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Study on Improvement of Poly(L-lactic acid) by Blending of Poly(ε -Caprolactone)

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Abstract: Poly(L-lactic acid) (PLA) was blended with poly(ε -Caprolactone) (PCL) using a single-screw extruder in order to modify poor characteristic of these polymers. Furthermore, when the polymer was blended, the copolymer (LA-CL copolymer) consisted of L-lactide (L-LA) and ε -caprolactone (ε -CL) was used as a compatibilizer. The biodegradability, mechanical properties, and surface morphology of the extruded fibers and films were determined. For the PLA/PCL blend systems, from the enzymatic degradation test, we found following results. There was a vast difference in the weight loss of pure PCL samples and the PLA/PCL=20/80 blend and the residual weight ratio decreased with an increase in PCL content. This fact suggested that Lipase (Rizopus delemar) was selectively degraded PCL, which has a flexibility, more alternatively than PLA, which has a rigidity. Moreover, the same tendency was also seen with the blend films. From the result of tensile test, we found that the maximum strength increased with an increase in PLA content with some exceptions. SEM photographs showed that the various pattern of degradation was observed in the PLA/PCL blend systems. For example, The formation of fibril and exfoliation of the surface were observed.
Key words: Blending, Improvement, Poly(L-lactic acid), Poly(ε-Caprolactone)

1. INTRODUCTION

Recently, aliphatic polyesters such as poly(L-lactic acid) (PLA), poly(ε -Caprolactone) (PCL), poly (Butylenesuccinate) (PBS) and so on have been noticed because of their bio-degradability. However, these polymers do not have enough properties for practical application. For example, PLA is too rigid and brittle, PCL has too low melting temperature and PBS is too flexible. Then, we tried to improve these disadvantages by blending each other.

Concretely, in our laboratory, PLA was blended with PCL or PBS using a single-screw extruder in order to modify poor characteristic of these polymers. Furthermore, when the polymer was blended, the copolymer (LA-CL block copolymer) consisted of L-lactide (L-LA) and ε -caprolactone (ε -CL) was used as a compatibilizer. And then, we could spin the blend fibers and prepare the blend films of PLA/PCL and PLA/PBS having uniform thickness [1], [2].

In this paper, the enzymatic degradation test by lipase (Rhizopus delemar), which degrades PCL selectively, of the PLA/PCL blend fibers were performed and characterized their enzymatic degradable properties. Moreover, the enzymatic degradable property and the mechanical property of the PLA/PCL blend films were also characterized.

2. EXPERIMENTAL

2.1. Materials

PLA (LACEA H-100), PCL (Celgreen P-H7), were purchased from Mitsui Chemicals, Inc. and DAICEL CHEMICAL INDUSTRIES, LTD. respectively and were used as received. Their molecular weights of were determined by GPC as shown in Table I.

The copolymer (LA-CL block copolymer) consisted of L-LA and ε -CL was synthesized previously at our laboratory and used as a compatibilizer [1].

2.2. Preparation of blends

The PLA/PCL blend fibers were prepared using a melt-spinning machine at 180~200℃. The PLA/PCL blend films were prepared using a single -screw extruder at 180~200 ℃ . Simultaneously, the compatibilizer (1wt% of total polymer) was added to the blends. PLA/PCL blending ratios were 100/0, 80/20, 60/40, 50/50, 40/60, 20/80, and 0/100 by weight.

2.3. Enzymatic degradation test

In the case of the PLA/PCL blend fibers, the enzymatic degradation of the blends was carried out at 37℃ in a 5ml of 0.05M acetate buffer solution (= pH5.6) containing 7mg of lipase {*Rhizopus delemar* (SEIKAGAKU Co.)} and 1.75ml of 0.1M$CaCl_2$ solution. The PLA/PCL blend fibers with an initial weight about 20 (100/0) or 50mg and length 50mm were placed in a test tube containing the buffer solution. The test tube was incubated at 37℃ in a water bath for a fixed interval. The fiber washed with distilled water and then dried to constant weight. Simultaneously, pH of the buffer solution was also measured using pH meter (HORIBA, Ltd. Twin pH).

Table I Molecular weights of PLA and PCL.*

Polymer	$M_n(\times10^{-4})$	$M_w(\times10^{-4})$	M_w/M_n
PLA	9.8	17.5	1.8
PCL	7.0	11.9	1.7

*Determined by G.P.C.

Moreover, as a control run, the hydrolysis of PLA/PCL blend fibers was carried out at 37℃ in a 5ml of 0.05M acetate buffer solution (= pH5.6). The following procedures were the same as the procedure described previously.

In the case of the PLA/PCL blend films, the enzymatic degradation of the blends was carried out at 37℃ in a 10ml of 0.05M acetate buffer solution (= pH5.6) containing 5mg lipase (*Rhizopus delemar*) and 1.0ml of 0.1M$CaCl_2$ solution. The PLA/PCL blend films with an initial weight about 150 (100/0) or 300mg and dimensions 10mm×70mm were placed in a test tube containing the buffer solution. The test tube was incubated at 37℃ in a water bath for a fixed time interval. The buffer solution was changed every 2weeks to restore the original level of enzymatic activity. The film washed with distilled water and then dried to constant weight.

2.4. Measurement

Thermal properties of the blends were measured by DSC analysis using SHIMADZU DT-30DSC instrument. The blend fibers were heated from 25℃ to 200℃ at a rate of 10℃min^{-1} for 9~10mg sample.

The number and weight average molecular weight (respectively, M_n and M_w) and molecular weight distribution (M_w/M_n) were determined by gel permeation chromatography (GPC) using a TOSOH-8020 instrument and chloroform as an eluent. The GPC system was calibrated with the polystyrene standard.

Surface and cross-sectional morphologies of the blends before and after enzymatic biodegradation were observed by scanning electron microscopy (SEM) using a HITACHI S-4300 Scanning Electron Microscope Type G. The electron gun voltage was 2~15kV. The samples were coated with gold before observation.

The tensile tests were done on a TMI UTM-3 tensile testing machine according to JIS K7161. The mechanical properties of blend films were measured using the tester at 20℃ with at a cross-head speed of 20mm min^{-1}.

3. RESULTS AND DISCUSSION

3.1. Thermal properties of the PLA/PCL blend fibers

The influence of composition on thermal properties of the PLA /PCL blend fiber were studied using DSC.

The DSC thermograms of six samples (excluding plain PCL) show two endothermic peaks and one exothermic peak when heated from 25℃ to 200℃. The endothermic peak at 59-63℃ represents the fusion of the PCL phase or the glass transition of the PLA phase. And the endothermic peak at 159-164℃ represents the fusion of the PLA phase. The exothermic peak represents the crystallization of the PLA phase. These results are shown in Table II. The crystallization temperature of the PLA phase decreased with an increase in the PCL content. It is because the crystallization of the PLA component was promoted by the molecular motion of the fusion of the PCL component. This was due to a micro-phase separation in this blend system. However, no change of $T_{m,PLA}$ and $T_{m,PCL}$ showed that they were immiscible each other.

3.2. Enzymatic degradation of the PLA/PCL blend fibers

Residual weight ratio of the blend fibers was obtained according to the following equation:

$$\text{Residual weight ratio\%} = W_t/W_0 \quad (1)$$

where W_0 is the initial weight, and W_t is the dry weight of the specimens after the enzymatic degradation. Residual weight ratio data of the seven samples after the enzymatic degradation are shown in Figure 1. For PLA and PCL homopolymer, only the PCL fiber showed complete degradation within 7 days and the PLA fiber did not undergo any change in weight. Moreover, there was a vast difference in the weight loss of the PCL fiber and the PLA/PCL=20/80 blend and the residual weight ratio decreased with an increase in PCL content.

On the other hand, residual weight ratio data of the seven samples after the hydrolysis are shown in Figure 2. All samples did not undergo any change in weight. This result suggests that these samples were not hydrolyzed and that enzymatic degradation predominantly occurred.

3.3. Enzymatic degradation of the PLA/PCL blend films

Weight loss of the blend films was obtained according to the following equation:

$$\text{Weight loss} = (W_0 - W_t)/S \quad (2)$$

where W_0 is the initial weight, W_t is the dry weight of the specimens after the enzymatic degradation, and S is the surface area of the specimens. Weight loss data of seven samples are shown in Figure 3. The behaviors of blend films were the almost same as blend fibers as shown in section 3.1. These results showed that Lipase was selectively degraded PCL, which has more flexibility than that of PLA.

Table II Thermal properties of the PLA/PCL blend fiber.

PLA/PCL	T_mPCL*1	T_gPLA*2	T_cPLA*3	T_mPLA*4
	℃	℃	℃	℃
100/0	–	63	110	159~160
80/20	59	–	92~94	163
60/40	60	–	88~89	163
50/50	60	–	90~91	164
40/60	61	–	86~88	163
20/80	59	–	84~86	162
0/100	60	–	–	–

*1 Melting temperature of PCL *2 Glass transition temperature of PCL
*3 Crystallization temperature of PLA *4 Melting temperature of PLA

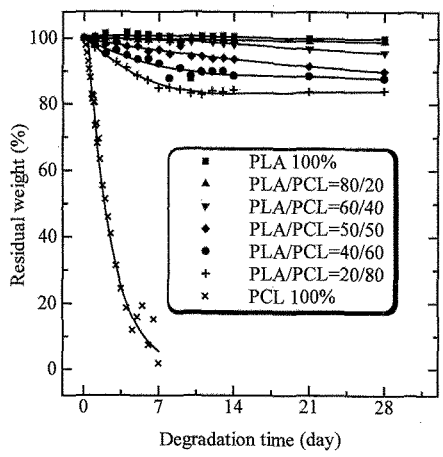

Figure 1 Residual weight of the PLA/PCL blend fiber as a function of the enzymatic degradation time.

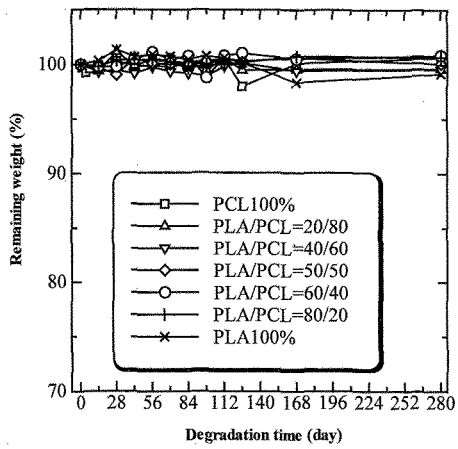

Figure 2 Residual weight of the PLA/PCL blend fiber as a function of degradation time.

Furthermore, we found that the amount of weight losses of PLA homopolymer was almost the same as that of PLA/PCL=80/20. These results showed that there is no difference both in the surface composition of PLA homopolymer and in that of PLA/PCL=80/20. Moreover, this is also suggested from the surface analytical result by X-ray photoelectron spectroscopy (XPS) [2].

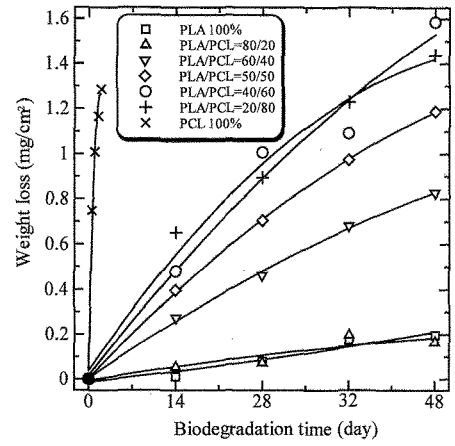

Figure 3 Weight loss of the PLA/PCL blend film as a function of the enzymatic degradation time.

3.4. Mechanical properties of the PLA/PCL blend films

The mechanical properties such as Young's modulus (*E*), maximum strength (σ_{max}), elongation at maximum strength (ε_{max}) and elongation at break (ε_b) were evaluated from stress-strain curves. The experimental results were listed in Table III.

According to the data, for PLA and PCL homopolymer films, the maximum strength of PLA was greater than that of PCL, while the elongation at break of PCL was greater than that of PLA. As the results of DSC also showed, it is because T_g of PLA is higher than the room temperature and is in a glass state at room temperature [3]. Moreover, it is because the molecular chain of PLA is relatively rigid and the entanglement density is small. On the contrary, since T_g of PCL is below the room temperature and it is flexible at the room temperature, therefore, the maximum strength shows the low value.

For the blend films, the maximum strength increased with an increase in PLA content with some exceptions. And, the elongation at break increased with an increase in PCL content. Thus, blending of PLA could improve the strength of PCL, while blending of PCL could improve the elongation of PLA.

3.5. Change of pH during the degradation of buffer solutions.

pH of the buffer solutions was measured before and after enzymatic degradation of the blend fibers. The measured results were listed in Table IV.

Table III Mechanical properties of the PLA/PCL blend films.

PLA/PCL	Maximum strength (σ_{max})	Elongation at maximum strength (ε_{max})	Elongation at break (ε_b)	Young's modulus (E)
	MPa	%	%	GPa
100/0	55.2	2.9	4.2	2.0
80/20	52.5	2.4	6.3	2.3
60/40	53.7	2.4	6.3	2.3
50/50	38.5	3.1	10.7	1.3
40/60	38.6	3.6	13.7	1.1
20/80	30.9	3.4	13.7	0.9
0/100	20.5	9.8	314.0	0.2

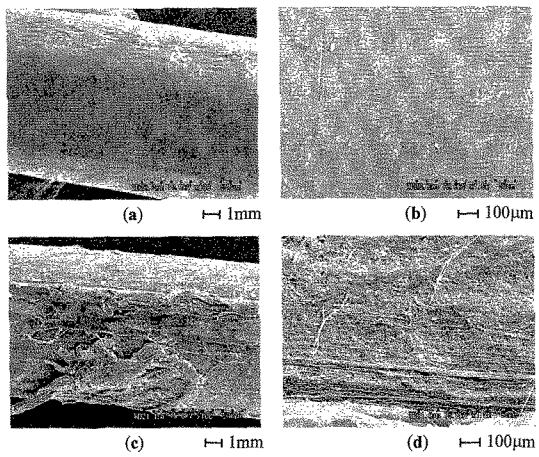

Figure 3 SEM of surface of PCL fibers before (**a** and **b**) and after (**c** and **d**) the enzymatic degradation for 1day.

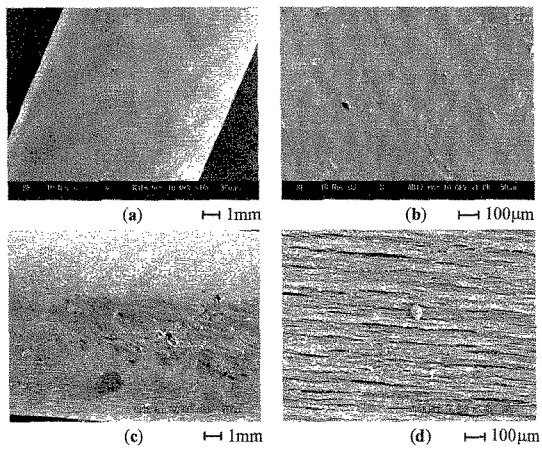

Figure 4 SEM of surface of PLA/PCL=50/50 fibers before (**a** and **b**) and after (**c** and **d**) the enzymatic degradation for 1week.

Table IV pH change of the buffer solution containing PLA/PCL blend fiber as a function of degradation time.

PLA/PCL	Initial	1day	7days	14days	21days
100/0		5.4-5.5	5.6	5.7	5.6
80/20		5.5	5.4	5.6	5.5
60/40	5.6-5.7 →	5.5	→ 5.6	→ 5.5	→ 5.5
50/50		5.5	5.5	5.4	5.3
40/60		5.4	5.5	5.3	5.2
20/80		5.4	5.3	5.2	5.2
	Initial	0.5day	1day	4days	7days
0/100	5.6-5.7 →	5.3-5.4 →	5.0 →	4.7 →	4.7

For the PLA homopolymer and the blend fibers, pH of these buffer solutions decreased slightly. For PCL homopolymer, however, pH decreased to 4.7 in a week. This result shows that the PCL is selectively degraded, according to the result of 3.2 and 3.3. It is due to the dissolution of the acidic low molecular weight compounds, which were generated by the enzymatic degradation of the PCL.

3.6. Surface morphology of the PLA/PCL blend fibers

Figure 3 show SEM photographs of the surface of the PCL fiber before and after the enzymatic degradation for 1 day. A clear change was observed in the surface morphology of the blend fiber before and after the enzymatic degradation. The morphology change was various and the formation of fibril, the exfoliation of the surface were observed.

Figure 4 show SEM photographs of the surface of the PLA/PCL=50/50 fibers before and after the enzymatic degradation for 1 week. Compared with the PCL fiber, the change of morphology was monotonous after the enzymatic degradation. However, the change of surface morphology was observed as shown in Figure 4 (**c**) and (**d**). In addition, the same tendency was also seen with the other composition.

4. CONCLUSION

By the enzymatic biodegradation test of the PLA/PCL blend fibers using Lipase (Rizopus delemar), residual ratio of weight decreased with an increase in PCL content. This fact showed that PCL having flexibility was degraded more alternatively than PLA having rigidity. Moreover, the same tendency was also seen with the blend film.

For the blend fiber, it was cleared that the molecular chain of polymer was cut after the enzymatic degradation, since reduction of pH were observed.

A clear change was observed in the surface morphology of the blend fiber before and after the enzymatic degradation. The morphology change was various and the formation of fibril, exfoliation of the surface, and so on were observed. On the other hand, a change was not observed in the cross sectional morphology of the blend fiber before and after the enzymatic degradation. Therefore, we found that the initially state of the degradation occurred over the fiber surface.

From the result of the tensile test, it was cleared that the mechanical properties of the blend film was improved.

Acknowledgment.

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