer composed of blocks that are each miscible with one of the homopolymers. These so-called *compatibilizers*, which often tend to concentrate at the interface as emulsifiers,

have turned some otherwise incompatible blends into compatible and useful materials.²³

In this article, the miscibility of i-PHB with block copolymers of PCL and poly(ethylene glycol) (PEG), PCL-*b*-PEGs, was studied, and, subsequently, the effect of adding PCL-*b*-PEGs to the blends of PCL and i-PHB was investigated. As an extension of the initial thinking, a-PHB was synthesized through anionic polymerization and was also blended with PCL using PCL-*b*-PEGs as compatibilizers. The miscibility of a-PHB with PCL-*b*-PEGs and the effect of PCL-*b*-PEGs as compatibilizers were studied the same way. Because a-PHB is a totally amorphous polymer without a film-forming property, blending of a-PHB with other biodegradable polymers, such as PCL, should be an appropriate approach to obtain some useful materials with improved mechanical properties.

EXPERIMENTAL

Materials

The molecular characteristics of polymer samples are shown in Table I. Bacterial isotactic PHB (i-PHB), purchased from Aldrich (Tokyo, Japan), was purified by precipitation into ethanol from a 1,2-dichloroethane solution. The PCL sample was kindly supplied by Daicel Chemical Industries, Ltd. (Tokyo, Japan).

PEG with a molecular weight of 20,000 (PEG20000) and monomethoxy-PEG with a molecular weight of 750 (MPEG750) were obtained from Aldrich. They were used as macroinitiators and were purified in advance by precipitation into hexane from tetrahydrofuran (THF) solutions followed by being dried for 8 h at 60°C under reduced pressure before use. ϵ -Caprolactone (from TCI, Tokyo, Japan) was purified by vacuum-distillation over CaH₂. Stannous(II) octoate (from Wako Pure Chemical Industries Ltd., Tokyo, Japan) was used as received. β -Butyrolactone and 18-crown-6 ether (from TCI) were purified as reported.^{11,24} Potassium oleate (from TCI) was dried for 6 h at 40°C under reduced pressure. All the solvents used were of analytical grade.

Synthesis of Block Copolymer of PEG and PCL (Scheme 1)

Typically, under the protection of dry nitrogen, the calculated amount of ϵ -caprolactone and stan-

Table I M_n , M_w/M_n , Solubility Parameter, and Composition of the Samples

Sample	M_n	M_w/M_n	Solubility Parameter (MPa ^{1/2})	Block Copolymer Composition PCL : PEG (Mol Ratio) ^a
i-PHB	2.38×10^5	1.99	19.8 ^b	—
PCL	7.87×10^4	1.47	20.3 ^c	—
PEG20000	2.0×10^4	—	20.2 ^d	—
MPEG750	750	—	—	—
PCL- <i>b</i> -PEG	6.2×10^4	1.86	—	45 : 55
PCL- <i>b</i> -MPEG	4.4×10^4	1.45	—	96 : 4
a-PHB	4.5×10^4	1.17	—	—

M_n and M_w are number-averaged and weight-averaged molecular weights, respectively.

^a Calculated from the molecular weight.

^b Ref. 28.

^c Estimated with the group contribution methods (ref. 29).

^d Ref. 30.

nous(II) octoate were added into the reaction flask containing preweighted and predried PEG (PEG20000 or MPEG750). The flask purged with dry N₂ was sealed. Subsequently, the reaction mixture was heated to 115°C and was kept at this temperature for 24 h in an oil bath. The polymerization product was twice purified by a process of dissolving the polymer in chloroform followed by precipitating the polymer in methanol. The purified polymer was finally dried to a constant weight *in vacuo* at 40°C.

The purified polymer was characterized by ¹H-NMR, and the molecular weights were estimated by GPC measurement. A PEG20000-based block copolymer with $M_n = 6.2 \times 10^4$ and $M_w/M_n = 1.86$ and an MPEG750-based block copolymer with $M_n = 4.4 \times 10^4$ and $M_w/M_n = 1.45$ were obtained.

It is noted here that the ¹H-NMR spectra showed good agreement with the expected structures of the block copolymers, and the GPC curves of all purified copolymers exhibited the unimodal distribution. Therefore, ¹H-NMR and GPC measurements confirmed not only the copolymerization but also the fact that no or only a negligible

amount of the homopolymer (PEG and PCL) remained in the purified product of the block copolymer.

Synthesis of Atactic PHB (a-PHB)

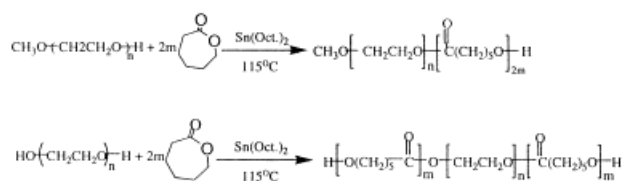
a-PHB was synthesized through anionic polymerization²⁵ in bulk with a potassium oleate/18-crown-6 ether complex (molar ratio = 1:1) as an initiator. The required amount of 18-crown-6 ether and β-butyrolactone were transferred under dry nitrogen to the reaction vial containing preweighted and predried potassium oleate. The vial was then sealed, and the anionic polymerization of β-butyrolactone was allowed to react at 25°C for 2 weeks. The polymer was twice purified by precipitation into ethanol from the THF solution; then, it was dried to a constant weight *in vacuo* at room temperature.

The polymer structure was proved by the ¹H-NMR measurement. From the GPC measurement, the molecular weight and molecular weight distribution were estimated to be 4.5×10^4 and 1.17, respectively.

Preparation of Blend Films

The prepared blend films (thickness 70–110 μm) are as follows: blends of i-PHB and PCL-*b*-PEG, blends of a-PHB and PCL-*b*-PEG, blends of i-PHB and PCL with or without PCL-*b*-PEG, and blends of a-PHB and PCL with or without PCL-*b*-PEG. The blend films were cast onto Teflon dishes from 2.5% sample solutions in chloroform. The solvent was allowed to evaporate at room temperature, and, subsequently, the films were dried *in vacuo* for 2 weeks at room temperature and another 2

Scheme 1: synthesis of block copolymers of PEG and PCL



Scheme 1 Synthesis of block copolymers of PEG and PCL.

Table II Thermal Properties of Blends of i-PHB and PCL-*b*-PEG Based on PEG20000

Composition ^a (i-PHB/Copolymer)	i-PHB					Block Copolymer (PCL- <i>b</i> -PEG)		
	T_{cc} (°C)	T_g (°C)	T_m (°C)	ΔH_f (J/g _{i-PHB})	χ_c (%)	T_g (°C)	T_m (°C)	ΔH_f (J/g _{copolymer})
0/100						-60.3	64.4/48.8	80.51
10/90	30.5	nd ^b	174.0/158.6	74.50	50.82	-61.9	64.3/48.0	69.67
30/70	26.2	-18.3	174.3/158.0	68.64	46.82	-61.7	65.0/45.5	58.01
50/50	26.3	-11.8	174.7/158.0	64.74	44.16	nd	63.6/45.1	52.06
70/30	28.3	-5.3	174.3/158.6	68.40	46.66	nd	58.9	40.11
90/10	38.0	1.6	175.3/158.2	74.06	50.52	nd	nd	nd
100/0	50.9	5.3	177.6/159.9	77.86	53.11			

T_{cc} and T_g are the cold-crystallization temperature and the glass transition temperature, respectively, obtained in the second heating run of DSC measurement. T_m , ΔH_f , and χ_c are the melting temperature, enthalpy of fusion, and degree of crystallinity, respectively, obtained in the first heating run of DSC measurement.

^a Indicating the weight ratio.

^b Indicating "not detected."

weeks at 40°C. With compression-molding equipment (Mini Test Press-10, Toyoseiki, Japan), blend films suitable for measurements of the mechanical properties were prepared by a further compression-molding process of the solution-cast films at 160°C under a pressure of 5 MPa.

Instrumentation

GPC measurements of block copolymers and *a*-PHB were carried out with chloroform as the eluent at a rate of 1.0 mL/min using a Toso HLC-8020 GPC system equipped with a TSK gel GMH \times L*2+2000H \times L column and a Toso SC-8010 controller and a refractive detector. Polystyrenes with narrow polydispersity were employed as the standards to generate the calibration curve. A volume of a 10- μ L sample solution in chloroform (concentration 1.0 g/L) was injected.

¹H-NMR spectra of samples (block copolymers or *a*-PHB) in CDCl₃ solutions were recorded on a JEOL SX-500 spectrometer at room temperature. A SEIKO-DSC 220U differential scanning calorimeter calibrated with indium was used to analyze the thermal properties of the blends. The sample was heated from a low temperature (established in accordance with sample, e.g., -100°C) to a high temperature (established in accordance with sample, e.g., 250°C) at a heating rate of 20°C/min. It was annealed for 1 min and quenched to a low temperature (established in accordance with a sample, e.g., -120°C). The sample was subsequently heated again to a high temperature (established in accordance with sample, e.g., 250°C) at a heating rate of 10°C/min. The thermograms of the first and the second heating

runs were both recorded. The cold-crystallization temperatures (T_{cc} 's) and the melting temperatures (T_m 's) were taken as the top values of the crystallization exotherms and the top values of the melting endotherms, respectively. The enthalpies of fusion (ΔH_f 's) were calculated from the integral of the endothermic melting peaks in the DSC curves. The glass transition temperatures (T_g 's) in the second heating run DSC curves were taken as indicated by the differentiation of the DSC (DDSC) peak.

Dynamic mechanical thermal analysis (DMTA) was performed on a SEIKO-DMS210 instrument in the tensile mode. The flat-casting films (length 30 mm, width 8 mm, and thickness 60–100 μ m) were tested from a low temperature to a high temperature at 5 Hz and a thermal scanning rate of 2°C/min. The ranges of measurement temperature were established in accordance with the samples.

Measurements of mechanical properties of specimens were performed at room temperature with a SHIMADZU (Japan) EZ Test machine at a crosshead speed of 3 mm/min. Each value reported is an average of three specimens.

RESULTS AND DISCUSSION

In Table II are summarized the results of the DSC measurements for the blends of i-PHB and PEG20000-based PCL-*b*-PEG. The enthalpy of fusion of each component was calculated by $\Delta H_f = \Delta H_f^a/W$, where ΔH_f^a is the apparent melting enthalpy corresponding to the fusion of each com-

Table III Thermal Properties of Blends of i-PHB and PCL-*b*-PEG Based on MPEG750

Composition (i-PHB/Copolymer)	i-PHB					Block Copolymer (PCL- <i>b</i> -PEG)		
	T_{cc} (°C)	T_g (°C)	T_m (°C)	ΔH_f (J/g _{i-PHB})	χ_c (%)	T_g (°C)	T_m (°C)	ΔH_f (J/g _{copolymer})
0/100						-62.7	63.3	69.57
10/90	43.5	nd	174.8	72.40	49.39	-61.8	64.5	67.12
30/70	43.2	0.5	175.1/178.3	68.63	46.81	-60.7	61.9	69.30
50/50	42.6	1.6	174.8/157.0	73.25	49.97	-61.9	59.9	69.52
70/30	43.0	2.5	176.8/157.6	79.32	54.11	nd	57.2	67.99
90/10	45.5	3.2	177.9/159.4	74.97	51.14	nd	nd	nd
100/0	50.9	5.3	177.6/159.9	77.86	53.11			

See the footnotes to Table II.

ponent indicated directly in the DSC thermogram and W is the weight fraction of the component in the blend. The crystallinity (χ_c) of i-PHB in the blends was calculated by assuming the thermodynamic melting enthalpy per gram of completely crystalline i-PHB to be 146.6 J/g.¹⁷

In the first heating run of the DSC measurement, bimodal T_m 's were obtained for both the pure i-PHB and i-PHB phases in the blends. It was suggested that the bimodal T_m 's of i-PHB were due to the fusion of crystals formed during the sample preparation and the fusion of crystals reformed during the heating run in the DSC measurement.²⁶ In Table II, the T_m 's of i-PHB and the T_m 's of PCL-*b*-PEG almost stand unchanged around 175/158°C (bimodal) and 64°C, respectively, in spite of the changes of the blend composition. Because pure PCL is not miscible with i-PHB (ref. 21) and PCL-*b*-PEG is a copolymer with two segments (PCL and PEG) possessing almost the same T_m (ca. 60°C) and T_g (ca. -60°C), it is unsuitable to conclude that the melting process and the crystalline phase structure of PCL-*b*-PEG were not affected at all by i-PHB in the blends from the unchanged T_m 's corresponding to the copolymer phase. Indeed, the constant T_m of i-PHB independent of the blend composition does imply that the melting process and crystalline structure of i-PHB were little affected by the addition of the copolymer. This is also demonstrated by the quite constant crystallinity of i-PHB in the blends as shown in Table II. On the contrary, the enthalpies of fusion assigned to PCL-*b*-PEG in the blends decrease significantly with increase of the i-PHB content. From these results, it is reasonable to suppose that the crystallization of PEG segments of PCL-*b*-PEG was much suppressed

upon adding i-PHB, while the crystallization of PCL segments of the copolymer was little affected.

The cold-crystallization temperature (T_{cc}) of pure i-PHB is observed at 50.9°C. In contrast, those of i-PHB in the blends are lower than that of pure i-PHB (see Table II). It seems that the crystallization of i-PHB becomes easier upon blending with PCL-*b*-PEG. However, the crystallinity of i-PHB in the blends does not differ too much from that of pure i-PHB as mentioned already; moreover, it is noteworthy that i-PHB in other blends, except that with a composition of $W_{i-PHB}/W_{PCL-b-PEG} = 90/10$, have very close T_{cc} 's almost independent of the composition of the blend.

Table III shows the thermal properties of blends of i-PHB and MPEG750-based PCL-*b*-PEG. Similarly, two series of T_m 's assigned, respectively, to the crystalline phase of i-PHB and the crystalline phase of PCL segments of the copolymer do not show significant changes with the composition. The T_g 's of the PCL segment phase in the blends may be regarded as the same as that of pure PCL. The crystallinity of i-PHB in the blends is almost constant at a range of 46–53%. Therefore, it is clear that well-separated PHB and PCL phases exist in these blends. The decrease of the T_g 's assigned to the i-PHB-rich amorphous region with increase of the i-PHB content should indicate that the PEG chains of the copolymer have penetrated into the amorphous region of i-PHB. However, the PEG segments of the MPEG750-based copolymer are very short in these blends; in other words, the PEG content in a blend containing the MPEG750-based copolymer is much lower than that of a blend containing the PEG20000-based copolymer even at the same

Table IV T_g 's and T_m 's of Blends of *a*-PHB and PEG20000-based PCL-*b*-PEG

Composition (a-PHB/PCL- <i>b</i> -PEG)	T_g (a-PHB phase) (°C)	T_g (PCL phase) (°C)	T_m (°C)	T_m (°C)
0/100		-59.3	64.4	58.7
30/70	-19.0	-61.7	61.9	57.4
50/50	-8.9	-60.4	62.0	56.9
70/30	-4.6	-61.2	60.2	55.9
100/0	0.6			

See the footnotes to Table II.

composition of $W_{i\text{-PHB}}/W_{\text{PCL-}b\text{-PEG}}$. Therefore, the T_g decrements of the *i*-PHB phase upon blending with an MPEG750-based copolymer are much less in comparison with blending with a PEG20000-based copolymer. As another result of the low content of PEG, the apparent melting enthalpies of MPEG750-based PCL-*b*-PEG are almost the same for all the blends. The apparent melting enthalpies of MPEG750-based PCL-*b*-PEG are thus mostly contributed by the PCL segment phase rather than by the PEG segment phase, which could be affected by *i*-PHB upon blending as discussed already.

The miscibility of *a*-PHB and PCL-*b*-PEG was also studied. According to the results of the DSC measurement (see Table IV), *a*-PHB synthesized in this report is a completely amorphous polymer with T_g at 0.6°C. Upon blending with the PEG20000-based PCL-*b*-PEG, the glass transition temperature of the *a*-PHB phase was much lower (see Table IV). The changes in the T_g 's and T_m 's relevant to the composition are similar to those found in the blends of *i*-PHB and PCL-*b*-PEG. Therefore, it is concluded that the isolated PCL segment domains comprising amorphous and crystalline phases exist in these blends, while the PEG segment phase of the copolymer is mixed with *a*-PHB in the amorphous region.

In the DSC thermograms of the second heating run, the significant changes in the T_g values assigned to the *i*-PHB-rich phase in the blends were observed. The T_g of the *i*-PHB-rich phase, depending on the blend composition, declines linearly from 5.3°C of pure *i*-PHB to -18.3°C of the blend with the composition of $W_{i\text{-PHB}}/W_{\text{PCL-}b\text{-PEG}} = 10/90$ (see Table II and Fig. 1). In addition, another series of quite constant T_g 's close to that of pure PCL (-60°C) were recognizable in the expanded thermograms of blends with a relatively high copolymer content, although they are very obscure even in the expanded DSC thermograms (not shown in this report due to the exhi-

bition of clearer DMTA thermograms). Furthermore, this series of T_g 's around -60°C are clearly observed in DMTA curves of the loss tangent versus temperature, as shown in Figure 2. From these results, on the one hand, it should be safe to conclude that isolated PCL domains including amorphous and crystalline phases exist in the blends. On the other hand, in these blends, *i*-PHB in its amorphous region is miscible with the amorphous region of PEG domains of PCL-*b*-PEG. Therefore, it is clear that the penetration of PEG chains, other than PCL chains, of PCL-*b*-PEG into the *i*-PHB amorphous region has caused the decrease of T_g of the *i*-PHB phase. It is not clear at

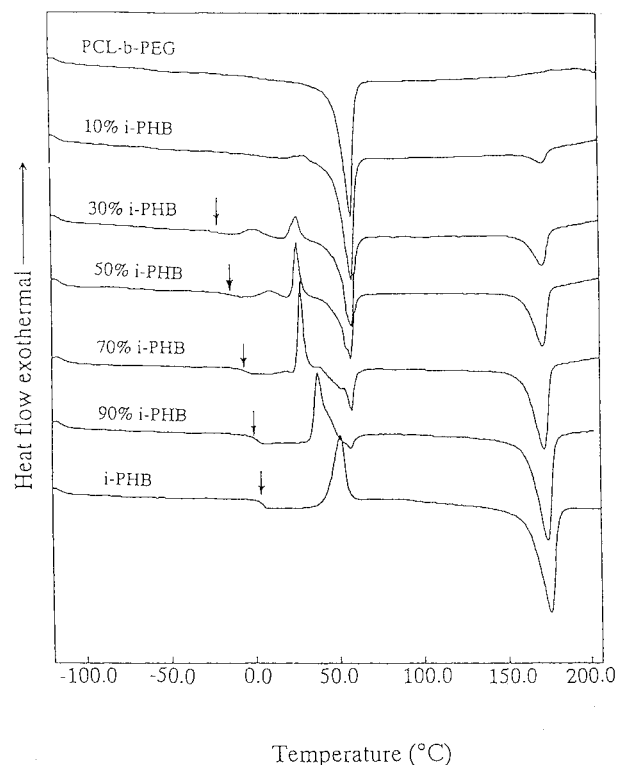


Figure 1 Second heating run DSC thermograms of *i*-PHB, PEG20000-based PCL-*b*-PEG, and their blends

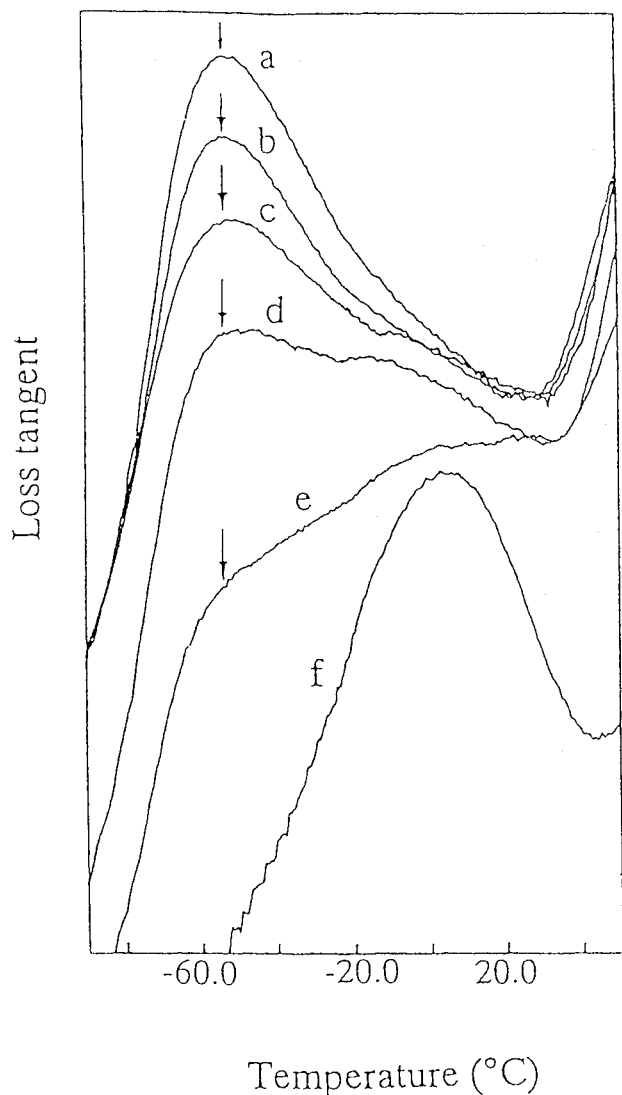


Figure 2 Loss tangent as a function of temperature for (f) i-PHB, (a) PEG20000-based PCL-*b*-PEG, and their blends: (b) 10% i-PHB, (c) 30% i-PHB, (d) 50% i-PHB; (e) 70% i-PHB.

the moment if a small proportion of short PCL chains close to the junctions of PCL blocks and PEG blocks were brought into the i-PHB amorphous region; however, it is certain that the PCL segment phase of PCL-*b*-PEG on the whole is still immiscible with i-PHB, as homo-poly(ϵ -caprolactone) is immiscible with i-PHB.

As mentioned in the Introduction of this report, a block copolymer suitable for compatibilizing an immiscible binary blend should possess the character of two segments separately miscible with the blend components so that the copolymer tends to concentrate at the interface as an emulsifier.

Recently, the block copolymers of PLA and PEG were reported to be added as a compatibilizer into the blends of i-PHB and PLA in consideration of the miscibility of PEG and i-PHB; unfortunately, the mechanical properties of the PLA/i-PHB blends were little improved. It was explained²⁷ that the molecular weight of the block copolymer was not high enough. On the other hand, PLA with a lower molecular weight was also found to be miscible with i-PHB. Therefore, most of the block copolymers were located in either the i-PHB or PLA phase rather than the interface between PLA and i-PHB.

Compared to this published case, the miscibility of PHB with PCL-*b*-PEG is very different. These block copolymers of PCL and PEG should be effective compatibilizers in PCL/PHB blends according to the general principle which defines whether a block copolymer is suitable for being used as a compatibilizer. The tensile strength and percent elongation of PCL/PHB (a-PHB and i-PHB) blend films with and without the addition of PCL-*b*-PEGs are listed in Table V.

The tensile strength and elongation of most PHB/PCL blend films were much improved after adding the block copolymers. Especially, the i-PHB/PCL (weight ratio: 50/50) blend film containing 10% PEG20000-based PCL-*b*-PEG (weight content) shows an increase in tensile strength of about 8 MPa and an increase in elongation about 11% in comparison with the blend film containing no block copolymer. In contrast, i-PHB/PCL blends containing the MPEG750-based copolymer do not show significant increments in both tensile strength and elongation. These results are consistent with the phase structures of PCL-*b*-PEG/i-PHB and PCL-*b*-PEG/a-PHB blends revealed by the DSC measurements. Because the PEG segment phase of PCL-*b*-PEG is miscible while the PCL segment phase of the copolymer is immiscible with PHB, the block copolymers added to the blends should predominantly be concentrated in the interface region between PCL and PHB, unlike the published case of the PLA/PHB blends with PLA-*b*-PEGs as the compatibilizer. Therefore, the interfacial adhesion between PCL and PHB was reinforced. When the MPEG750-based block copolymer was used as the compatibilizer, the PEG segment might be too short to bring about sufficient improvement in the interfacial adhesion between i-PHB and PCL; thus, the mechanical properties of the PCL/i-PHB blend films were not significantly improved upon adding the MPEG750-based PCL-*b*-PEG.

Table V Mechanical Properties of PCL, PHB, and Their Blends

PHB Type	Composition ^a (PHB/PCL)	Compatibilizer Based On ^a	Compatibilizer Amount (wt %)	Tensile Strength (MPa)	Elongation at Break (%)
—	0/100	—	—	14.57	690.30
i-PHB	50/50	—	0	11.36	6.61
i-PHB	50/50	PEG20000	5	17.98	14.13
i-PHB	50/50	PEG20000	10	19.42	17.33
i-PHB	50/50	MPEG750	5	12.06	6.98
i-PHB	50/50	MPEG750	10	11.84	7.50
i-PHB	100/0	—	—	26.99	5.04
a-PHB	30/70	—	0	4.68	118.53
a-PHB	30/70	PEG20000	5	7.94	350.12
a-PHB	30/70	PEG20000	10	8.99	382.75

^a Indicating weight ratio.

CONCLUSIONS

Analyses of the thermal properties of PCL-*b*-PEG/*i*-PHB and PCL-*b*-PEG/*α*-PHB blends demonstrated that the PEG phase of the block copolymer is miscible with PHB; on the contrary, the PCL phase of the copolymer, on the whole, is still immiscible with PHB, although it is difficult to exclude that some of the PCL short chains close to the junction of the PEG blocks and the PCL blocks may be brought into the PHB amorphous region by the PEG. However, it is certain that isolated PCL domains free of PHB chains still exist in the blends of the copolymer and PHB when the PEG chains of the copolymer are mixed into the amorphous region of PHB. The improvement in the mechanical properties of the blends containing PCL-*b*-PEGs demonstrated the expectation that PCL-*b*-PEGs are suitable for compatibilizing the immiscible PCL/*i*-PHB and PCL/*α*-PHB blends.

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