Blends of Aliphatic Polyesters. III. Biodegradation of Solution-Cast Blends from Poly(L-lactide) and Poly(ε-caprolactone)

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ABSTRACT: Phase-separated blend films were prepared with the solution casting method from poly(L-lactide) (PLLA) and poly(ε-caprolactone) (PCL) with different PLLA contents [X_{PLLA} (w/w) = PLLA/(PCL + PLLA)] and their biodegradation was investigated in soil up to 20 months by gravimetry, gel permeation chromatography, tensile testing, differential scanning calorimetry, and scanning electron microscopy. The nonblended PCL film and the blend film with X_{PLLA} = 0.25 disappeared in 4 and 12 months, respectively, while most of the initial mass remained for the blend film of X_{PLLA} = 0.75 and the nonblended PLLA film. The decrease in weight remaining, molecular weight, tensile strength, and elongation-at-break was higher for blend films of low X_{PLLA}. The melting temperature of PLLA in blend films of X_{PLLA} = 0.5 and 0.75, and of nonblended film, remained around 179°C upon biodegradation in soil for 20 months. The preferred biodegradation of PCL in blend films resulted in formation of microspheres of a PLLA-rich phase at the surface for the blend film of X_{PLLA} = 0.25 and the porous structure for blend films of X_{PLLA} = 0.5 and 0.75. Comparison of the weight loss of blend films in biodegradation in soil with that of the nonenzymatic hydrolysis in phosphate-buffered solution revealed preferred enzymatic degradation of PCL and insignificant attack to PLLA in the blends. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2259–2268, 1998

Key words: polylactide; polycaprolactone; polymer blends; biodegradation

INTRODUCTION

In a previous paper of this series, we investigated nonenzymatic hydrolysis of blend films from poly(L-lactide) (PLLA) and poly(ε-caprolactone) (PCL) in a phosphate-buffered solution of pH 7.4 as a model of phase-separated aliphatic polyester blends.[1] The work disclosed the following.

1. Hydrolysis of PLLA was much faster than that of PCL, even when the molecular weight of PLLA was higher than that of PCL.
2. A small amount of PCL accelerated the hydrolysis of PLLA in the blend films, probably because of the increased concentration of the terminal carboxyl group in the film by the addition of low-molecular-weight PCL.
3. Hydrolysis of PLLA in the blend films of high PCL contents was greatly retarded probably due to prevention of water diffusion into the PLLA-rich phase dispersed

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in the continuous hydrophobic PCL-rich phase.
4. Hydrolysis of PCL was not strongly influenced by the presence of PLLA.

On the contrary, in natural environments such as in soil, biodegradation of PCL has been reported to take place more rapidly than that of PLLA because of enzymes from microbes present in the environments,[2–5] although Torres et al. reported that oligomeric poly(DL-lactide) (PDLLA) plates underwent invasion of some filamentous fungi at the surface and into the bulk.[6] Not enzymatic hydrolysis in natural environments, but pure enzymatic hydrolysis of the phase-separated blends from enzymatically hydrolyzable and nonhydrolyzable aliphatic polyesters has been studied by Doi and coworkers for the pairs of poly[(R)-3-hydroxybutyrate] (PHB) with PCL, or poly(ε-caprolactone-*co*-lactide) (PCL–LA).[7,8] They revealed that the hydrolysis rate per unit weight of PHB by PHB–depolymerase was increased by addition of PHB–depolymerase nonhydrolyzable PCL or PCL-LA and that the difference in enzymatic hydrolyzability between the two polymers in the phase-separated blends resulted in formation of porous surface structure.

In the present work, biodegradation of phase-separated aliphatic polyester blends from PLLA and PCL, having different polymer mixing ratios, will be studied in soil up to 20 months using gravimetry, gel permeation chromatography (GPC), tensile testing, differential scanning calorimetry (DSC), and scanning electron microscopy (SEM). The nonenzymatic hydrolysis in blend films must be slower in soil than in phosphate-buffered solution because of lower temperature and water concentration in soil than in phosphate-buffered solution. Therefore, comparison of biodegradation of the blends in soil with nonenzymatic hydrolysis in phosphate-buffered solution will make clear the effect of enzymes from microbes in natural environments on the degradation of phase-separated blends.

EXPERIMENTAL

Materials

PLLA and PCL used in this work were synthesized and purified as described in previous papers.[1,9–12] Molecular characteristics and physical properties of PLLA and PCL obtained by ring-opening bulk polymerization are listed in Table I. Blend films with the thickness of 50 μm were prepared with the method described in previous papers.[1,9] Briefly, methylene chloride solutions of different PLLA and PCL concentrations were prepared to have a total polymer concentration of 1.0 g/dL and then cast onto flat glass plates, followed by solvent evaporation at room temperature for approximately 1 week. To avoid reaching a dried state of quasi-equilibrium, solvent evaporation was performed very slowly as reported in previous articles.[1,9,13–15] The resulting films were dried *in vacuo* for 1 week and stored at room temperature for more than 1 month to the equilibrated state. The thickness of films was fixed to 50 μm since nonenzymatic hydrolysis is reported to proceed homogeneously in phosphate-buffered solution along the cross section of the film if its thickness is below 2 mm.[16]

Biodegradation

Biodegradation test was performed at Toyohashi City, Aichi prefecture, Japan, using blend films of 1.8 × 3.0 × 50 μm in leaf mold purchased in the market. The water content and relative humidity of the soil (leaf mold) were 45 ± 10 and 98 ± 2%, respectively. The water content of the soil was calculated as follows:

$$\text{Water content of soil (wt \%)} = (1 - W_a/W_b) \times 100 \quad (1)$$

where W_b and W_a are the weight of soil before and after drying *in vacuo* for 1 week, respectively. The pH(H_2O) and pH(KCl) of the soil were 7.3 and 6.8, respectively, suggesting that there should be insignificant pH effect for the film degradation in the soil compared with that in phosphate-buffered solution at pH 7.4. The total carbon contents of the soil was 5.7%, which was calculated based on the following equation:

$$\text{Total carbon content of soil (wt \%)} = [0.458 \cdot (W_1 - W_2) - 0.4]/W_1 \times 100 \quad (2)$$

where W_1 and W_2 are the weight of the soil heated at 105°C for 5 h and at 375°C for 16 h, respectively. The heating at 375°C for 16 h was performed after heating at 105°C for 5 h.

In order to investigate what kind of soil microbes is responsible for biodegradation, the nonblended PCL and PLLA films were buried at 25°C for 1 week in the soil with and without addition of

Table I Characteristics of Blend Films of Different X_{PLLA} Before and After Hydrolysis for 20 Months

X_{PLLA}	$\bar{M}_w/10^5$ (g/mol)		$\bar{M}_w/\bar{M}_n$		σ_β (kg/mm^2)		ε_β (%)		$T_{m,\,PCL}$ (°C)		$x_{c,\,PCL}$ (%)		$T_{m,\,PLLA}$ (°C)		$x_{c,\,PLLA}$ (%)		$x_{c,\,tot}$ (%)	
	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After
0	2.63		2.0		1.1	0	245	0	65.0		67						67	
0.25	4.01		2.5		1.7	0	50	0	64.8		68		176		17		55	
0.5	5.50	5.00	2.7	2.4	1.4	0.2	34	0–0.1	64.6	63.1	55	[a]	179	178	47	[a]	51	[a]
0.75	7.95	4.14	3.1	3.9	4.0	0.3	393	0–0.1	64.5	63.8	54	[a]	179	178	52	[a]	53	[a]
1	11.88	7.64	2.6	2.0	4.9	5.1	23	5					179	179	51	49	51	49

[a] Not estimated because X_{PLLA} could not be evaluated after hydrolysis.

streptomycin (1 mg/g soil) or chlorothalonil (Daconil; 1 mg/g soil). Streptomycin and chlorothalonil are antibiotic against general bacteria and fungicide, respectively. A significant weight loss was observed for the nonblended PCL film buried in the soil with streptonycin (2.2 μg/mm^2, 8.5%) and no additives (7.2 μg/mm^2, 33.4%), while no weight loss was observed when the nonblended PCL film was buried in the soil with chlorothalonil (0 μg/mm^2, 0%), strongly suggesting that enzymes from fungi are mainly responsible for biodegradation of PCL. On the other hand, no weight loss was recognized for the nonblended PLLA film, independent of the soil additives, suggesting insignificant attack by the enzymes from microbes in the soil.

The biodegradation test started on April 23, 1995. After biodegradation of films in the soil for predetermined periods of time, the films were washed twice in double distilled water at room temperature, followed by drying *in vacuo* for at least 2 weeks.

Measurements

The crystallization and melting temperature (T_c and T_m, respectively) and the enthalpy of crystallization and melting (ΔH_c and ΔH_m, respectively) of blend films were determined by differential scanning calorimetry (DSC) with a Shimadzu DT-50. For DSC measurements, films were heated at a rate of 10°C/min under a nitrogen gas flow, and DSC results were calibrated using indium as the standard. The crystallinity of PCL ($x_{c,PCL}$) in the blend films before biodegradation was calculated under the assumption that the enthalpy of glass transition of PLLA in blend films ($\Delta H_{g,PLLA}$) was constant, irrespective of the mixing ratio of the two polymers and the same as that of the nonblended PLLA film before biodegradation ($\Delta H_{g,PLLA}$ = 3 J/g of PLLA). Under this assumption, x_c of PLLA, PCL, and the total polymer in the films ($x_{c,PLLA}$, $x_{c,PCL}$, and $x_{c,tot}$, respectively) were calculated for the blend films of different PLLA contents (X_{PLLA}) by the following equations.[9,10]

$$x_{c,\,PLLA}\,(\%) = 100 \times (\Delta H_{m,\,PLLA} + \Delta H_{c,\,PLLA})/(X_{PLLA} \cdot 93) \quad (3)$$

$$x_{c,\,PCL}\,(\%) = 100 \cdot (\Delta H_t - \Delta H_{g,\,PLLA} \cdot X_{PLLA})/[(1 - X_{PLLA}) \cdot 142] \quad (4)$$

$$x_{c,\,\mathrm{tot}}\,(\%) = x_{c,\,\mathrm{PLLA}} \cdot X_{\mathrm{PLLA}} + x_{c,\,\mathrm{PCL}} \cdot (1 - X_{\mathrm{PLLA}}) \quad (5)$$

$$X_{\mathrm{PLLA}}\,(\mathrm{w/w}) = \mathrm{PLLA}/(\mathrm{PCL} + \mathrm{PLLA}) \quad (6)$$

where ΔH_t (J/g of polymer) is the enthalpy of overall transition, including $\Delta H_{g,\mathrm{PLLA}}$ and ΔH_m of PCL appearing around 60°C. $\Delta H_{c,\mathrm{PLLA}}$ (J/g of polymer) is ΔH_c of PLLA around 100°C, while 93 J/g of PLLA and 142 J/g of PCL are the enthalpy of fusion of PLLA and PCL crystals having the infinite crystal thickness reported by Fischer et al.[17] and Crescenzi et al.,[18] respectively.

Tensile properties of the blend films were measured at 25°C and 50% relative humidity using a tensile tester at a crosshead speed of 100%/min. The initial length of specimens was always kept at 20 mm.

Molecular weight distribution of blend polymers was evaluated in chloroform at 40°C with a Tosoh GPC system equipped with TSK Gel columns ($\mathrm{GMH_{XL}} \times 2$) using polystyrene as standard. Morphology of biodegraded blend films was studied with a Hitachi SEM (S-2300) after coating with carbon to a thickness of about 20 nm.

RESULTS AND DISCUSSION

Weight Remaining

It has been reported that biodegradation of aliphatic polyesters is accelerated by microbe enzymes present in soil.[2–8,19–22] In such enzyme-accelerated biodegradation, hydrolysis of materials will proceed by surface erosion mechanism because it is unlikely that macromolecular enzymes can readily diffuse into the interior of such hydrophobic polyesters. When blend films obtained from aliphatic polyesters undergo hydrolysis through their main chain scission, weight loss of the films will take place, but it becomes detectable only when water-soluble oligomers are produced by microbes and then diffuse into the surrounding soil. Figure 1 shows the film weight remaining after biodegradation of blend films in soil performed for different periods of time. Apparently, weight becomes almost zero in 4 and 12 months for the nonblended PCL film ($X_{\mathrm{PLLA}} = 0$) and the blend film of $X_{\mathrm{PLLA}} = 0.25$, respectively, where a PCL-rich phase forms a continuous phase in the initial films.[1] Even after 20 months of biodegradation, only a small weight loss is observed for the blend film of $X_{\mathrm{PLLA}} = 0.75$ and the nonblended PLLA film ($X_{\mathrm{PLLA}} = 1$), where a PLLA-rich phase forms a continuous phase.[1] The weight of blend film of $X_{\mathrm{PLLA}} = 0.5$ decreases slowly in the first 12 months, but then the decrease becomes significant. When compared at 20 months of biodegradation, the blend film of $X_{\mathrm{PLLA}} = 0.75$ and the nonblended PLLA film have only slightly lost their initial weight (1 and 6%, respectively), whereas the nonblended PCL and the blend films of $X_{\mathrm{PLLA}} = 0.25$, 0.5 have lost 100, 100, and 46% of the initial weight, respectively. This indicates that the weight loss in soil increases with an increase in the PCL content in the blends. The mass loss around 50% of blend of $X_{\mathrm{PLLA}} = 0.5$ suggests that a PCL-rich phase as well as a PLLA-rich phase forms a continuous phase in this blend. If a PCL-rich phase forms a dispersed phase, biodegradation of a PCL-rich phase will occur only at the surface of the film, resulting in a much smaller weight loss than 50%.

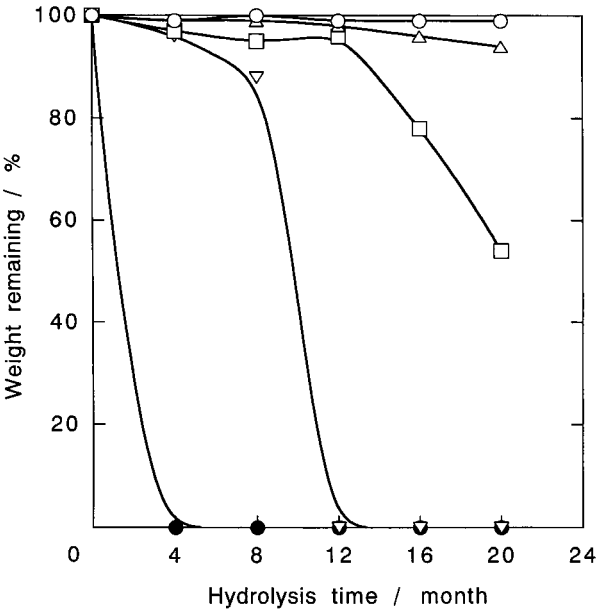

Figure 1 Weight remaining for blend films of different X_{PLLA} as a function of hydrolysis time. X_{PLLA} equals (●) 0, (▽) 0.25, (□) 0.5, (△) 0.75, and (○) 1.

It is interesting to note that the weight of the blend film of $X_{\mathrm{PLLA}} = 0.25$, where a very small amount of PLLA molecules dispersed in the continuous PCL-rich phase,[1] decreased slowly compared to that of the nonblended PCL. This suggests that a small amount of PLLA molecules existing in the continuous PCL-rich phase has suppressed biodegradation of the PCL molecules. Probably, the PLLA molecules in the PCL-rich phase might hinder binding of enzymes to PCL molecules. In contrast, the weight loss rate per

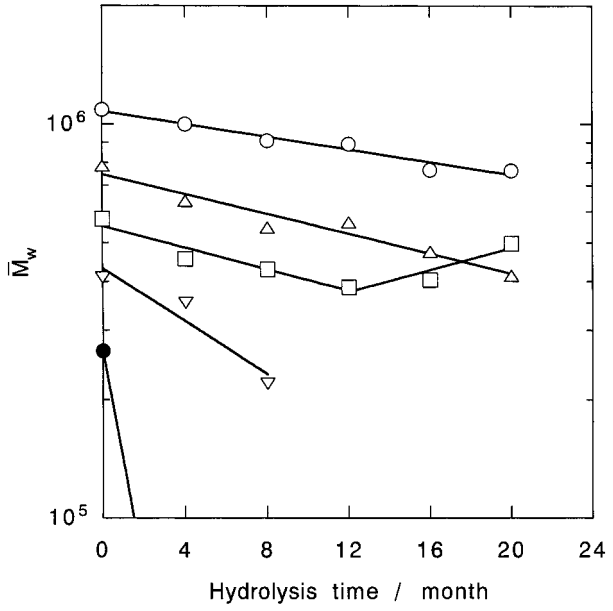

Figure 2 A semilogarithmic plot of $\bar{M}_w$ against hydrolysis time for blend films of different X_{PLLA}: X_{PLLA} equals (●) 0, (▽) 0.25, (□) 0.5, (△) 0.75, and (○) 1.

unit weight of an enzymatically hydrolyzable polyester was reported to increase upon addition of an enzymatically nonhydrolyzable polyester, even when the two aliphatic polyesters were phase-separated. The example includes enzymatic hydrolysis of PHB by PHB-depolymerase upon addition of a small amount (approximately 25 wt %) of PCL[7] or PCL–LA.[8]

Molecular Weight Change

Figure 2 shows a semilogarithmic plot of $\bar{M}_w$ of the blend films against the biodegradation time in soil. The molecular weight of films of $X_{PLLA} = 0$ and 0.25 could not be measured when biodegradation was performed for longer than 4 and 12 months, respectively, because they were rapidly degraded, and no material remained in soil. It is seen that $\bar{M}_w$ decreases monotonously with the biodegradation time except for the blend film of $X_{PLLA} = 0.5$, which showed delayed biodegradation after 16 months. A slight change in the slope of log $\bar{M}_w$ may be explained by selective degradation and removal of PCL molecules of low molecular weights in the blend film, leaving PLLA of high molecular weights. Generally, the initial slope of log $\bar{M}_w$ increases with the decreasing X_{PLLA}.

The molecular weight distribution of the blend films after 0, 8, and 20 months of biodegradation, shown in Figure 3, provides us with further information concerning the biodegradation of blend films in soil. Despite the rapid degradation of PCL molecules in the blends, any specific GPC peak due to PCL crystalline residue was not observed during biodegradation of blend films of $X_{PLLA} = 0.25$ and 0.5, probably because the crystalline thickness of PCL in the blend films as well as in the nonblended PCL film was too small to leave any crystalline residue, in contrast to that reported for the nonenzymatic alkaline hydrolysis of the nonblended PCL film.[5] We also found that the specific peak position due to the crystalline residue and the ratio of the specific peak area to the main peak area in GPC spectra strongly depended on the crystalline thickness and crystallinity of the initial film, respectively.[23]

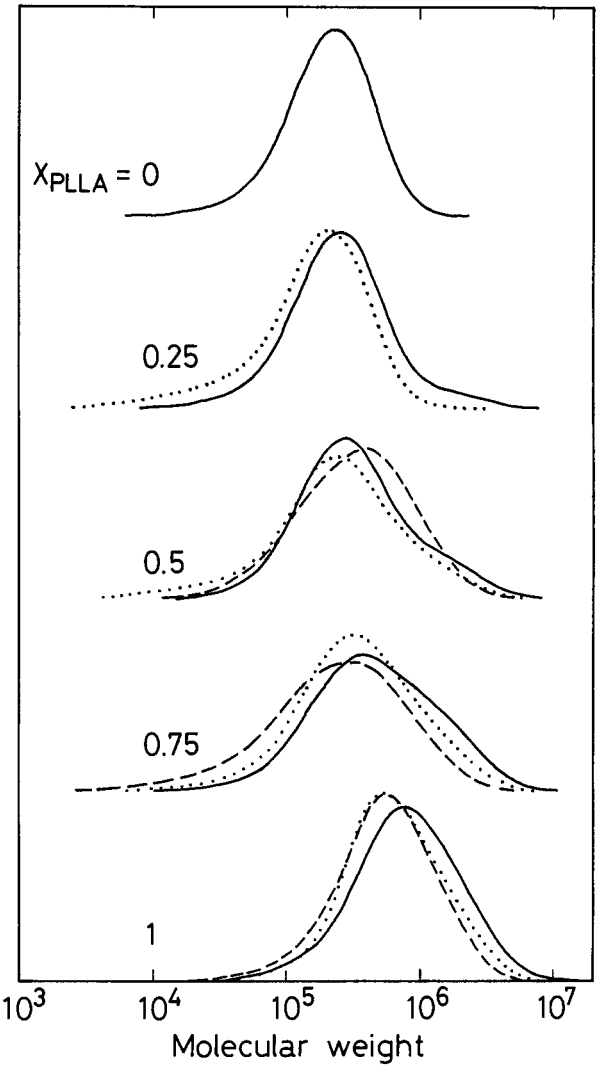

Figure 3 Molecular weight distribution of blend films of different X_{PLLA} subjected to hydrolysis for 0, 8, and 20 months: (——) 0, (····) 8, and (---) 20 months.

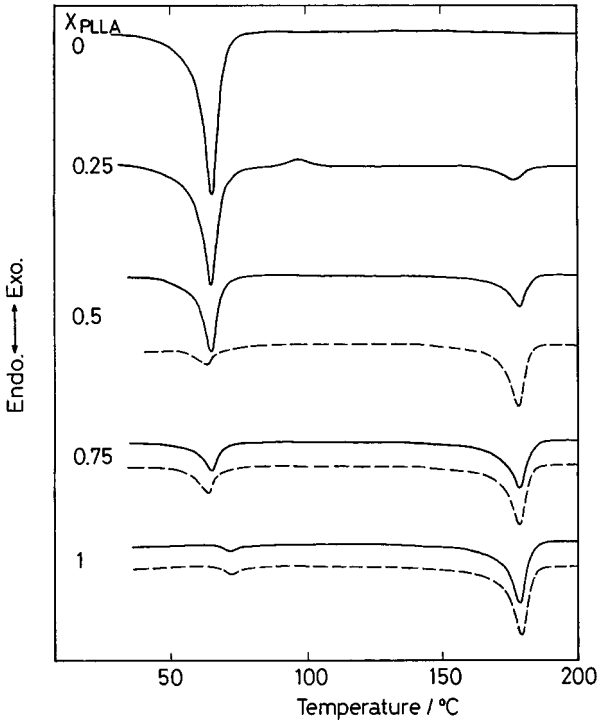

Figure 4 DSC thermograms of blend films of different X_{PLLA} before and after hydrolysis for 20 months: (——) before; (----) after.

Such a specific peak was observed for neither the nonblended PLLA film nor the blend film of X_{PLLA} = 0.75, probably because of very low biodegradability of PLLA in soil, though specific peak formation was reported for nonenzymatic hydrolysis in a phosphate-buffered solution of compression-molded crystallized PLLA[24] and solution-cast crystallized poly(D-lactide) (PDLA),[25] for nonenzymatic alkaline hydrolysis of melt-crystallized PLLA,[23] and also for *in vivo* hydrolysis of as-polymerized crystallized PLLA,[26] when hydrolysis was allowed to proceed to a great extent.

The molecular weight peak of the blend film of X_{PLLA} = 0.5 after biodegradation for 20 months seemingly shifted to higher molecular weight than that after biodegradation for 8 months. This may be because solely low-molecular-weight PCL was enzymatically degraded, leaving high-molecular-weight PLLA, as mentioned above.

Crystalline Structure Change

DSC thermograms for the blend films of different X_{PLLA} before and after biodegradation for 20 months are shown in Figure 4. An insignificant change was observed on the DSC thermogram for the blend of X_{PLLA} = 0.25 after biodegradation for 8 months (data not shown). Evidently from Figure 4, the area of the melting peak of PCL around 65°C decreases with the increasing X_{PLLA} before biodegradation, while that of PLLA around 179°C increases with an increase in X_{PLLA}. Table I summarizes the thermal properties of blend films evaluated from the DSC measurements. The T_m of PLLA and PCL ($T_{m,PLLA}$ and $T_{m,PCL}$, respectively) in the blend films before biodegradation is practically constant, irrespective of X_{PLLA}, when they are major components in the blend films. These findings provide evidence for the phase-separation of PCL and PLLA into PCL-rich and PLLA-rich phases in the initial blend films.

It has been reported that a decrease in melting temperature is observed in DSC charts of polymers at the late degradation stage when hydrolysis occurs in their crystalline region.[24–26] On the contrary, an insignificant decrease or a slight increase of melting temperature of degradable polymers will appear in their DSC chart if hydrolysis has taken place solely in their amorphous region at the initial stage, resulting in crystallite growth.[24–26] The decrease and increase in the melting peak area of PCL and PLLA, respectively, observed in the blend film of X_{PLLA} = 0.5 after biodegradation for 20 months, suggests that PCL molecules have been readily enzymatically degraded and removed from the blend film, leaving PLLA molecules, in agreement with the result of GPC. On the other hand, this trend was not recognized for the blend film of X_{PLLA} = 0.75, probably because enzymatic degradation of PCL molecules in the PCL-rich phase dispersed in the continuous PLLA-rich phase occurred solely at the surface of the film. The melting temperature

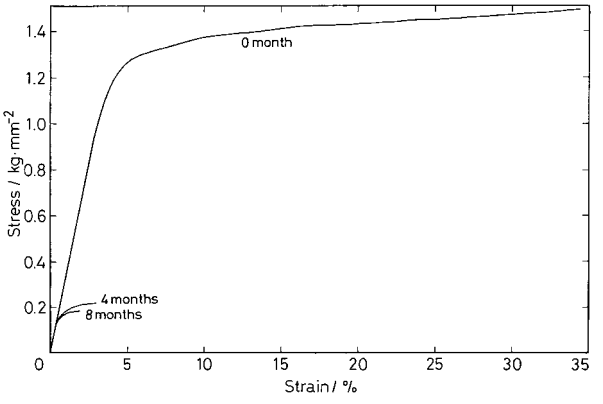

Figure 5 Strain–stress curves for blend film of X_{PLLA} equals 0.5 at different hydrolysis times.

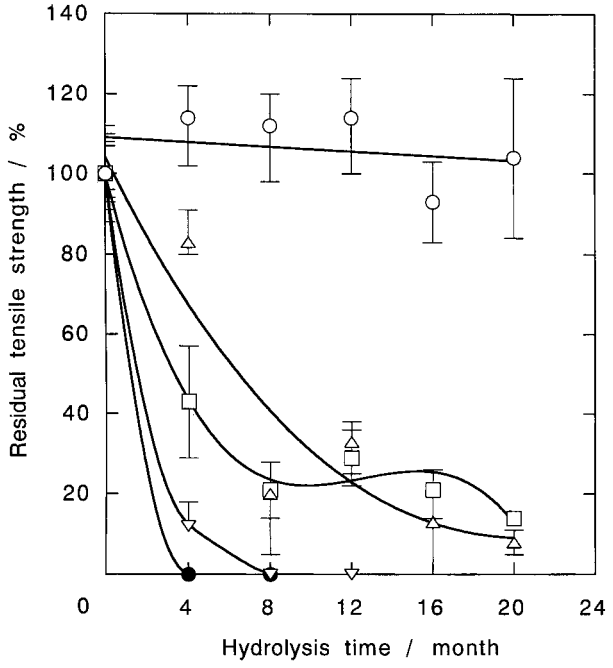

Figure 6 Residual tensile strength of blend films of different X_{PLLA} as a function of hydrolysis time: X_{PLLA} equals (●) 0, (▽) 0.25, (□) 0.5, (△) 0.75, and (○) 1.

and peak area of PLLA in the nonblended PLLA film and the blend film of X_{PLLA} = 0.75 did not practically change by biodegradation for 20 months, probably due to very low biodegradation in soil.

Mechanical Properties Change

Figures 5 illustrates typical strain–stress curves for the blend film of X_{PLLA} = 0.5 at different hydrolysis times. Tensile strength and elongation-at-break dramatically decreased in the first 4 months. Figures 6 and 7 show the residual tensile strength and elongation-at-break for the blend films biodegraded in soil as a function of the biodegradation time. As can be seen in Figure 6, the tensile strength of the nonblended PLLA film remains unchanged for 20 months, while that of nonblended PCL film rapidly decreases to zero in 4 months. As seen in Figure 7, the elongation-at-break of the nonblended PCL film rapidly becomes zero within 4 months of biodegradation, while that of nonblended PLLA slowly decreases to 20% of the initial value in 20 months of biodegradation. The intermediate blends show a gradual and intermediate decrease in both tensile strength and elongation-at-break.

The tensile strength and elongation-at-break of the blend film of X_{PLLA} = 0.75 decrease monotonously but more rapidly than that of the nonblended PLLA, indicating that the presence of a small amount of PCL molecules accelerated degradation of tie molecules in the amorphous region of the continuous PLLA-rich phase. This is probably due to the increased density of terminal carboxyl group supplied by low-molecular-weight PCL.[1] On the other hand, the tensile strength and elongation-at-break of the blend film of X_{PLLA} = 0.25 shows a different decrease profile, retaining a slightly higher value than that of the nonblended PCL. This finding suggests that a small amount of PLLA molecules existing in the continuous PCL-rich phase hindered the biodegradation of tie molecules present in the amorphous region of the PCL-rich phase.

It should be noted that a significant decrease in tensile strength and elongation-at-break was observed for the blend films of X_{PLLA} = 0.5 and 0.75, which had the PLLA-rich phase as the continuous phase and showed a very small decrease in molecular weight, as seen in Figure 3. Comparison of the residual tensile strength with the residual elongation-at-break of the nonblended PLLA shows that the residual elongation-at-break is more sensitive to the scission of tie molecules in the amorphous region between the crystalline lamellae than the residual tensile strength.

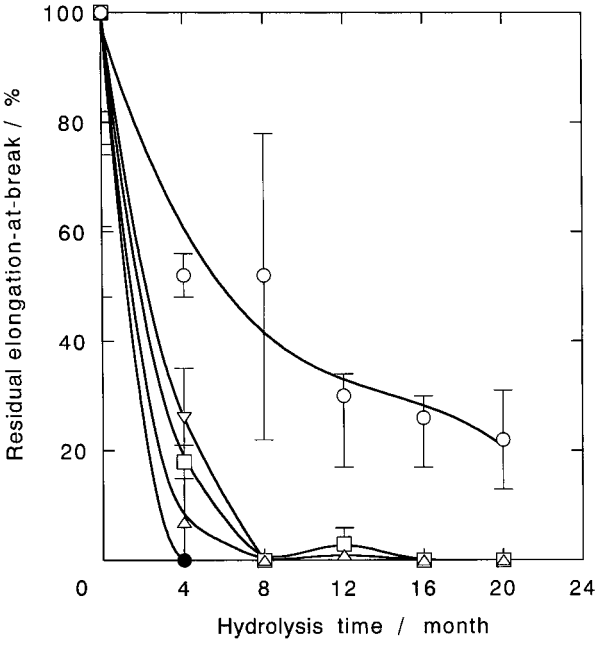

Figure 7 Residual elongation-at-break of blend films of different X_{PLLA} as a function of hydrolysis time: X_{PLLA} equals (●) 0, (▽) 0.25, (□) 0.5, (△) 0.75, and (○) 1.

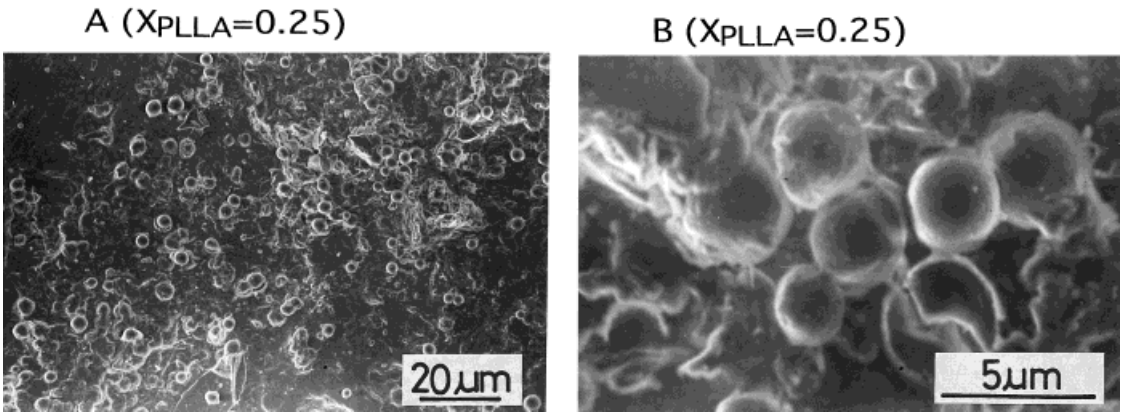

Figure 8 SEM photomicrographs of the blend film of X_{PLLA} = 0.25. (B) is a magnification of (A).

Morphology

SEM photomicrographs are shown in Figures 8 and 9 for the blend film of X_{PLLA} = 0.25 after 4 months of biodegradation in soil, along with those of blend films of X_{PLLA} = 0.5 and 0.75 and the nonblended PLLA film after 20 months of biodegradation in soil. As seen in Figure 8, numerous microspheres with diameters of 2 to 4 μm are

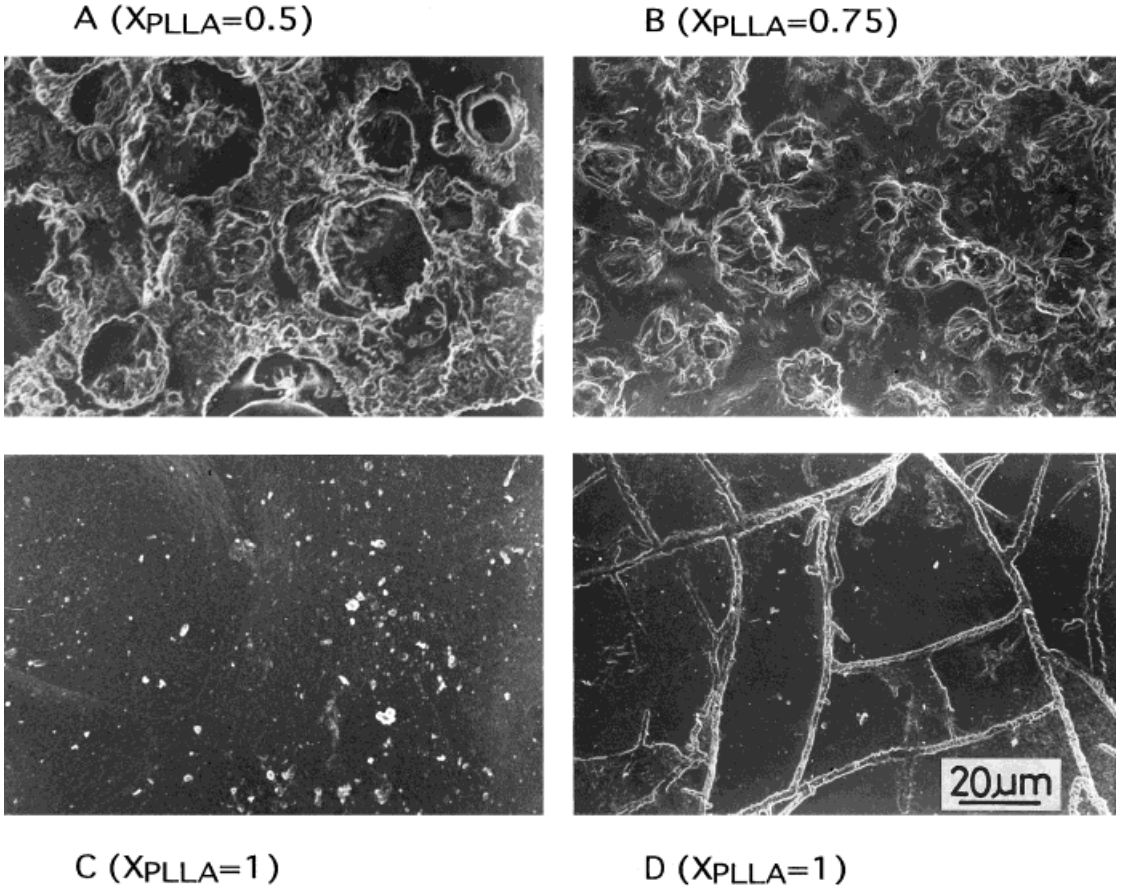

Figure 9 SEM photomicrographs of blend films of X_{PLLA} equals (A) 0.5 and (B) 0.75 and nonblended PLLA film [(C) and (D)].

observed at the film surface. This may result from degradation and removal of the PCL-rich continuous phase, leaving the dispersed PLLA-rich phase in the state of microspheres at the surface of the film. This finding also suggests that biodegradation of the blend film of $X_{PLLA} = 0.25$ proceeds by enzymatic surface erosion. Observation of initial blend film of $X_{PLLA} = 0.25$ by polarizing optical microscope showed that a continuous PCL-rich phase was composed of PCL spherulites.[1] Preferred hydrolysis in the amorphous region and accumulation of the crystalline region of the spherulite will elucidate the shape of spherulite. Such accumulation of crystalline residue was not observed for the blend film of $X_{PLLA} = 0.25$, in contrast with alkaline surface erosion of PCL[5] and PLLA film.[23] There may be a small difference between biodegradation rates of amorphous and crystalline region, or accumulation of microspheres of a PLLA-rich phase may hide the crystalline residue of PCL spherulites.

On the other hand, microporous structure with pore sizes of about 20 and 10 μm is observed for the blend films of $X_{PLLA} = 0.5$ and 0.75, respectively. These pores may be ascribed to removal of the PCL-rich phase dispersed in the initial blend films by biodegradation, and the pore size difference between the two biodegraded blend films must be due to the size difference of the PCL-rich phase in the initial blend films. Biodegradation of the PCL-rich phase in the blend film of $X_{PLLA} = 0.75$ must have occurred only at the surface. If not, the weight loss after 20 months of biodegradation should have approached 25%, not 6%, as shown in Figure 1.

No formation of specific structure was observed at most of the surface from nonblended PLLA, as shown in Figure 9(C). However, a part of the nonblended PLLA film surface was invaded by filamentous fungi, as shown in Figure 9(D), in good agreement with the finding by Torres et al. for poly(DL-lactide) and PLLA when biodegraded in soil.[6]

It is interesting to note that the preferred removal of PCL molecules of the blend films in soil gives further evidence for phase-separated structure of blend films from PLLA and PCL before biodegradation, in addition to the evidence by DSC, viscoelastic measurements, and polarizing optical microscopy,[1] and revealed the domain size and morphology of the PLLA-rich and the PCL-rich phase in the initial blend films, which could not be determined by polarizing optical microscopy before biodegradation.

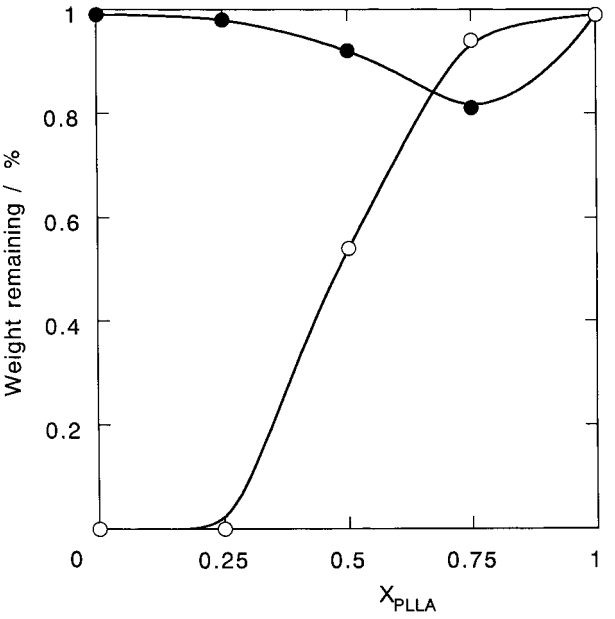

Figure 10 Weight remaining for blend films hydrolyzed in soil (○) and in phosphate-buffered solution (●) as a function of X_{PLLA}.

Comparison of Biodegradation in Soil with Hydrolysis in Phosphate-Buffered Solution

To compare the biodegradation of blend films in soil with the nonenzymatic hydrolysis of blend films in phosphate-buffered solution, the weight of films remaining after 20 months of biodegradation and hydrolysis is shown in Figure 10 as a function of X_{PLLA}. The hydrolysis test was performed in 0.15*M* phosphate-buffered solution of pH 7.4 at 37°C. The nonenzymatic hydrolysis in blend films must be slower in soil than in phosphate-buffered solution because of lower temperature and water concentration in soil than in phosphate-buffered solution. Therefore, comparison of biodegradation of the blends in soil with nonenzymatic hydrolysis in phosphate-buffered solution will demonstrate the effect of enzymes from microbes in natural environments on the degradation of blends.

Clearly, there is a large difference between the biodegradation in soil and the hydrolysis in phosphate buffered solution, again confirming the preferred enzymatic degradation of PCL and the insignificant enzymatic attack to PLLA in the blend films. The weight loss becomes more prominent with the decreasing X_{PLLA} for the biodegradation test, whereas the weight loss becomes maximum at $X_{PLLA} = 0.75$ for the nonenzymatic hydrolysis. The maximum weight loss is larger for the bio-

degradation in soil than for the hydrolysis in buffered solution, indicating a strong effect of enzymes from microbes on the degradation of blends containing PCL.

CONCLUSION

It can be concluded that biodegradation of blend films containing a large amount of PCL, where the PCL-rich phase forms the continuous phase, was accelerated in soil, compared to hydrolysis in phosphate-buffered solution, probably due to the enzymatic degradation of PCL molecules. Microsphere formation at the surface of blend films of low X_{PLLA} may be due to rapid enzymatic surface erosion and, hence, removal of the PCL-rich continuous phase, leaving the dispersed PLLA-rich phase of the initial blend film. The results of mechanical measurements revealed that the phase separation between PLLA and PCL was imperfect and that a small amount of PLLA molecules existing in the continuous PCL-rich phase delayed the biodegradation of PCL.

In contrast, no accelerated biodegradation was observed for the blend films containing a small amount of PCL, where the PCL-rich phase was dispersed in the continuous PLLA-rich phase. The enzymatic degradation and removal of the PCL-rich phase dispersed in the PLLA-rich phase resulted in formation of pores in the blend films. Catalytic effect of PCL molecules on the hydrolysis of PLLA molecules in the continuous PLLA-rich phase caused a more rapid decrease in mechanical properties than that of the nonblended PLLA film as observed for the nonenzymatic hydrolysis in phosphate-buffered solution.

Comparison of the weight loss of blend films in biodegradation in soil with that of the nonenzymatic hydrolysis in phosphate-buffered solution revealed selective enzymatic degradation of PCL and an insignificant attack to PLLA in the blend films.

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