Melt-Processed Biodegradable Polyester Blends of Poly(L-lactic acid) and Poly(ε-caprolactone): Effects of Processing Conditions on Biodegradation

Hideto Tsuji,[1] Gen Horikawa,[1] Shinichi Itsuno[2]

[1]*Department of Ecological Engineering, Faculty of Engineering, Toyohashi University of Technology, Tempaku-cho, Toyohashi, Aichi 441-8580, Japan*
[2]*Department of Materials Engineering, Faculty of Engineering, Toyohashi University of Technology, Tempaku-cho, Toyohashi, Aichi 441-8580, Japan*

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ABSTRACT: Biodegradable polyester blends were prepared from poly(L-lactic acid) (PLLA) and poly(ε-caprolactone) (PCL) (50/50) by melt-blending, and the effects of processing conditions (shear rate, time, and strain) of melt-blending on proteinase-K- and lipase-catalyzed enzymatic degradability were investigated using gravimetry, differential scanning calorimetry, and scanning electron microscopy. The proteinase-K-catalyzed degradation rate of the blend films increased and leveled off with increasing the shear rate, time, or strain for melt-blending, except for the shortest shear time of 60 s. The optimal processing conditions of melt-blending giving the maximum rate of lipase-catalyzed degradation were 9.6×10^2 s^{-1} and 180 s, whereas a deviation from these conditions caused a reduction in lipase-catalyzed enzymatic degradation rate. At the highest shear rate of 2.2×10^3 s^{-1}, PCL-rich phase was continuous in the blend films, irrespective of the shear time (or shear strain), whereas PLLA-rich phase changed from dispersed to continuous by increasing the shear time (or shear strain). This study revealed that the biodegradability of PLLA/PCL blend materials can be manipulated by altering the processing conditions of melt-blending (shear rate, time, or strain) or the sizes and morphology of PLLA-rich and PCL-rich domains. The method reported in the present study can be utilized for controlling the biodegradability of other biodegradable polyester blends. J Appl Polym Sci 104: 831–841, 2007

Key words: biodegradable polyesters; blends; degradation; enzymes; shear

INTRODUCTION

The polymer blending of aliphatic polyesters is commercially advantageous for producing biodegradable materials with different physical properties and biodegradability. Among biodegradable polyester blends, those from glassy poly(L-lactic acid) (PLLA) or poly(DL-lactic acid) (PDLLA) with relatively low environmental degradability and rubbery poly(ε-caprolactone) (PCL) with relatively high environmental degradability have attracted much attention because of their wide variety of physical properties and biodegradability.[1–12] The effects of polymer blending ratio, molecular characteristics, compatibilizers, coupling agents, and preparation method and conditions of the blends on their morphology (phase structure), crystallization, thermal, mechanical, and drug release properties, and enzymatic and nonenzymatic degradation have been studied for PLLA (or PDLLA)/PCL blends.

With respect to the enzymatic degradation of PLLA (or PDLLA)/PCL blends, the effects of blending ratio,[13–16] compatibilizer,[17] and coupling agents[18] have been investigated. The following results have been disclosed: (1) Proteinase-K-catalyzed enzymatic degradation was enhanced in the presence of PCL for solution-cast blends,[15,16] whereas disturbed for melt-processed blends;[18] (2) The addition of poly(L-lactide-*co*-ε-caprolactone) as a compatibilizer between PLLA and PCL reduced lipase- or proteinase-K-catalyzed enzymatic degradation rate of solution-cast blends;[17] and (3) The coupling agents enhanced proteinase-K-catalyzed enzymatic degradation of the melt-processed blends.[18]

The purpose of this study was to develop an industrially versatile method for preparing biodegradable polyester blends having different biodegradability at a fixed polymer blending ratio. For this purpose, we prepared PLLA/PCL blends as model biodegradable polyester blends under various processing conditions of melt-blending, such as shear rate, time, and strain, at a fixed blending ratio of 50/50 (w/w), and investi-

Correspondence to: H. Tsuji (tsuji@eco.tut.ac.jp).

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gated the effects of processing conditions on proteinase-K- or lipase-catalyzed enzymatic degradation.

EXPERIMENTAL

Materials

PLLA pellets (radius of about 18 ± 3 mm) were kindly supplied by Unitika (Kyoto, Japan), while PCL pellets ($M_w = 6.5 \times 10^4$ g mol^{-1}, radius of about 19 ± 2 mm) were purchased from Sigma-Aldrich. The PLLA and PCL were purified by extraction with methanol, followed by drying *in vacuo* for at least 1 week. The blend films with thickness of about 2.5 mm were prepared by melt-blending of PLLA and PCL [PLLA/PCL (w/w) = 50/50] with a kneading extruder (Type 1172, Imoto Machinary, Kyoto, Japan). The melt-blending was carried out at 200°C and different shear rates (3.2×10^2, 9.6×10^2, and 2.2×10^3 s^{-1}) for various times (60, 180, and 600 s). After the melt-blending process, the blends were extruded and then compressed between two Teflon sheets to a thickness of 2.5 mm using Teflon spacers of the same thickness.

Enzymatic degradation

Proteinase-K-catalyzed enzymatic degradation of the films ($10 \times 10 \times 2.5$ mm^3, ~ 400 mg) was performed according to the procedure reported by Reeve et al.,[19] and modified by us.[16] In brief, each of the films was placed in a vial filled with 5 mL of 0.05*M* Tris-HCl-buffered solution (pH 8.6) containing 1.0 mg of sodium azide (Nacalai Tesque, Kyoto, Japan). Air on the surfaces of the films and in the gaps between PLLA and PCL-rich domains was removed under a reduced pressure for 3 min. Then each of the films was moved to a vial filled with 5 mL of Tris-HCl-buffered solution containing 1.0 mg of proteinase K (lyophilized powder, 80% protein; Sigma–Aldrich) and 1.0 mg of sodium azide. Proteinse K-catalyzed degradation of the films was performed at 37°C for periods up to 9 days in a rotary shaker.

The *Rhizopus arrhizus* lipase-catalyzed enzymatic degradation of the films ($10 \times 10 \times 2.5$ mm^3, ~ 400 mg) was performed according to the aforementioned procedure under the conditions reported by Pranamuda et al.,[20] and modified by us.[15] In brief, each of the films was placed in a vial filled with 20 mL of 0.02*M* phosphate-buffered solution (pH 7.0) containing 0.005 wt % of Plysurf A210G (Dai-Ichi Kogyo Seiyaku, Kyoto Japan). Air on the surfaces of the films and in the gaps between PLLA-rich and PCL-rich domains was removed under a reduced pressure for 3 min. Then each of the films was moved to a vial filled with 20 mL of 0.02*M* phosphate-buffered solution (pH 7.0) containing 2000 units of lipase [Type XI, *R. arrhizus*, suspension in 3.2*M* $(NH_4)_2SO_4$ and 10 m*M* potassium phosphate solution; Sigma–Aldrich] and 0.005 wt % of Plysurf A210G, which stabilizes the suspended state of the lipase. Lipase-catalyed degradation of the films was performed at 30°C for periods up to 9 days in a rotary shaker.

The enzymatically degraded films were rinsed thoroughly with distilled water at 4°C to stop further enzymatic degradation, followed by drying under a reduced pressure for at least 2 weeks. The distilled water used for preparing the Tris-HCl and phosphate-buffered solutions and rinsing the film was of HPLC grade (Nacalai Tesque).

Measurements and observation

The weight– and number–average molecular weights (M_w and M_n, respectively) of the purified polymers were evaluated in chloroform at 40°C by a Tosoh GPC system (refractive index monitor: RI-8020) with two TSK Gel columns (GMH_{XL}) using polystyrene standards. The molecular characteristics of the purified polymers are listed in Table I. The molecular structural changes of PLLA and PCL by melt-blending were determined from the 300 MHz ^{1}H NMR the and the 75.5 MHz ^{13}C NMR spectra obtained in deuterated chloroform (50 mg mL^{-1}) by a Varian Mercury 300 Spectrometer using tetramethylsilane as an internal standard.

The glass transition, cold crystallization, and melting temperatures (T_g, T_{cc}, and T_m, respectively), and

TABLE I
Molecular Characteristics of Polymers Used in This Study

Polymer	M_w (g mol^{-1})	M_w/M_n	$[\alpha]^{25}_{589}$[a] (deg dm^{-1} g^{-1} cm^3)	Reported δ[b] (MPa$^{1/2}$)
PLLA	2.4×10^5	1.6	−153	19.2–21.3[c]
PCL	6.6×10^4	1.5	–	19.0–20.5[d] 20.8[e]

[a] The specific optical rotation ($[\alpha]^{25}_{589}$) value was measured in chloroform in Ref. 21.
[b] Solubility parameter.
[c] The values reported for poly(DL-lactic acid) in Ref. 22.
[d] The values for PLLA reported in Ref. 23.
[e] The value reported in Ref. 24.

TABLE II
Physical Properties of Blend Films before and after Proteinase-K-catalyzed Enzymatic Degradation

Shear rate (s^{-1})	Shear time (s)	Shear strain[a]	Enzymatic degradation time (days)	M_w (10^5 g mol^{-1})	M_w/M_n	T_m(PCL)[b] (°C)	T_{cc}(PLLA)[c] (°C)	T_m(PLLA)[b] (°C)	X_c(PCL)[d] (%)	X_c(PLLA)[d] (%)
3.2×10^2	60	1.9×10^4	0	1.10	1.60	58.9	102.1	168.5	50.3	2.2
			9	1.09	1.71	62.1	96.7	168.2	77.2	4.0
	180	5.8×10^4	0	1.20	1.66	59.5	106.2	168.5	54.5	0.9
			9	1.12	1.95	62.4	106.7	168.5	85.7	5.0
	600	1.9×10^5	0	1.09	1.64	59.7	100.0	165.8	47.3	3.6
			9	0.87	1.79	61.7	100.5	166.0	57.0	0.4
9.6×10^2	60	5.8×10^4	0	1.31	1.53	56.9	99.8	168.4	36.5	1.2
			9	1.06	1.80	61.3	95.9	168.4	61.5	0.1
	180	1.7×10^5	0	1.06	1.73	59.5	101.1	168.3	58.3	1.9
			9	1.11	1.63	63.3	98.7	168.4	73.2	1.2
	600	5.8×10^5	0	1.05	1.68	60.7	97.9	165.9	46.2	0.6
			9	1.03	1.77	62.7	94.9	165.5	59.7	3.4
2.2×10^3	60	1.3×10^5	0	1.13	1.69	58.0	97.8	168.2	42.4	3.6
			9	1.03	1.79	62.0	95.0	168.2	56.8	3.4
	180	4.0×10^5	0	1.04	1.91	60.0	103.9	168.9	49.9	5.3
			9	0.93	1.93	62.4	98.8	168.4	67.5	7.6

[a] The shear strain is the product of shear rate multiplied by shear time.
[b] T_m(PCL) and T_m(PLLA) are melting temperatures of PCL and PLLA respectively.
[c] T_{cc}(PLLA) is cold crystallization of PLLA.
[d] X_c(PCL) and X_c(PLLA) are crystallinity values of PCL and PLLA respectively.

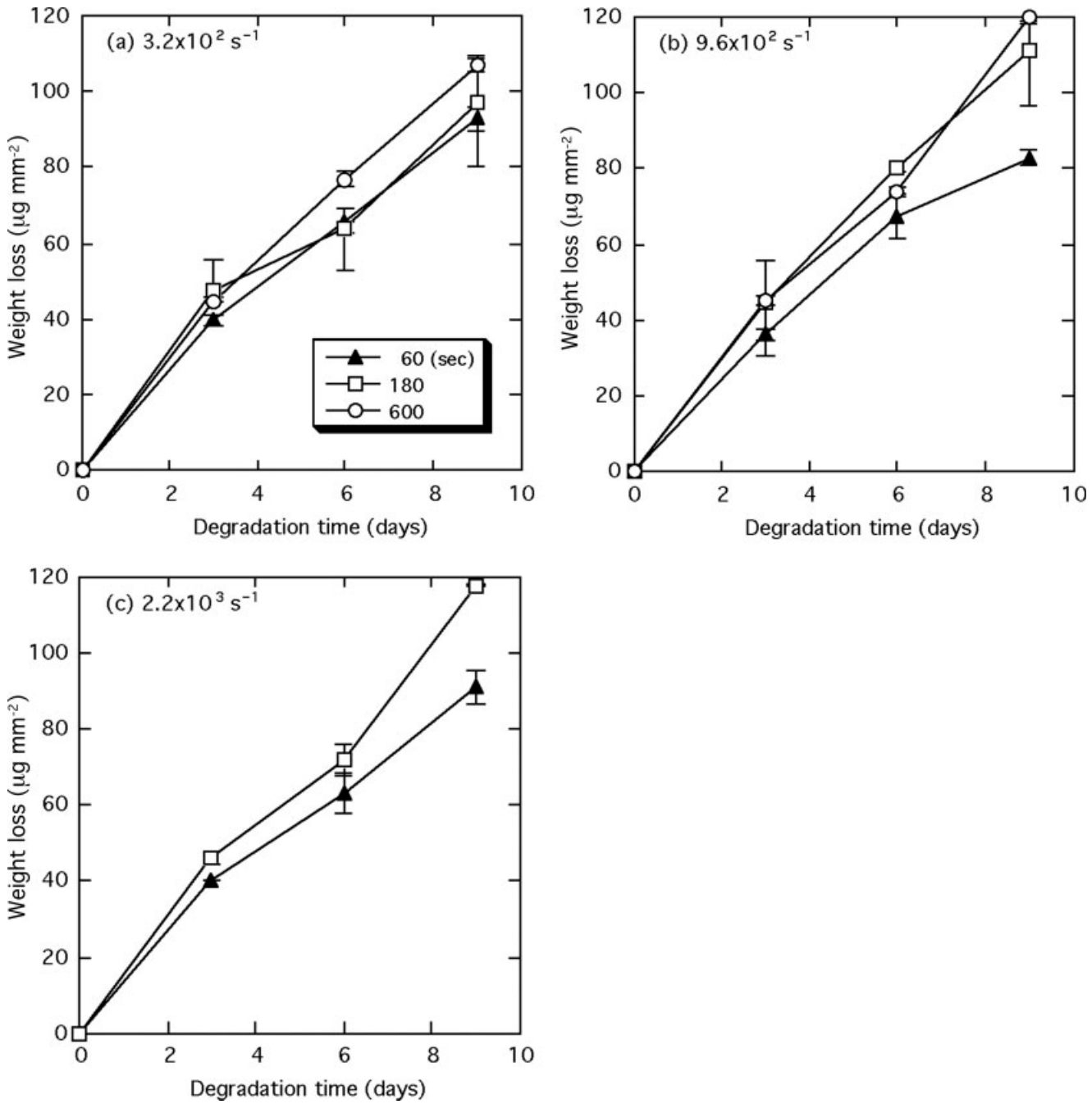

Figure 1 Weight loss of blend films prepared at shear rates of 3.2×10^2 s^{-1} (a), 9.6×10^2 s^{-1} (b), and 2.2×10^3 s^{-1} (c) in the presence of proteinse K as a function of degradation time.

enthalpies of cold crystallization and melting (ΔH_{cc} and ΔH_m, respectively) of the films were determined by a Shimadzu DSC-50 differential scanning calorimeter (DSC) equipped with a cooling cover (LTC-50). The films (sample weight of $\sim$ 3 mg) were heated from 10 to 180°C at a rate of 10°C min^{-1} under a nitrogen gas flow at the rate of 50 mL min^{-1}. DSC results were calibrated using benzophenone, indium, and tin as standards. The crystallinity values of PLLA [X_c(PLLA)] and PCL [X_c(PCL)] in a film [PLLA/PCL (w/w) = 50/50] were calculated using the following equations under the assumption that the endothermic peak observed around 60°C was ascribed to the melting of PCL:

$$X_c(\text{PLLA})(\%) = 100[\Delta H_m(\text{PLLA}) + \Delta H_{cc}(\text{PLLA})]/(0.5 \times 135) \quad (1)$$

$$X_c(\text{PCL})(\%) = 100\Delta H_m(\text{PCL})/(0.5 \times 142) \quad (2)$$

TABLE III
Weight Loss Values of Blend Films after Proteinase-K- and *Rhizopus arrhizus* Lipase-Catalyzed Enzymatic Degradation for 9 Days

	Conditions for film preparation			Weight loss	
Enzyme	Shear rate (s^{-1})	Shear time (s)	Shear strain[a]	Percentage weight loss (%)	Weight loss per unit surface area (μg mm^{-2})
Proteinase K	3.2×10^2	60	1.9×10^4	10.3	92.9
		180	5.8×10^4	9.7	97.2
		600	1.9×10^5	11.3	107.3
	9.6×10^2	60	5.8×10^4	8.7	82.7
		180	1.7×10^5	12.3	111.4
		600	5.8×10^5	12.4	119.9
	2.2×10^3	60	1.3×10^5	9.7	91.0
		180	4.0×10^5	12.7	117.7
Rhizopus arrhizus lipase	3.2×10^2	60	1.9×10^4	0.82	8.9
		180	5.8×10^4	1.15	11.1
		600	1.9×10^5	0.69	6.1
	9.6×10^2	60	5.8×10^4	1.12	10.5
		180	1.7×10^5	1.46	15.0
		600	5.8×10^5	0.79	7.4
	2.2×10^3	60	1.3×10^5	1.06	7.6
		180	4.0×10^5	1.12	9.9

[a] The shear strain is the product of shear rate multiplied by shear time.

where ΔH_{cc}(PLLA), ΔH_m(PLLA), and ΔH_m(PCL) (joule per gram of polymer) are ΔH_{cc} of PLLA at around 100°C, ΔH_m of PLLA at around 170°C, and ΔH_m of PCL at around 60°C, respectively; 135 (J g^{-1} of PLLA) and 142 (J g^{-1} of PCL) are the ΔH_m of PLLA and PCL crystals having infinite crystal thickness, respectively;[25,26] and 0.5 is the weight fraction of PLLA or PCL in the films. The morphology of the films was studied with a Hitachi (Tokyo, Japan) S-2300 scanning electron microscope (SEM). The films for SEM observation were coated with carbon to a thickness of about 20 nm.

In the presence of enzymes such as proteinase K and *R. arrhizus* lipase, it is known that PLLA and PCL specimens are degraded via a surface erosion mechanism.[15,16,17,19] Therefore, the weight loss per unit surface area was calculated by the following equation:

$$\text{Weight loss } (\mu g\ mm^{-2}) = (W_{before} - W_{after})/S_{before} \quad (3)$$

where W_{before} and W_{after} are the film weights before and after degradation, respectively, and S_{before} is the surface area of the film before degradation.

RESULTS AND DISCUSSION

Effects of melt-blending process on molecular characteristics and thermal properties

Table II summarizes the molecular characteristics and thermal properties of the blend films before and after proteinase-K-catalyzed enzymatic degradation. Here, the shear strain was the product of shear rate multiplied by shear time. Before degradation (i.e., after thermal treatment), the M_n values of films are in the range of (1.1–1.3) $\times 10^5$ g mol^{-1} and did not explicitly depend on the shear rate and time for melt-blending. Moreover, all the ^1H NMR and ^{13}C NMR peaks showed no significant change after the melt-blending process (data not shown here). These findings revealed that the melt-blending process had insignificant effects on molecular characteristics and structures. Furthermore, the X_c(PLLA) values of films were very close to 0, meaning that most of the PLLA-rich phase in films was composed of amorphous regions. Therefore, proteinase-K-catalyzed degradation was affected by the difference in morphology and sizes of the PLLA-rich and PCL-rich domains caused by altering the melt-blending conditions. In contrast, the X_c(PCL) values of films ranged from 37 to 58%. Therefore, in the lipase-catalyzed degradation depends on the X_c(PCL) as well as the morphology and sizes of the PLLA-rich and PCL-rich domains.

Proteinase-K-catalyzed enzymatic degradation

Figure 1 shows the weight loss of blend films in the presence of proteinase K as a function of degradation time. Here, only PLLA chains are enzymatically degraded in the presence of proteinase K.[16] Also, the weight loss values at 9 days are tabulated in Table III. The weight loss of films took place without any induction periods, irrespective of the shear rate and time for melt-blending. To investigate the effects of processing conditions of melt-blending, the weight loss

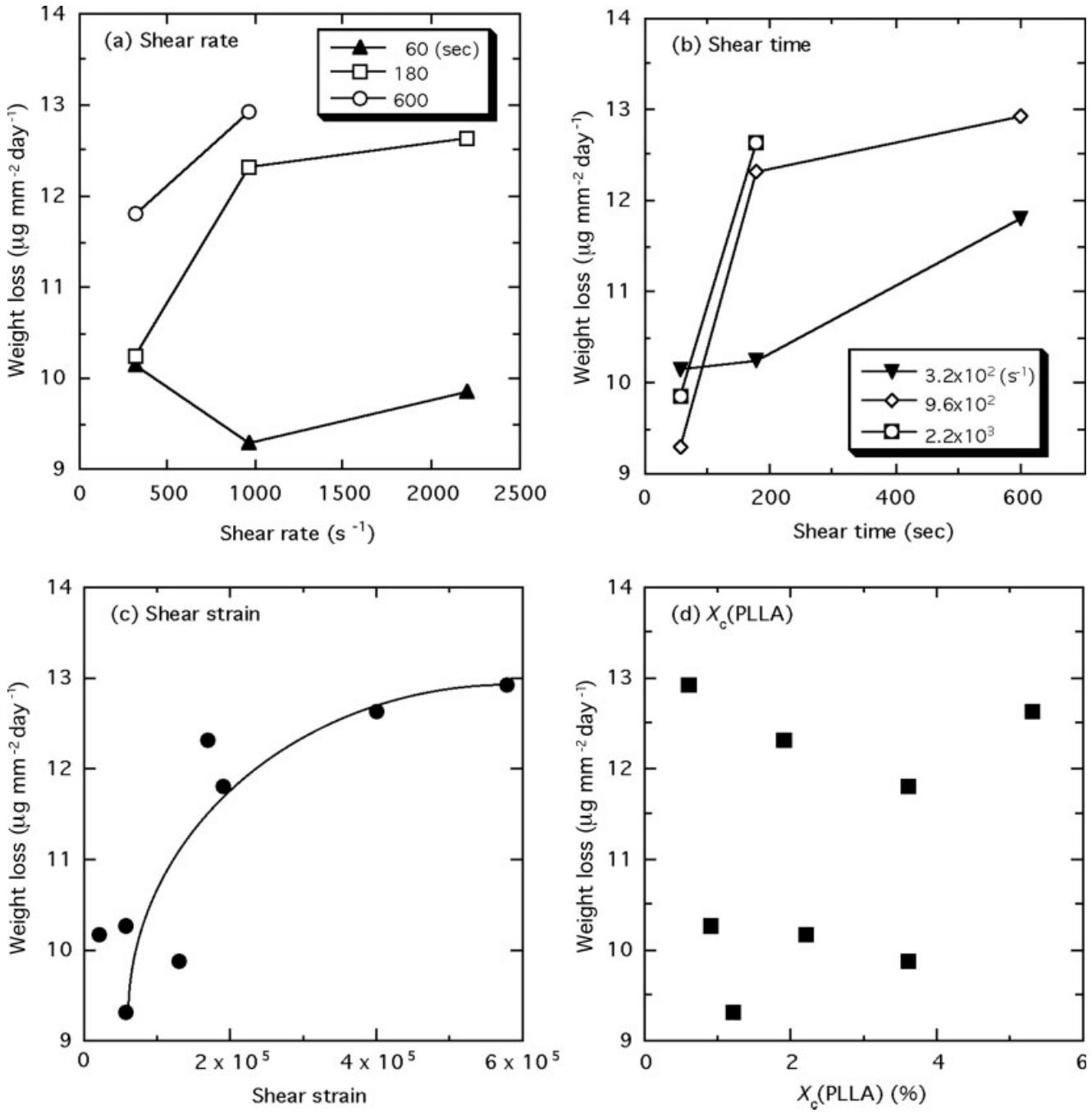

Figure 2 Weight loss rate of the blend films in the presence of proteinase K as a function of shear rate (a), time (b), strain (c), and crystallinity of PLLA [X_c(PLLA)] (d).

rate was estimated from the averaged slope of the weight loss values in Figure 1, and was plotted in Figure 2 as a function of shear rate and time, and strain. In this figure, the effects of X_c(PLLA) are shown for reference. As seen, the weight loss rate increased monotonically and leveled off around 12.5 μg mm^{-2} day^{-1} with the shear rate, time, or strain, except for 60 s in Figure 2(a). This trend indicates that the shear time and strain rather than the shear rate are crucial parameters to determine protainase K-catalyzed enzymatic degradation rate. However, the degradation rate has no explicit dependence on X_c(PLLA).

Figure 3 shows the DSC thermograms of blend films prepared at a shear rate of 9.6 $\times$ 10^2 s^{-1} for different shear times before enzymatic degradation and after enzymatic degradation for 9 days. As can be seen, the melting peak area and temperature of PCL at around 60°C were increased by enzymatic degradation. These caused significant increment in X_c(PCL) and T_m(PCL) after degradation (Table II). The increase

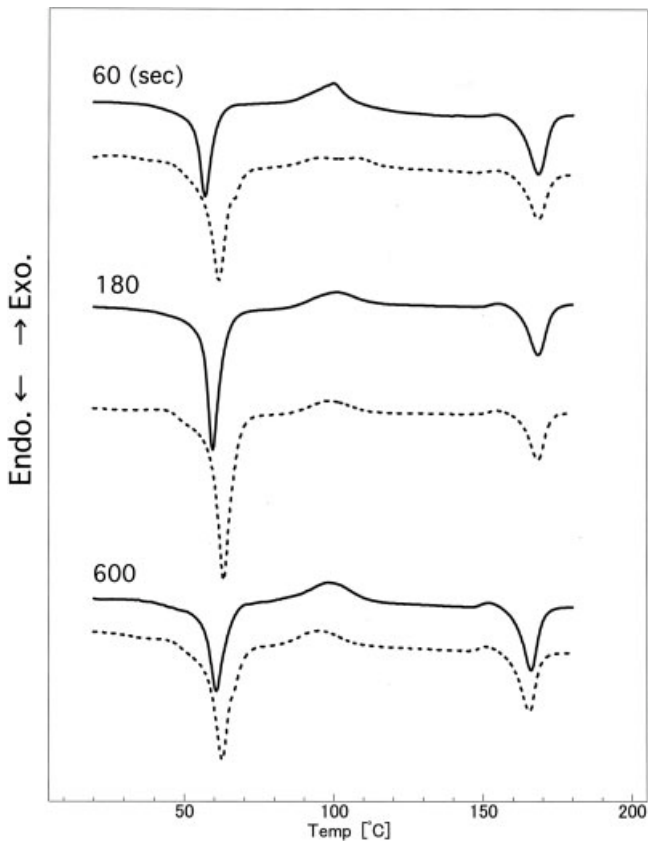

Figure 3 DSC thermograms of the blend films prepared at a shear rate of 9.6 × 10^2 s^{-1} for different shear times before degradation and after proteinase-K-catalyzed enzymatic degradation for 9 days.

in X_c(PCL) should have been caused by the enzymatic removal of PLLA chains or the crystallization of PCL. The increase in T_m(PCL) means an increase in crystalline thickness or a decrease in lattice disorder. Such crystalline growth can be caused by the increased chain mobility of PCL at an elevated temperature (37°C) in the presence of water as a plasticizer. This also agrees with the increase in X_c(PCL) by enzymatic degradation. In contrast, no significant change was noticed for PLLA crystallization and melting peaks after degradation, excluding a slight shift of crystallization peak to a lower temperature. Such shift can be explained by the nuclei formation of PLLA crystallites due to the elevated temperature and the presence of water during enzymatic degradation.

Figures 4(a) and 4(b) are SEM photomicrographs of the blend films prepared at a shear rate of 2.2 × 10^3 s^{-1} for 60 and 180 s before enzymatic degradation. The surface of the films was smooth before enzymatic degadradation. Figures 5(a) and 5(b) are SEM photomicrographs of the blend films enzymatically degraded in the presence of proteinase K for 9 days. As can be seen, the area eroded by enzymatic degradation was larger for the film melt-blended for 60 s than for that melt-blended for 180 s. This confirms that the proteinase-K-catalyzed enzymatic degradation rate increases with shear time and strain. In our previous study, a solution-casting method was used for the preparation of a blend film [PLLA/PCL (w/w) = 50/50].[16] In the reported case, the formation of pores with maximum size of 70 μm due to the removal of PLLA-rich phase was observed on the surface of the films after proteinase-K-catalyzed degradation for 5 days. The domain size of the PLLA-rich phase in the blend films before enzymatic degradation was larger for the solution-blended film than for the melt-blended film (domain size >5 μm). The higher mobility of PLLA and PCL chains in the presence of solvent molecules and the absence of shear force may have enhanced the formation of large-sized PLLA-rich phase during the solution-casting process.

In our previous study, we revealed that the proteinase-K-catalyzed degradation rate of PLLA was elevated by solution-blending with PCL.[16,17] This result strongly suggests that proteinase K can diffuse into the gaps between PLLA-rich and PCL-rich domains and the enzymatic degradation takes place not only on the film surface but also on the surface of the

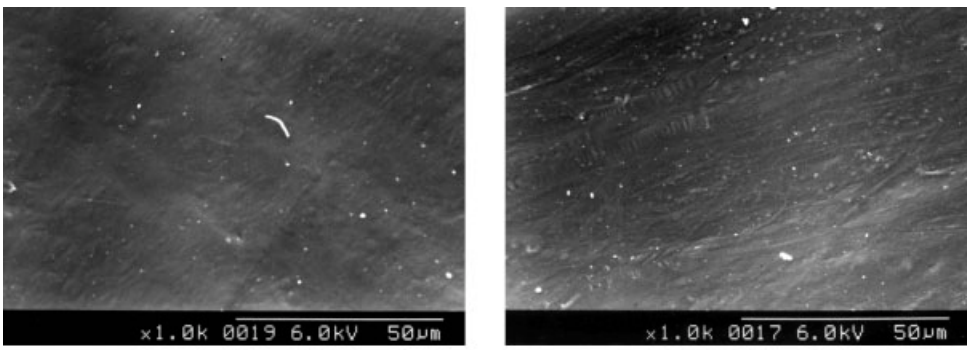

Figure 4 SEM photomicrographs of the blend films prepared at a shear rate of 2.2 × 10^3 s^{-1} for 60 s (a) and 180 s (b) before enzymatic degradation.

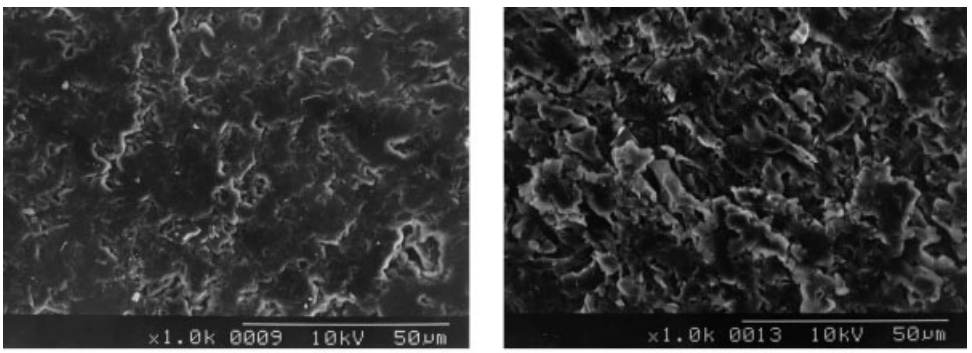

Figure 5 SEM photomicrographs of the blend films prepared at a shear rate of 2.2×10^3 s^{-1} for 60 s (a) and 180 s (b) and enzymatically degraded in the presence of proteinase K for 9 days.

PLLA-rich domains contacting PCL-rich domains inside the film. We have ascribed the rapid degradation of PLLA in the solution-cast blends rather than in a pure state to the larger degradable surface area per unit mass in the blends than that in the pure PLLA film. Therefore, Figures 1–4 show that the degradable surface area increases with the increasing the shear rate, time, or strain. In other words, the domain size of PLLA-rich phase decreases with increasing the shear rate, time, or strain. The results in this section strongly suggest that the proteinase-K-catalyzed degradation rate of PLLA/PCL blend films can be manipulated by the processing conditions for melt-blending.

Lipase-catalyzed enzymatic degradation

Figure 6 shows the weight loss of blend films in the presence of *R. arrhizus* lipase as a function of degradation time. Also, the weight loss values at 9 days are summarized in Table III. Here, only PCL chains are enzymatically degraded in the presence of *R. arrhizus* lipase.[16] Similar to the proteinase-K-catalyzed degradation, the weight loss rate was estimated from the averaged slope of the weight loss values in Figure 6, and was plotted in Figure 7 as a function of the shear rate, time, and strain. In this figure, the effects of X_c(PCL) are shown for reference. It is interesting to note that in marked contrast to the results for proteinase-K-catalyzed degradation, the lipase-catalyzed degradation rate reaches a maximum at 9.6×10^2 s^{-1} [Fig. 7(a)] and 180 s [Fig. 7(b)]. A deviation from these conditions reduces the lipase-catalyzed degradation rate. It should be noted that the shear strain for melt-blending has no explicit dependence on the lipase-catalyzed degradation rate [Fig. 7(c)]. This is also in marked contrast with the result for proteinase-K-catalyzed degradation, wherein the rate increased monotonically with the shear strain. The degradation rate is significantly decreased by increasing the X_c(PCL). Therefore, it is difficult to specify which parameter among shear rate, time, or X_c(PCL) is dominant to determine the degradation rate. For the blend films after lipase-catalyzed degradation, we did not carry out the DSC measurements, because the actual percentage weight loss values were below 2% (Table III), which should have caused very small changes in thermal properties.

Figures 8(a) and (b) are the SEM photomicrographs of the blend films prepared at a shear rate of 2.2×10^3 s^{-1} for 60 s and 180 s, respectively, and enzymatically degraded in the presence of *R. arrhizus* lipase. Numerous particles with diameters of 0.5–10 μm were observed on the surface of the film prepared with the shear time of 60 s. These particles are attributable to PLLA-rich phase. Therefore, the presence of such particles indicates that the PLLA-rich phase of the films was dispersed in the continuous PCL-rich phase before enzymatic degradation. On the other hand, no such particle was noticed for the blend films prepared with the shear time of 180 s. This reveals that the PLLA-rich phase as well as PCL-rich phase were continuous in the film. The disturbance effect of the formation of continuous PLLA-rich phase at the increased shear time may have overcome the enhancement effect of decreased domain size of PCL-rich phase. The latter enhancement effect is caused by an increase in degradable surface area of PCL-rich phase. The morphological change of PLLA from dispersed to continuous as well as the reduction in PLLA domain size, which were caused by the increase in shear time (or shear strain), must have enhanced the proteinase-K-catalyzed degradation of PLLA-rich phase. The PCL-rich and PLLA-rich domains in PLLA/PCL blends have been reported to be continuous and dispersed, respectively, at the blending ratio of 50/50 (w/w) when the blends were prepared by solution-casting.[14–16] The results in this section also indicate that the lipase-catalyzed degradation rate of PLLA/

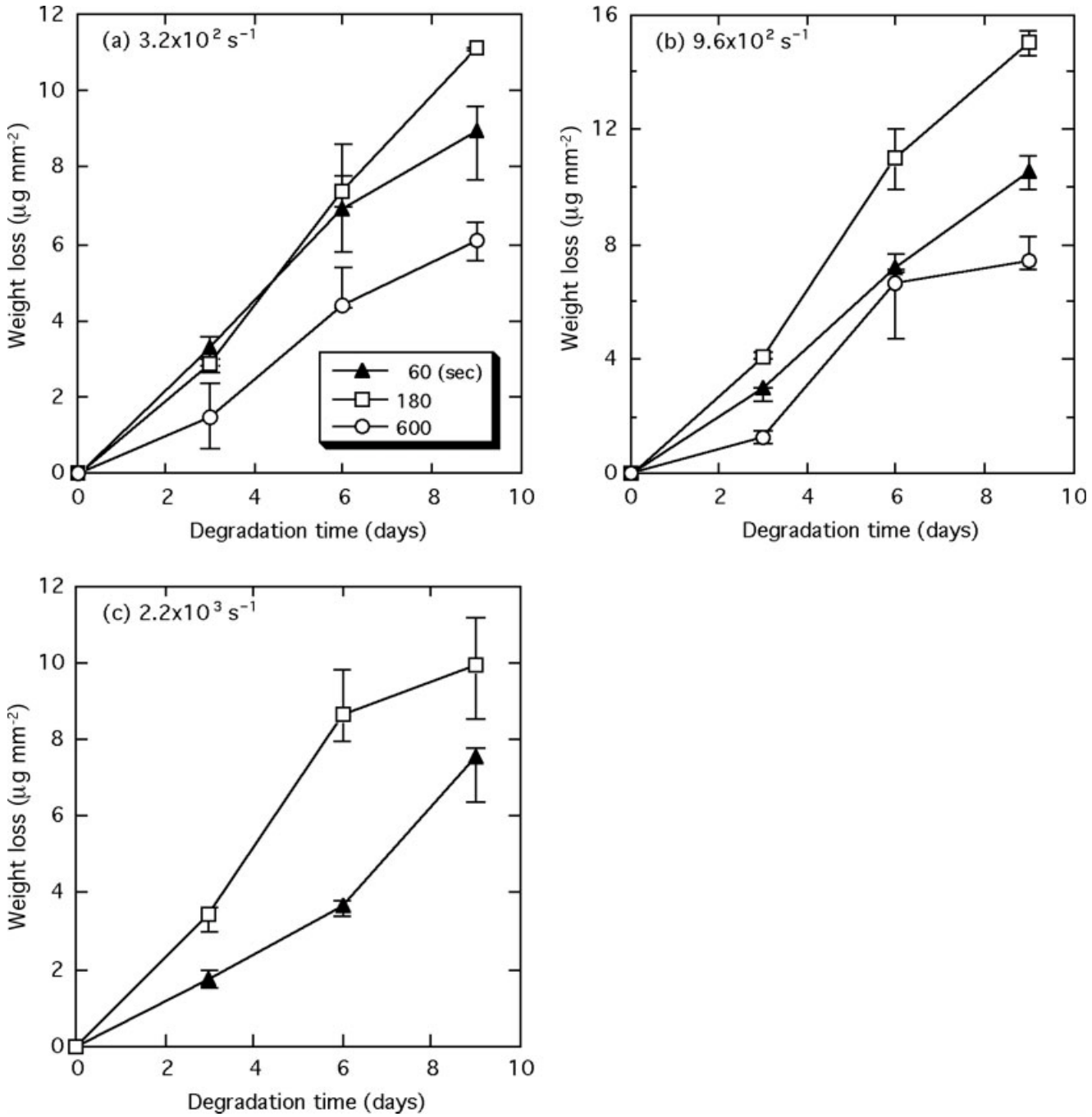

Figure 6 Weight loss of blend films prepared at shear rates of 3.2×10^2 s^{-1} (a), 9.6×10^2 s^{-1} (b), and 2.2×10^3 s^{-1} (c) in the presence of *Rhizopus arrhizus* lipase as a function of degradation time.

PCL blend films is controllable by altering the processing conditions for melt-blending. However, in the case of lipase-catalyzed enzymatic degradation the processing conditions must be accurately adjusted to control the biodegradability.

CONCLUSIONS

The following conclusions can be derived from the aforementioned experimental results in regard to the effects of processing conditions of melt-blending on enzymatic degradation of the PLLA/PCL (50/50) blend films:

1. The proteinase-K-catalyzed degradation rate of the blend films increased and leveled off by increasing the shear rate, time, or strain for melt-blending, except for the shortest shear time of 60 s.

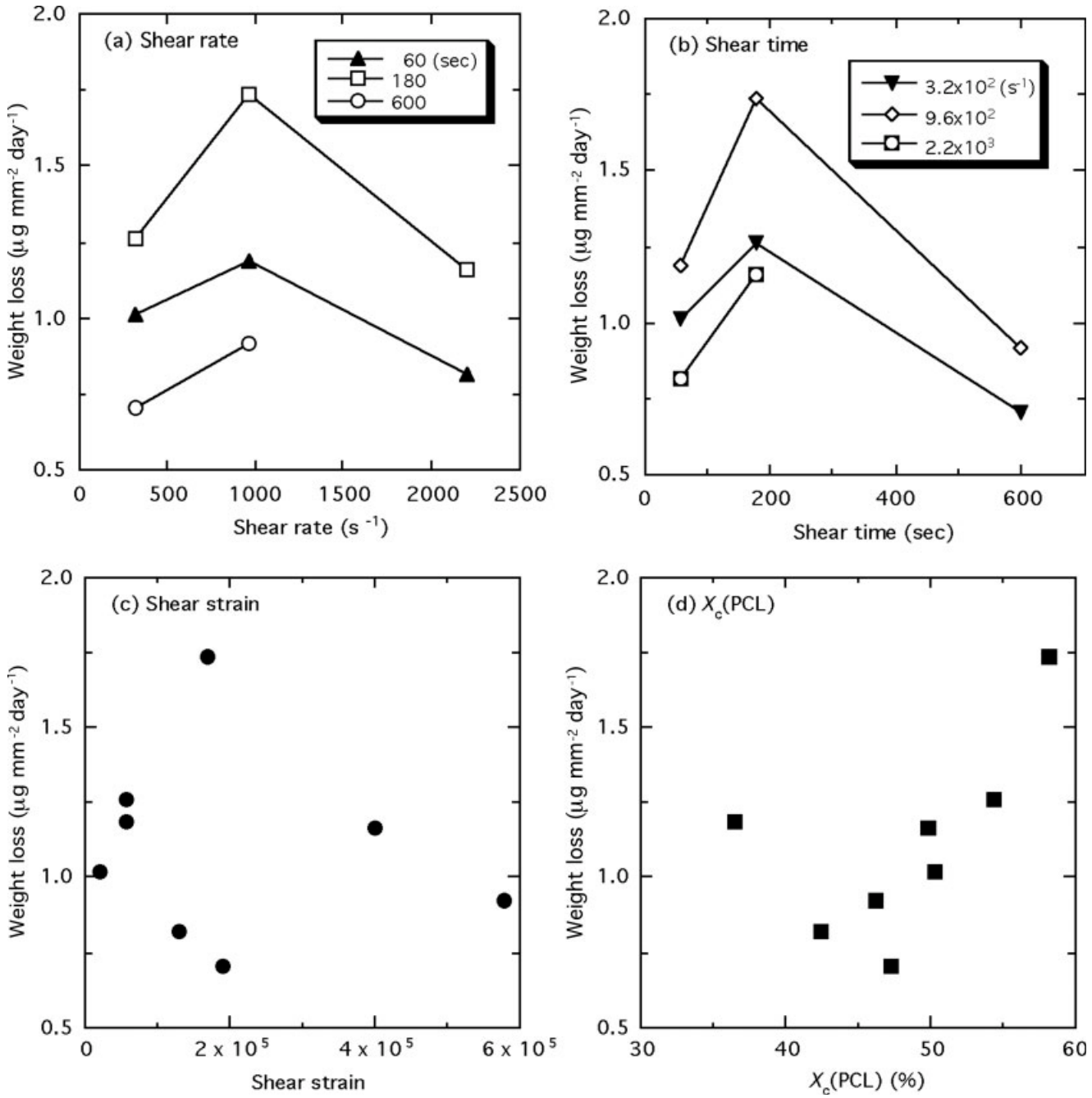

Figure 7 Weight loss rate of the blend films in the presence of *Rhizopus arrhizus* lipase as a function of shear rate (a), time (b), strain (c), and crystallinity of PCL [X_c(PCL)] (d).

2. The optimal processing conditions of melt-blending giving the maximum rate of lipase-catalyzed degradation were 9.6×10^2 s^{-1} and 180 s, and a deviation from these conditions caused a reduction in lipase-catalyzed degradation rate.
3. At the highest shear rate of 2.2×10^3 s^{-1}, PCL-rich phase was continuous in the blend films, irrespective of the shear time (or shear strain), whereas PLLA-rich phase changed from dispersed to continuous by increasing the shear time (or the shear strain).
4. The biodegradability of PLLA/PCL blend materials can be manipulated by altering the processing conditions of melt-blending (shear rate, time, or strain) or the sizes and morphology (dispersed or continuous) of PLLA-rich and PCL-rich domains. The method discussed in the present study can be utilized for controlling the biodegradability of other biodegradable polyester blends.

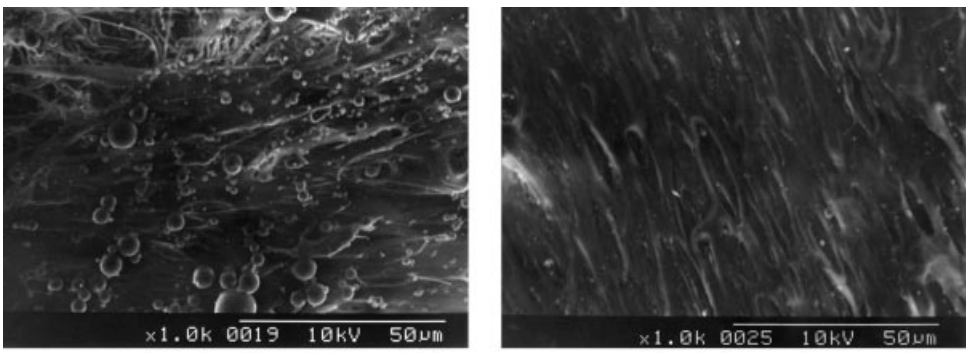

Figure 8 SEM photomicrographs of the blend films prepared at shear rate of 2.2×10^3 s^{-1} for 60 s (a) and 180 s (b) and enzymatically degraded in the presence of *Rhizopus arrhizus* lipase for 9 days.

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References

1. Kharas, G. B.; Sanchez-Riera, F.; Severson, D. K. In Plastics from Microbes; Mobley, D. P., Ed.; Hanser: New York, 1994; p 93.
2. Doi, Y.; Fukuda, K., Eds. Biodegradable Plastics and Polymers; Elsevier: Amsterdam, The Netherlands, 1994.
3. Coombes, A. G. A.; Meikle, M. C. Clin Mater 1994, 17, 35.
4. Vert, M.; Schwarch, G.; Coudane, J. J Macromol Sci Pure Appl Chem 1995, A32, 787.
5. Scott, G.; Gilead, D., Eds. Biodegradable Polymers. Principles and Applications; Chapman & Hall: London, 1995.
6. Hartmann, M. H. In Biopolymers from Renewable Resources; Kaplan, D. L., Ed.; Springer: Berlin, Germany, 1998; p 367.
7. Ikada, Y.; Tsuji, H. Macromol Rapid Commun 2000, 21, 117.
8. Albertsson, A.-C., Ed. Degradable Aliphatic Polyesters (Adv in Polymer Science, Vol. 157); Springer: Berlin, Germany, 2002.
9. Södergård, A.; Stolt, M. Prog Polym Sci 2002, 27, 1123.
10. Mochizuki, M. In Polyesters III. Biopolymers. Biology, Chemistry, Biotechnology, Applications, Vol. 4, Doi, Y., Steinbüchel, A., Eds; Wiley-VCH: Weinheim, Germany, 2002; pp 1–23, .
11. Tsuji, H. In Polyesters III. Biopolymers. Biology, Chemistry, Biotechnology, Applications, Vol. 4, Doi, Y., Steinbüchel, A., Eds.; Wiley-VCH: Weinheim, Germany, 2002. p 129.
12. Auras, R.; Harte, B.; Selke, S. Macromol Biosci 2004, 4, 835.
13. Gan, Z.; Yu, D.; Zhong, Z.; Liang, Q.; Jing, X. Polymer 1999, 40, 2859.
14. Liu, L.; Li, S.; Garreau, H.; Vert, M. Biomacromolecules 2000, 1, 350.
15. Tsuji, H.; Ishizaka, T. Int J Biol Macromol 2001, 29, 83.
16. Tsuji, H.; Ishizaka, T. Macromol Biosci 2001, 1, 59.
17. Tsuji, H.; Yamada, T. J Appl Polym Sci 2003, 87, 412.
18. Wang, L.; Ma, W.; Gross, R. A.; McCarthy, S. P. Polym Degrad Stab 1998, 59, 161.
19. Reeve, M. S.; McCarthy, S. P.; Downey, M. J.; Gross, R. A. Macromolecules 1994, 27, 825.
20. Pranamuda, H.; Tokiwa, Y.; Tanaka, H. J Environ Polym Degrad 1996, 4, 1.
21. Tsuji, H.; Tezuka, Y. Macromol Biosci 2005, 5, 135.
22. Brandrup, J.; Immergut, E. H.; Grulke, E. A.; Abe, A.; Bloch, D. R., Eds. Polymer Handbook, 4th ed.; Wiley: NewYork, 1999.
23. Tsuji, H.; Sumida, K. J Appl Polym Sci 2001, 79, 1582.
24. Cha, Y.; Pitt, C. G. Biomaterials 1990, 11, 108.
25. Miyata, T.; Masuko, T. Polymer 1998, 39, 5515.
26. Crescenzi, V.; Manzini, G.; Calzolari, G.; Borri, C. Eur Polym Mater 1972, 8, 449.