Morphologies and Mechanical Properties of Polylactide Blends with Medium Chain Length Poly(3-Hydroxyalkanoate) and Chemically Modified Poly(3-Hydroxyalkanoate)

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ABSTRACT: Blends of bacterial poly(3-hydoroxyalkanoate) (PHA) with a medium-length side chain and polylactide (PLA), and blends of the chemically modified PHA (ePHA) with PLA, were prepared. The morphologies, some physical properties, and thermal behavior of the blends based on PLA were investigated by electron microscopies, testing machines, and a differential scanning calorimeter, respectively. A blend of uncrystallized rubbery second components, PHA and ePHA, produced an increase in the impact toughness of the PLA blends in contrast to a decrease in the tensile strength value. PHA, especially, with an inserted epoxy group side chain was more effective in improving the morphology and the physical properties than PHA. The ePHA particles existed in the PLA domain as a dispersed phase having a size of 0.1–1 μm. The results of the biodegradation test demonstrated that the PLA blends still maintained their biodegradability and were more accessible to hydrolysis and microbial attack, resulting in a greater weight loss than the pure PLA. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 2363–2369, 2004

Key words: biopolymers; polyesters; biodegradable; blends; impact resistance

INTRODUCTION

With the increased interest in environmental protection, many biodegradable plastics were developed and investigated around the world. Aliphatic polyester is considered to be one of the most promising biodegradable plastics. Among them, polylactide (PLA) and poly(3-hydroxyalkanoate) (PHA) are best known as biodegradable thermoplastics produced from natural resources. Because they can be finally converted to water and carbon dioxide under environmental conditions, they are also known as renewable materials. A typical PHA, poly(3-hydroxybutyrate) (PHB), was first discovered as a naturally occurring storage material of *Bacillius megaterium* in 1925.[1] It is biosynthesized by numerous bacteria and accumulated in their body. Up to now, more than 150 different structural analogues of PHAs[2] have been reported, including alkyl pendant groups with 3 to 14 carbon atoms and functional groups in the side chain (halo-gens,[3] olefins,[4] aromatic,[5] thiophenoxy,[6] etc.). They are roughly divided into two groups according to their carbon numbers [i.e., short chain-length PHA (Scl-PHA) with shorter alkyl chains of C_3 to C_5 and medium chain-length PHA (Mcl-PHA) with longer alkyl chains of C_6 to C_{14}]. Mcl-PHA is a rubber-like material with properties such as biocompatibility, water insensitivity, and oxygen impermeability. Although Scl-PHA, poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate), was commercialized as Biopol, Mcl-PHA has not yet been industrialized but its attractive applications are being explored. Although PHAs with such functional groups have the possibility of wide applications, the yields from biomass are quite small, leading to a difficulty in industrialization. In contrast, one Mcl-PHA containing unsaturated bonds has a relatively high productivity[7] and the property by which functional groups can be introduced into the side chain by a chemical reaction. Because of these characteristics, Mcl-PHA has its own niche in application development. Until now, the applications to cheese coatings,[8] pressure-sensitive adhesives,[9] and biodegradable rubber[10,11] were reported. As Mcl-PHA seems likely an interesting candidate for the application of specific ally designed polymers in the future, further development of studies is considered valuable.

On the other hand, PLA is chemically synthesized from lactic acid which is produced by fermentation of renewable carbon sources such as sugars, cornstarch, or potato. It has attracted much industrial attention for many years because of its kinetic properties resembling those of polystyrene, biocompatibility, and high transparency. However, its brittleness, leading to low-impact resistance, limits its application. Therefore, many attempts were made to improve its physical properties for the potential growth of commercial markets for PLA. For instance, blending PLA with other polymers may be a more economical and more flexible technique for property improvements. So far, a variety of blends containing PLA have been studied, including binary blends with PHB,[12–14] polycaprolactone (PCL),[15–17] poly(ethylene oxide) (PEO),[18] and poly(butyrene succinate) (PBS).[19] The blends of PLA with natural biodegradable materials, such as cellulose[20] and poly(3-hydroxyoctanoate),[21] were also reported. Among them, the PCL blend became more flexible and the cellulose blend had an improved biodegradation speed. In the same way, a blend of PLA and rubbery PHA (denoted as Mcl-PHA later) would be expected to retain its biodegradability but has an improved impact toughness like polystyrene (PS) and an acrylonitrile–butadiene–styrene (ABS) blend. In this article, we attempted to develop a new application of PHA and investigate a polymer blend aimed at widening the practical use of PLA. The results concerning the morphology and thermal and physical properties of blends obtained by mixing PLA with uncrystallized rubbery components [i.e., PHA and epoxidized PHA (ePHA)] are described.

EXPERIMENTAL

Materials

PLA (Lacty) was provided by the Shimadzu Corp. (Kyoto, Japan) and then dried *in vacuo* at 30°C for 1 day. PHA was bacterially synthesized by *Pseudomonas putida* 27N01 by using a known fermentation procedure.[6] For bacterial growth and polymer accumulation, *P. putida* was cultivated under aerobic conditions at 30°C and pH 7.0 for 48 h in 100 L of medium containing defined mineral salts and 20 mM octanoic acid as the sole carbon substrate. The composition of the medium was as follows (per liter): 1.5 g $(NH_4)_2SO_4$, 1.4 g KH_2PO_4, 1.4 g Na_2HPO_4, 0.5 g $NaHCO_3$, and 0.3 g $MgSO_4\cdot7H_2O$ (all Aldrich); 0.3 g yeast extract (Difco); and 0.05 g ammonium iron (III) citrate (Wako Co., Tokyo). After the cells were harvested by centrifugation and lyophilized, the PHA was isolated by chloroform extraction at 60°C followed by precipitation into methanol. The PHA was dried *in vacuo* at 30°C before use.

Partly epoxidized PHA, ePHA, was prepared by chemical modification of the bacterial poly(3-hydroxy-alkanoate-*co*-3-hydroxyalkenonate) (PHAE). PHAE was biosynthesized from a fermentation process by using a mixture of 14 mM octanoic acid and 6 mM 10-undecenoic acid as the sole carbon source in the same way as the PHA production. After PHAE was extracted from cells in the same manner, the ratio of the unsaturated group was determined by ^{1}H-nuclear magnetic resonance (NMR) spectroscopy. Following a previous method,[22] the unsaturated side group in PHAE was converted into an epoxy group using *m*-chloroperbenozoic acid. The prepared ePHA was stored at −20°C before use.

Sample preparation

Mixtures of PLA-PHA and of PLA-ePHA were dissolved in the same solvent, chloroform/toluene (7/3), at 80°C for 1 h. After the polymer samples were precipitated by pouring the solutions into methanol, the samples for mechanical testing were prepared by using a hand-operated press-molding device (Instron, Japan, model 4505) at 190 ± 10°C.

Analysis

The ^{1}H- and ^{13}C-NMR spectra of the PHA samples were recorded by using a JNM-EX 400 FT-NMR spectrometer (JEOL Co.). The 400-MHz ^{1}H-NMR and the 100-MHz ^{13}C-NMR spectra were recorded at 25°C in $CDCl_3$. To determine the polymer composition, samples were decomposed to the methyl esters of PHA monomers by methanolysis. The methylesters were analyzed by GC-MS, 5890 system (Hewlett–Packard), and GC, GC-17 (Shimadzu Co.), equipped with a J&W Scientific capillary column (30 × 0.25 mm). The average molecular weight of the polymer was obtained at 30°C by gel permeation chromatography (Shodex GPC system 11; Showa Denko Co.) by using AC-800P, AC-80M, and AC803 sample columns. Chloroform was used as an eluant at the flow rate of 1.0 mL min^{-1}. Polystyrene standards with a low polydispersity rate were used to construct the calibration curve.

Thermal characterization was carried out by using a DSC-3100S (Mac Science) differential scanning calorimeter (DSC) equipped with an MTC 1000S data station. The sample was sealed in an aluminum pan, and analysis was carried out while maintaining a dry nitrogen purge. The polymer sample was analyzed at a heating rate of 20°C/min from −100 to 210°C. The sample was rapidly cooled by quenching in liquid nitrogen and then analyzed again during a second heating scan from −100 to 210°C.

Microscopy

The morphology of the PLA blends was investigated by using a JSM-5900LV (JEOL Co.) scanning electric
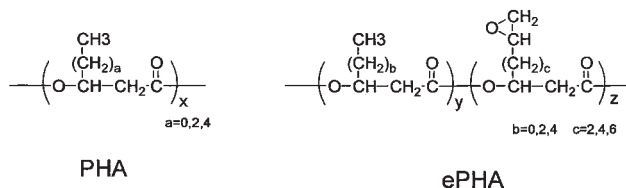
Figure 1 Chemical structure of PHA and ePHA.

microscope (SEM) equipped with a refrigerating unit and a JEOL 2000FX ATEM transmission electric microscope (TEM).

In the SEM investigation, the blend samples were broken at liquid nitrogen temperature on the unit and then the fracture surface was observed after coating with a 200 Å layer of Pt.

For the TEM experiment, specimens were trimmed and embedded in epoxy resin. After the epoxy cured, the cured block was further trimmed and then the trimmed block was faced off with a diamond knife. The thin block was stained by exposing it to a vapor of an aqueous RuO_4 solution. Ultrathin sections for the observations were prepared by cutting the thin block with a diamond knife.

Mechanical testing

The measurement values of all mechanical tests averaged for five specimens were reported. The tensile strength test of the blended samples was performed in accordance with ISO R527 without strain rate measurements at room temperature on an AG-50NG Tensilon tester (Shimadzu Co.) with a cross-head speed of 5 mm/min. The instrumented Charpy impact test was performed on a JT Toshi CI-8E equipped with an 8 J hammer. In the instrumented Charpy test, a pendulum's hammer was fitted with a load cell. The force–time data during the actual impact were stored in a high-speed data-acquisition data system. These data were used to draw load deflection curves showing force, energy, and deformation versus time. The crack initiation is defined to be the integrated area of curve before the maximum load value and the rest of the integrated area corresponds to the crack propagation. All samples ($45 \times 4 \times 3$ mm) were notched on a notching machine (Imoto Co.).

Biodegradation test

Each bone-shaped test piece was placed in a 300-mL baffle flask containing 80 mL of dilute activated sludge solution from a sewage-disposal plant in Nagoya City. The flask was incubated under aerobic conditions at 37°C on a reciprocating shaker for 4 months. During the incubation, the weight of each sample was measured every month. The degree of degradation was evaluated from the weight-loss measurement. The weight loss averaged for three test pieces was employed.

RESULTS AND DISCUSSION

PHA containing an unsaturated bond in the terminal side group was obtained from fermentation of *P. putida* 27N01. Chemical modification was thoroughly carried out and ePHA with $\sim$ 30% content of an epoxy group in the side chain was obtained. This reaction was monitored and confirmed by ^{1}H- and ^{13}C-NMR spectroscopies.[21] The chemical structures of PHA and ePHA are shown in Figure 1 and the characteristics of these polymers are listed in Table I. PHAs have a much lower crystallinity and higher elasticity than Scl-PHAs. PHA and ePHA show the same elastic behavior but ePHA crystallizes more slowly than PHA. In addition, ePHA easily undergoes gelation at room temperature because of the reaction of the epoxy groups.

TABLE I
Characterization of PHA and ePHA

	Repeating units composition (mol %)				T_m (°C)	T_g (°C)	$M_w{}^e$
	3HHx[a]	3HO[b]	3HD[c]	e3HA[d]			
PHA	14.6	76.5	8.9	—	51.5	−38.6	2.3×10^6
ePHA	9.7	53.1	7.8	29.4	50.5	−34.3	2.8×10^6

[a] 3-Hydroxyhexanoate.
[b] 3-Hydroxyoctanoate.
[c] 3-Hydroxydecanoate.
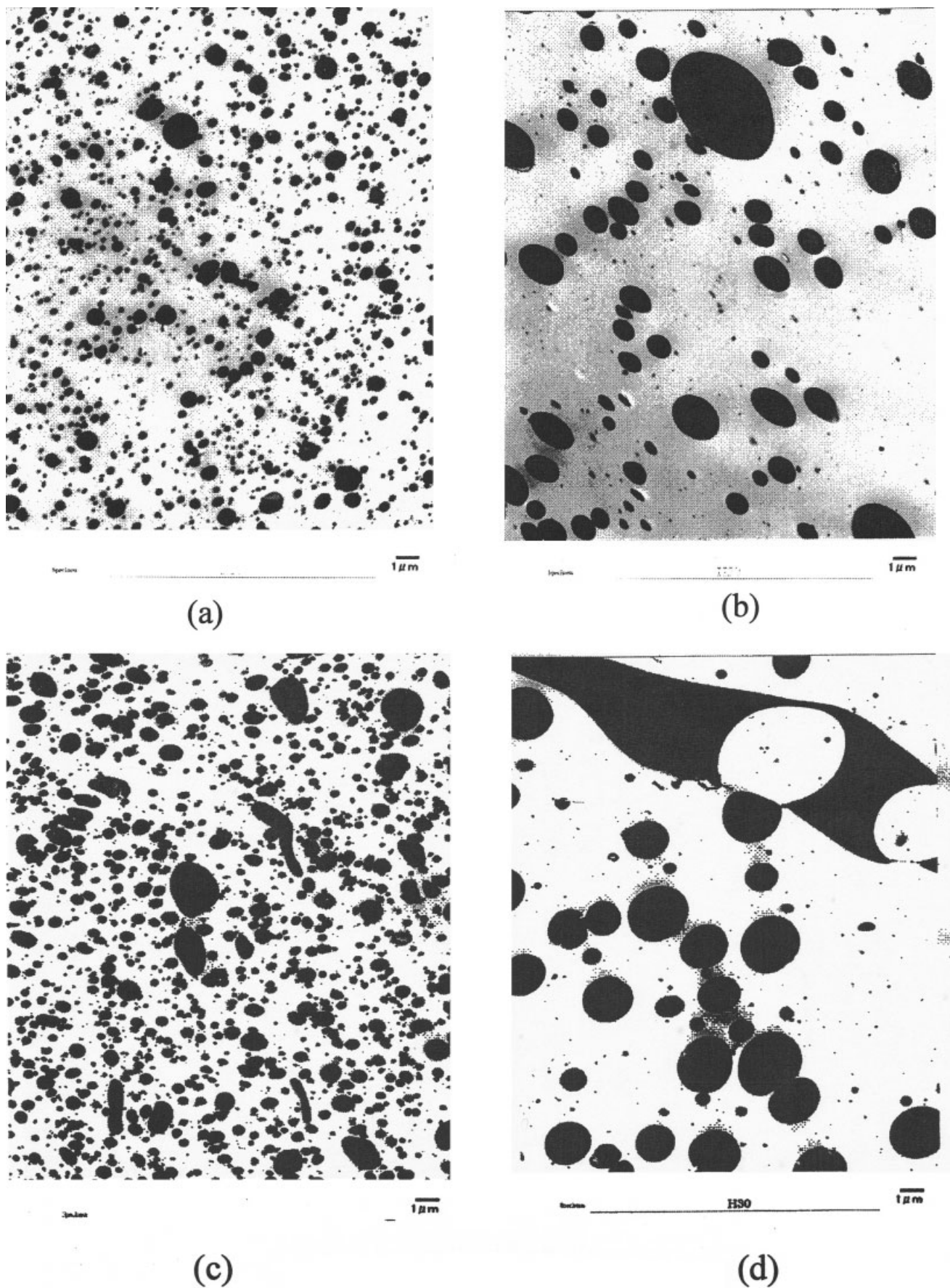[d] 3-Hydroxyalkanoate containing epoxy side group.
[e] Molecular weight.

Figure 2 Transmission electron micrographs of the PLA/ePHA blends: (a) 80/20; (c) 70/30; and the PLA/PHA blends: (b) 80/20; (d) 70/30.
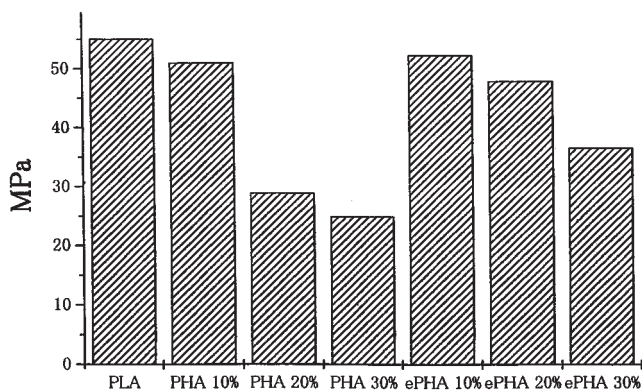
Figure 3 Mechanical tensile properties of PLA, PLA-PHA blends, and PLA-ePHA blends.

Polymer blend

Comparing the PHA-PLA blends to ePHA-PLA blends, there is a prominent difference in their appearance. Although the PHA blended has an opaque light-white color, the ePHA blend is transparent and colorless, which PLA also has. In addition, the PHA blends still have an adhesive surface. It may be safely assumed that the ePHA has a better compatibility for PLA than the nonepoxidized PHA. Thus, further information on the blends system was obtained from microscopic observations.

As shown in Figure 2(a), the dispersed granular size of the ePHA component in the PLA phase was ~ 0.05–2 μm based on TEM observations of the 20% ePHA blend. On the other hand, the size of the PHA component in the 20% PHA blend was ~ 1–7 μm [Fig. 2(b)]. Similar trends were observed from other ratios of the PHA and the ePHA blends [Fig. 2(c, d)]. The decrease in the particle size observed for the blends of PLA with modified PHA and with ePHA can be explained by the fact that the epoxy group might work on the PLA phase during the blend process. In other words, ePHA has some interaction with and penetrates into the PLA phase that causes the finer particle dispersion.

Mechanical properties

The tensile strength results for all the blend compositions are presented in Figure 3.

PLA has a higher tensile strength among the commercial biodegradable plastics. In this experiment, PLA itself had a value of 55.2 MPa.

Although the test values of the ePHA-blended samples decreased with an increase in the ePHA content of the blends, the rate of decrease is lower than those of the PHA blends. Thus, ePHA blended with PLA has a better effect on its physical properties than the PHA blend.

To confirm the improvement effect on the impact toughness of the PLA blends, a Charpy impact test was performed on the various blend compositions. It is reported that an elastic material blended into a stiff polymer improves the impact strength. A typical example of the improvement of the impact toughness of PS is the polymer blend, PS and ABS rubber, that is known as HIPS.[23] The same effect is applied to the PLA blend with a rubberlike plastic. The same improvement was observed for the impact strength of the two kinds of blend components. The results of the Charpy impact test is shown in Table II. The blend samples with ePHA and PHA have a higher impact strength than that of PLA itself. As the ratio of the elastic polymer in the blends increased, the total absorbance energy was increased. The impact toughness of the ePHA blend was superior to that of the PHA blend in same blend ratio, respectively. When comparing the two blends, the ePHA blend has a higher crack propagation value leading to the impact absorbing property. A 30% ePHA blend content especially had a 16 times higher value than PLA itself and was not broken after impact testing.

The fracture surfaces of these PHA blends and ePHA blends were investigated by SEM. As shown in Figure 4(a), the micrograph photo of the 20% PHA blend had spherical pores, which were from 1 to 5 μm in size all over the surfaces that were attributed to a phase-separated amorphous PHA. Correspondingly, in the micrograph of the 20% ePHA blend, less than a 1-μm pore size originating from ePHA was observed in the phase-separation structure [Fig. 4(b)]. These results suggest that dispersed elastic PHA or ePHA absorbs the impact force and finer ePHA is more effective than PHA for the PLA composite. According to many reports, the proper particle size in a polymer

TABLE II
Instrumented Charpy Impact Test of Pure PLA, PHA, and ePHA Blends

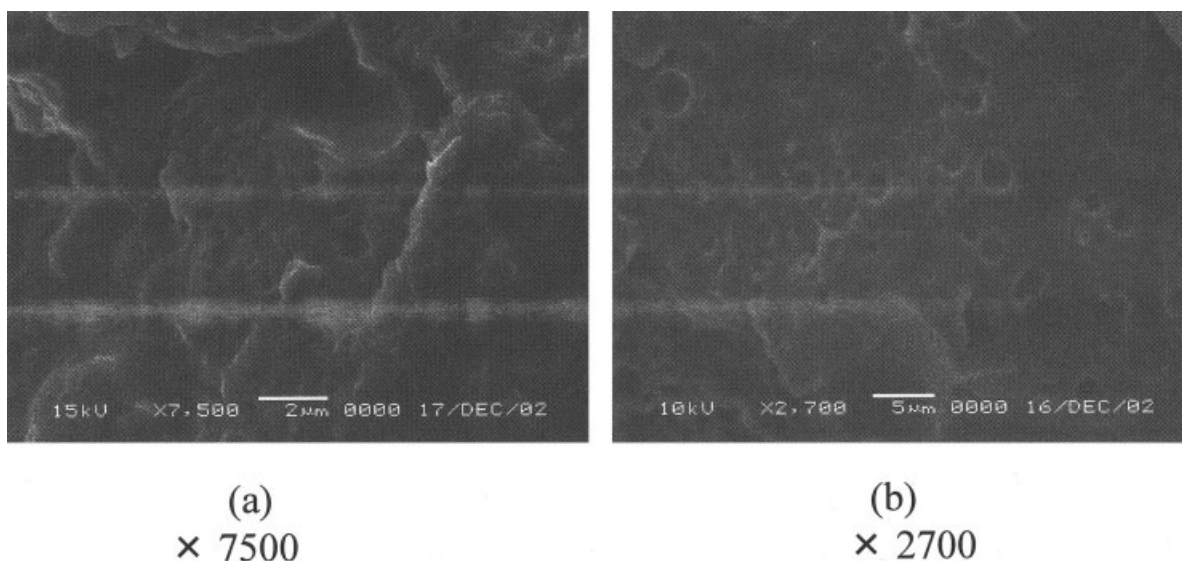| Sample	Total absorbed energy (J)	Crack initiation (J)	Crack Propagation (J)
PLA	5.2×10^{-2}	4.6×10^{-2}	0.5×10^{-2}
PLA/PHA 90/10	8.1×10^{-2}	7.3×10^{-2}	0.7×10^{-2}
PLA/PHA 80/20	13.7×10^{-2}	12.7×10^{-2}	1.0×10^{-2}
PLA/PHA 70/30	16.1×10^{-2}	14.7×10^{-2}	1.3×10^{-2}
PLA/ePHA 90/10	8.9×10^{-2}	8.1×10^{-2}	0.8×10^{-2}
PLA/ePHA 80/20	16.9×10^{-2}	14.6×10^{-2}	2.3×10^{-2}
PLA/ePHA 70/30	26.0×10^{-2}	17.6×10^{-2}	8.4×10^{-2}

Figure 4 Scanning electron micrographs of the fracture surface of the (a) PLA/ePHA 80/20 and (b) PLA/PHA 80/20. Bar: (a) 2 μm; (b) 5 μm.

blend to improve the impact toughness is determined by the type of polymer. It is assumed that around a 10^{-1}-μm rubber particle size is suitable for improving the mechanical properties.

Thermal analysis

DSC was carried out to determine the compatibility of ePHA in PLA. The melting temperature (T_m) due to PLA is almost unchanged with the increasing ePHA and PHA contents. Two distinctive glass transition temperatures (T_g) peak in the curves and T_g due to the PLA component appeared ~ 60°C for both pure PLA and the blends, supporting the fact that the two kinds of blends are not miscible in the amorphous state over these studied composition ranges. Table III shows the T_g of each phase blend samples. Compared with the T_g

TABLE III
Glass-Transition Temperatures of Two Phases in PLA Blends

Blend ratio	T_g of PLA phase (°C)	T_g of PHA phase (°C)
(a) PLA/PHA blends		
100/0	57.7	—
90/10	57.5	—
80/20	57.0	−38.2
70/30	56.9	−38.0
(b) PLA/ePHA blends		
100/0	57.7	—
90/10	56.8	—
80/20	56.5	−33.5
70/30	55.7	−32.8

of the pure component in blends, the T_g's of each component in the blends shift slightly toward each other. The shift in the T_g values of the ePHA blends was greater than that of PHA blends, which implied that an interaction between the ePHA phase and the PLA phase took place.

Biodegradation

Biodegradation of PLA in the usual natural environment is slower than other commercial biodegradable plastics. However, in a compost, PLA is easily hydrolyzed and then immediately biodegraded. It is reported that a biodegradable plastic blend with another highly biodegradable material sometimes exhibits better biodegradability than the pure plastic itself.[24] Because microbial PHA is one of the representative highly biodegradable plastics, its blends are supposed to undergo faster degradations. To confirm the biodegradability of ePHA and PHA in the PLA blends, biodegradation test was performed. Test samples of all the blends and PLA were incubated for 120 days in an activated sludge solution under aerobic conditions at 30°C. The mass loss of the samples and their appearance were observed. The time course of the degradation of the samples for 120 days is shown in Figure 5. For the initial 30 days, no weight change was observed in the all samples and their surfaces were smooth. Distinct cavities due to the degradation processes were visible in the PHA and the ePHA blend samples after the incubation period of 70 days. After 120 days, the PLA still had a smooth surface and showed no weight loss, whereas the ePHA and the PHA blends were partly biodegraded with 8 and 6.5% weight losses, respectively. For both blend samples,
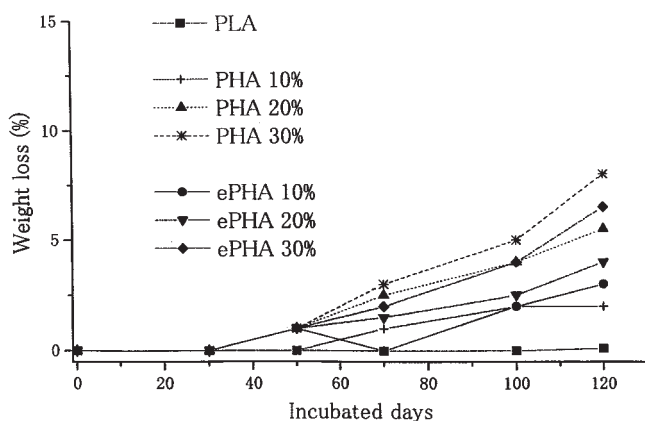
Figure 5 Weight loss of PLA, PHA blends, and ePHA blends in activated sludge solution.

the degradation increased with an increase in the ePHA and the PHA ratio, respectively. As similar weight loss processes were observed between the ePHA blend and the PHA blend, there seems to be no apparent correlation between the rate of biodegradation and the presence of epoxy groups in the polymer. According to a previous study, the hydrolysis of PLA was accelerated by a phase-separated blend structure rather than a miscible structure due to the enhanced occurrence of enzymatic hydrolysis. Although no evidence of PLA biodegradation was found in our result, the hydrolytic degradation is supposed to be increased by the expanded surface area in the blends after biodegradation.

CONCLUSION

Although the PLA-PHA and the PLA-ePHA blends were found to be immiscible in the amorphous state, it was found that elastic biodegradable polymers, PHA and ePHA, could enhance the impact toughness of the PLA blend. The ePHA had a more significant effect than PHA in the blends and existed as a finer particle phase in the phase-separated structure. It is possible to conclude that there is a difference between the compatibility of PHA and ePHA in the PLA phase in the blends. The partly inserted epoxy group in the side chain is supposed to provide a better effect on the morphology of the ePHA blend. A possible explanation is that the epoxy group is not stable and therefore tends to combine with the hydroxyl group of PLA in the end group. This could increase the interaction between phases. Results obtained from the biodegra-

dation test indicated that the addition of PHA or ePHA to PLA resulted in an increased degradation rate. To our knowledge, only a few kinds of plastics, which have elastic, water insensitivity, and biodegradable properties, were reported. PHA and its derivatives are some of the promising candidates for the second component in PLA blends.

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