Melt Spinning of Poly(L-lactic acid) and Its Biodegradability

Yoshiro Nishimura, Akinori Takasu, Yoshihito Inai, Tadamichi Hirabayashi

Department of Environmental Technology and Urban Planning, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan

ABSTRACT: The melt spinning and melt drawing of poly(L-lactic acid) (PLLA) were carried out with a melt-spinning machine, and the mechanical properties, structure, and biodegradability of PLLA fiber were investigated. PLLA fiber with a tensile strength of 0.81 GPa was successfully obtained through two steps of drawing at a draw ratio of 18 in hot water. This fiber had enough tensile strength for common engineering use. The fiber could be degraded under controlled composting conditions at 70°C for 1 week. In scanning electron microscopy observations of the fiber, a regular pattern of cracks running along the vertical direction to the fiber axis was clearly observed. This suggested that the PLLA fiber built up a highly ordered structure arranged along the direction of the fiber axis. After the fiber was left to lie in the ground for 1 year, however, the surface of the fiber was still smooth, and the tensile strength did not decrease much. This PLLA fiber could not be hydrolyzed after 1 month of steeping in a buffer solution at 37°C, but it was rapidly hydrolyzed at more than 60°C. It was suggested that the degradation (hydrolysis) rate of PLLA depended on the glass-transition temperature. Upon hydrolysis at 80°C for 48 h, a regular crack along the vertical direction to the fiber axis was found that was very similar to that observed in degradation under composting conditions. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 2118–2124, 2005

Key words: biodegradable; drawing; fibers; melt

INTRODUCTION

In recent years, plastic disposal has become a serious environmental problem. One approach to solving the problem is the extensive utilization of biodegradable plastics that can be degraded by microorganisms in nature. Poly(L-lactic acid) (PLLA) is a typical biodegradable polymer and is superior in its tensile strength, elasticity, transparency, and moldability. Moreover, starting materials of PLLA can be obtained as agricultural and biochemical products, independently of petroleum. Fibers made of PLLA have already been supplied for resolvable sutures. However, there are few fibrous PLLA products in the industrial plastic market. It is thought that PLLA fiber can be applied widely in agriculture, the fishing industry, civil engineering, and so on.

Several investigators have reported PLLA fibers[1–6] prepared by melt spinning or solution spinning. Eling et al.[1] obtained melt-spun and solution-spun PLLA fibers with tensile strengths of 0.5 and 1.0 GPa, respectively. Pennings et al.[2] obtained melt-spun and solution-spun PLLA fibers with tensile strengths of 0.53 and 2.3 GPa, respectively. The strength of melt-spun fibers tends to be lower than that of solution-spun fibers. Actually, PLLA fiber manufactured with a melt-spinning machine does not have enough tensile strength for industrial applications.[7] However, the solution-spinning method is industrially unfavorable because many organic solvents are required in the process. In this study, we produced PLLA fiber with a high strength by operating a melt-spinning machine under a high draw ratio.

Several investigators[8–15] have reported the degradability of PLLA in the molded or film state. However, the degradation behavior of PLLA fibers is hardly known. When a biodegradable fiber is used, the environment in which the fiber is placed is very important. The degradation of the fiber is influenced by not only its chemical structure but also its crystallinity, molecular size, and thermal stability.

This article presents the production process with a melt-spinning machine and the mechanical properties, structure, and degradability of PLLA fiber. In particular, the degradation rate and degradation mode of PLLA fiber in soil, under controlled composting conditions and *in vitro*, are examined in detail.

EXPERIMENTAL

Materials

PLLA was obtained by the ring-opening polymerization of L-lactide (optical purity = 98%) in the presence

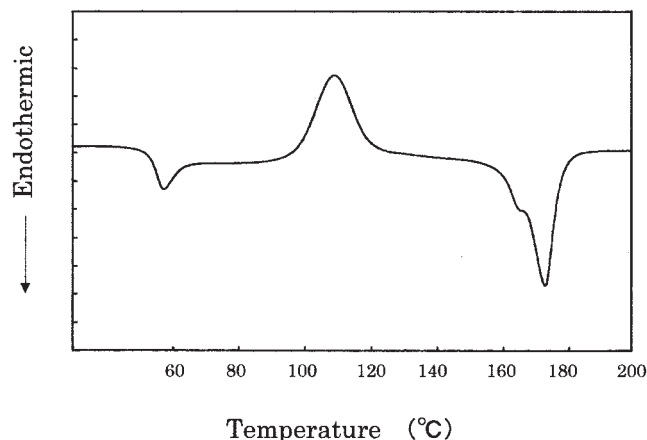*Correspondence to:* T. Hirabayashi (t-hirabayashi@nitech. ac.jp).

Figure 1 DSC thermograph of the PLLA resin.

of stannous octanoate as a catalyst The viscosity-average molecular weight (M_v) of the polymer was determined from the intrinsic viscosity ($[\eta]$) of its solution in chloroform at 25°C with the following equation:[16]

$$[\eta] = 5.45 \times 10^{-4} M_v^{0.73} \tag{1}$$

The residual lactide in the polymer was measured with a Shimazu Ltd., AM300 FT-NMR instrument (Japan). Figure 1 shows a differential scanning calorimetry (DSC) chart of the polymer. The glass-transition temperature (T_g), crystallization temperature (T_c), and melting temperature (T_m) of the polymer were determined from the DSC thermograph and are summarized in Table I, as well as M_v and the purity. Table II presents the data of the melt flow rate of PLLA obtained by the extrusion of the molten polymer through a capillary 0.5 mm in diameter under a constant load of 21.18 N.

Melt spinning and melt drawing

Figure 2 gives an outline of the melt-spinning machine used in this study. At the end of a 35-mm single-screw extruder (length/diameter = 28), a spinning nozzle with 12 holes (1.0 mm in diameter) was placed. The melt extrusion temperature was kept at 220°C for all samples. The melted PLLA was extruded into water (45°) in a cooling bath at the output speed of 12 g/min. The take-up speed for the melt-spun fiber was 8 m/min. The as-spun fiber was then drawn on drawing

TABLE II
Melt Flow Rate of the PLLA Resin

	Temperature (°C)				
	190	200	210	220	230
Melt flow rate (g/10 min)	0.05	0.13	0.23	0.44	1.07

machines kept at 98°C. Drawing ratios of 6–18 were employed. The fineness of the fiber was adjusted from 10 to 40 tex, which corresponded to a diameter of 0.1–0.2 mm.

Characterization of the fibers

The mechanical properties of the fibers were measured with a Tensilon instrument (UTM-3-200, Toyo Baldwin Co., Japan) at 20°C and a relative humidity of 65%; the crosshead speed was set at 200 mm/min, and the length of the specimen was 200 mm. All the tensile properties given in this article represent average values of 10 trials.

DSC was measured with a Rigaku-Denki TAS-100 differential scanning calorimeter (Japan) at a heating rate of 10°C/min under nitrogen gas. The degree of crystallization (X_c^{DSC}) was estimated from the endothermic calorific values for crystallization, with a value of 93 J/g assumed for the heat of fusion of the perfect crystal:[16]

$$X_C^{DSC}(\%) = 100(\Delta H_m + \Delta H_c)/93 \tag{2}$$

where ΔH_m and ΔH_c represents heat of melting and crystallizaiton, respectively. Birefringences were measured with the optical retardation technique with a BHFS polarized light microscope (Olympus Co., Japan).

Wide-angle X-ray diffraction (WAXD) under Cu Kα irradiation was measured on a Shimazu XD-D1 apparatus operated at 40 kV and 30 mA. The degree of crystallization ($X_c^{X\text{-ray}}$) was evaluated according to the following equation:

$$X_c^{x\text{-ray}}(\%) = 100 \times I_{crystal}/(I_{crystal}+I_{amorphous}) \tag{3}$$

where $I_{crystal}$ is the intensity of the crystalline peak area and $I_{crystal} + I_{amorphous}$ is the overall intensity for both the amorphous and crystalline areas.

The density of the fiber was determined from various gradient mixtures of ligroin and bromobenzene at 30°C.[16]

Biodegradability

For the examination of the degradation behavior in soil, the PLLA fiber was buried 10 cm under the surface of the test field of the Mikawa Textile Research
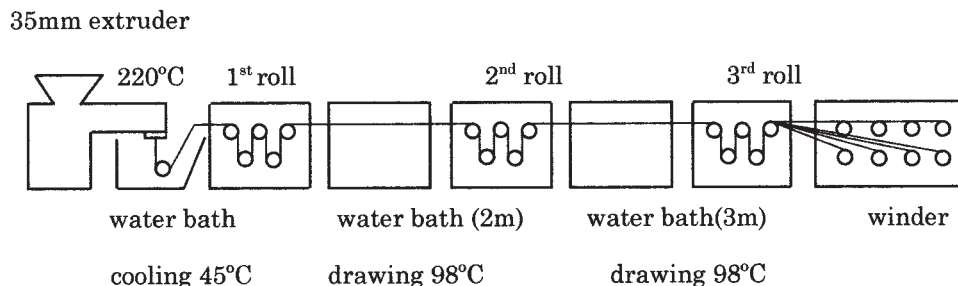
TABLE I
Characteristics of the PLLA Resin

T_g (°C)	T_m (°C)	T_c (°C)	M_v	Monomer (ppm)
56	171	117	1.7×10^5	50

Figure 2 Outline of the production line for melt spinning and melt drawing.

Institute in Gamagori City. The chemical hydrolysis was carried out as follows. The PLLA fiber was placed in a phosphate buffer solution (KH_2PO_4/K_2HPO_4, pH 7.4) at 37, 60, and 80°C for an adequate time. The examination of the degradation under controlled composting conditions was performed in a municipal composting plant in Atsumi Town, in which the feces and urine of a horse and a cow were disposed. The temperature of the compost reached 70°C. The degraded PLLA fiber was washed thoroughly with distilled water and then was dried under reduced pressure for at least 1 week. Subsequently, the tensile strength, molecular weight, and degree f crystallization were measured. The molecular weights of the samples were measured with a Tosoh Co. HLC-8020 gel permeation chromatography (GPC) system (Japan) calibrated by standard polystyrene samples. Chloroform was used as an eluting solution at a rate of 1 cm^3/min. Also, the fiber surface was observed with a JEOL JSM-5200 scanning electron microscope (Japan).

RESULTS AND DISCUSSION

Melt spinning and melt drawing

The melt-spinning and melt-drawing conditions of the PLLA fiber are shown in Table III. It is necessary in a melt-spinning process of PLLA to dry the starting PLLA resin at 70°C in a vacuum oven because the PLLA resin tends to hydrolyze even in the presence of a trace amount of water. A melt extrusion temperature of 180–

220°C was suitable. However, above 230°C, the thermal degradation of PLLA took place and resulted in a reduction of its viscosity; therefore, any fiber of good quality could not be obtained. The temperature of the cooling water (bath) had to be set at 45°C because the fiber began to swing in the bath during operation below 40°C and evenness could not be maintained.

Samples 5–8 were drawn fully (twice). However, sample 1 was the as-spun fiber, and samples 2–4 were the fibers drawn only once (the first stage). When the as-spun fiber was subjected to the first stage of drawing under the draw ratio of 8, it changed from transparent to white and opaque (sample 4). Drawing had to be carried out in hot water; otherwise, there would not have been enough energy to dry the fiber.

It was possible to set the maximum draw ratio to 18 for sample 8, which gave us a PLLA fiber drawn under a high draw ratio for the first time. The first drawing process was very important. The as-spun fiber melted in a bath at 98°C during relaxation. After the as-spun fiber was drawn and changed into the strained fiber, it never melted under the aforementioned conditions. The as-spun fiber was drawn at a low temperature (in concrete, from 80 to 90°C), and so it was strained and became white. After the drawing temperature was raised to 98°C, the fiber became transparent.

Properties of the PLLA fibers

The properties of the PLLA fibers are summarized in Table IV. The tensile strength increased with an in-

TABLE III
Melt-Spinning and Melt-Drawing Conditions of PLLA Fiber

	Sample							
	1	2	3	4	5	6	7	8
Extruder temperature (°C)	220	220	220	220	220	220	220	220
Cooling temperature (°C)	45	45	45	45	45	45	45	45
First drawing temperature (°C)	—	98	98	98	98	98	98	98
First draw ratio	—	6.0	7.0	9.0	7.0	7.0	7.0	7.0
Second drawing temperature (°C)	—	—	—	—	98	98	98	98
Second draw ratio	—	—	—	—	1.3	1.6	1.9	2.6
Total draw ratio	1.0	6.0	7.0	9.0	9.0	11.0	13.0	18.0

TABLE IV
Properties of PLLA Fibers with Different Draw Ratios

Sample	Total draw ratio	Tensile strength (GPa)	Elongation at break (%)	Tensile modulus (GPa)	Knot tensile strength (GPa)	Loop strength (GPa)	Birefringence	Density (g/cm^3)	Crystallinity	
									X-ray (%)	DSC (%)
1	1.0	0.06	4	2.7	0.03	0.04	0.0000	1.249	18.8	46.6
2	6.0	0.39	42	6.5	0.22	0.23	0.0302	1.255	62.1	66.3
3	7.0	0.45	41	7.3	0.24	0.23	0.0317	1.255	60.4	64.6
4	9.0	0.31	21	8.2	0.18	0.15	0.0326	1.249	63.4	65.5
5	9.0	0.56	38	7.9	0.28	0.25	0.0325	1.255	64.0	70.1
6	11.0	0.65	35	8.3	0.31	0.26	0.0343	1.258	66.3	67.3
7	13.0	0.73	31	8.9	0.34	0.25	0.0357	1.259	63.4	68.5
8	18.0	0.81	28	10.7	0.44	0.34	0.0380	1.269	70.9	67.7

crease in the draw ratio of drawing, and the highest one (0.81 GPa for sample 8) was achieved after the second drawing stages under the draw ratio of 18. The tensile modulus, knot tensile strength, and loop strength also increased with the increasing draw ratio. Sample 8 had good enough tensile properties for common engineering purposes.

When drawing was stopped at only one stage, the fiber changed from being transparent to being white and opaque at the draw ratio of about 9, and its tensile strength was low (sample 4). Our maximum tensile strength for the PLLA fiber was considerably higher than that (0.5 GPa) found by Eling et al.[1] Nevertheless, the molecular weights of the two starting PLLA resins were almost the same. The difference in the tensile strength must be due to the different drawing procedures.

The density of the fiber increased with the increasing draw ratio. When the sample was drawn only once under the draw ratio of 9, its density was rather low (sample 4). Figure 3 shows a typical scanning electron microscopy (SEM) photograph for a cross section of the white PLLA fiber. Many microholes can be observed in the SEM photograph. It is clear that many
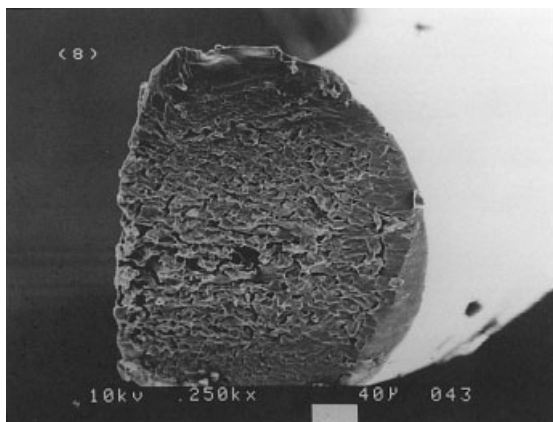

Figure 3 SEM photograph of the cross section of the PLLA fiber (white fiber).

microcracks were generated in the fiber in the course of the drawing process because of overdrawing and resulted in low density and whitening.

The birefringence also increased with the increasing draw ratio, and this suggested an increase in the orientation or chain crystallization. However, the degree of crystallization was approximately constant (60–70%) for draw ratios above 6. The tensile strength increased significantly after the degree of crystallization leveled off. This can be reasonably explained by the fact that the increase in the tensile strength of the fiber was due to an increase in the extended chain crystals and tie molecules in the amorphous regions between the crystalline ones.

Biodegradation manner

A degradation test was investigated for PLLA samples for which the diameter was about 0.1 mm at the draw ratio of 9 (sample 5). The tensile strength of the PLLA fiber did not decrease as much after the burial in soil for 1 year as before the test. As shown in the SEM photograph of Figure 4(a), the surface of the buried fiber was still smooth. The biodegradation of the PLLA fiber did not take place in practice through soil burial even for 1 year.

Figure 4(b) presents an SEM photograph of the surface of the PLLA fiber treated under controlled composting conditions for 1 week. A regular pattern of cracks can be observed running in the vertical direction to the fiber axis. Similar cracks were reported by Hyon[15] in the course of hydrolysis of as-spun and drawn PLLA fibers. Figure 5 shows GPC profiles of the PLLA fibers before and after degradation under composting conditions. After 1 week, the peak not only shifted toward a low-molecular-weight side but also split into two peaks. This indicated clearly that the polymer chain in the fiber broke down quickly under composting conditions. Figure 6 shows WAXD profiles of the PLLA fibers before and after degradation under composting conditions. After the degradation test, the degree of crystallization increased by
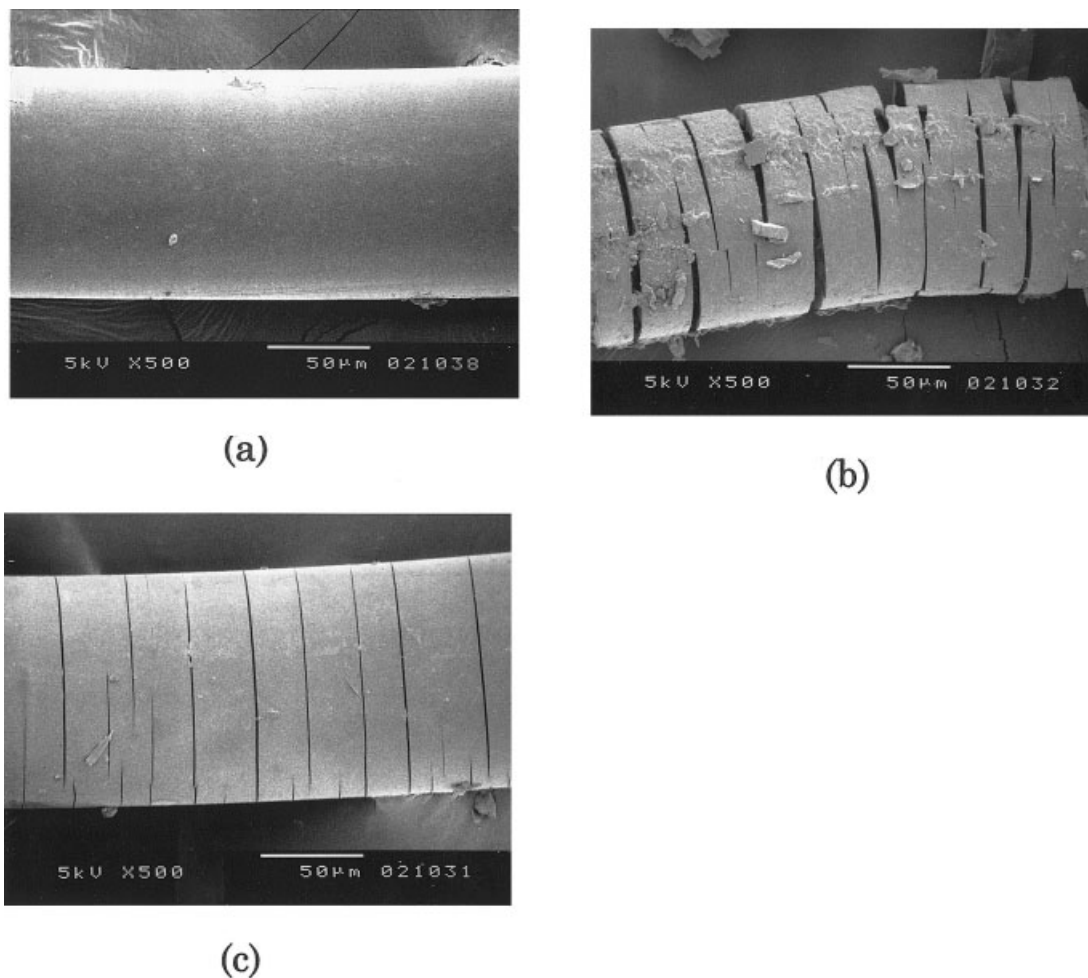
Figure 4 SEM photographs of the surface of the PLLA fiber: (a) after soil burial for 1 year, (b) after decomposition under composting conditions for 1 week, and (c) after hydrolysis at 80°C for 48 h.

about 20%. The amorphous region of the sample might be more sensitive to biodegradation than the crystalline region, and so the degree of crystallization

in the sample rather increased after the test. It is reasonable for us to propose a reliable structure of this PLLA fiber and the degradation mechanism, as shown
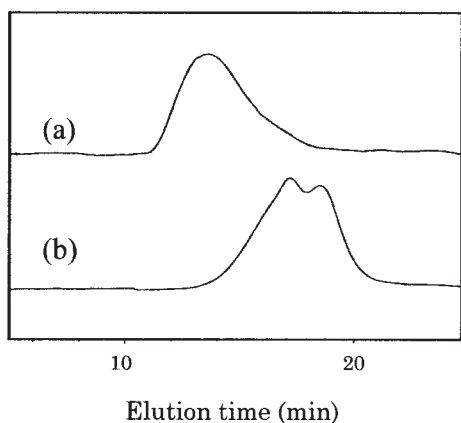

Figure 5 GPC profile of the PLLA fiber: (a) before and (b) after decomposition under composting conditions for 1 week.
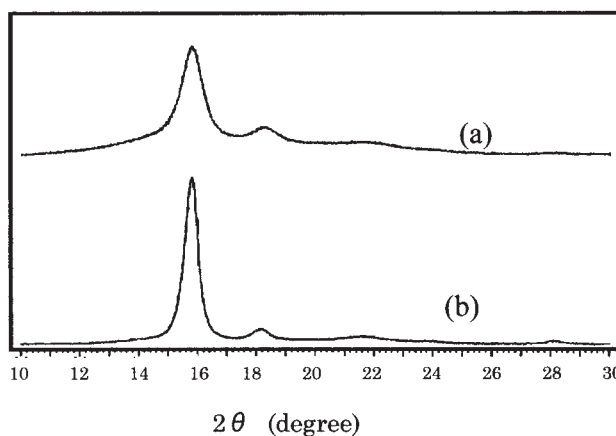

Figure 6 WAXD patterns of the PLLA fiber: (a) before and (b) after decomposition under composting conditions for 1 week.
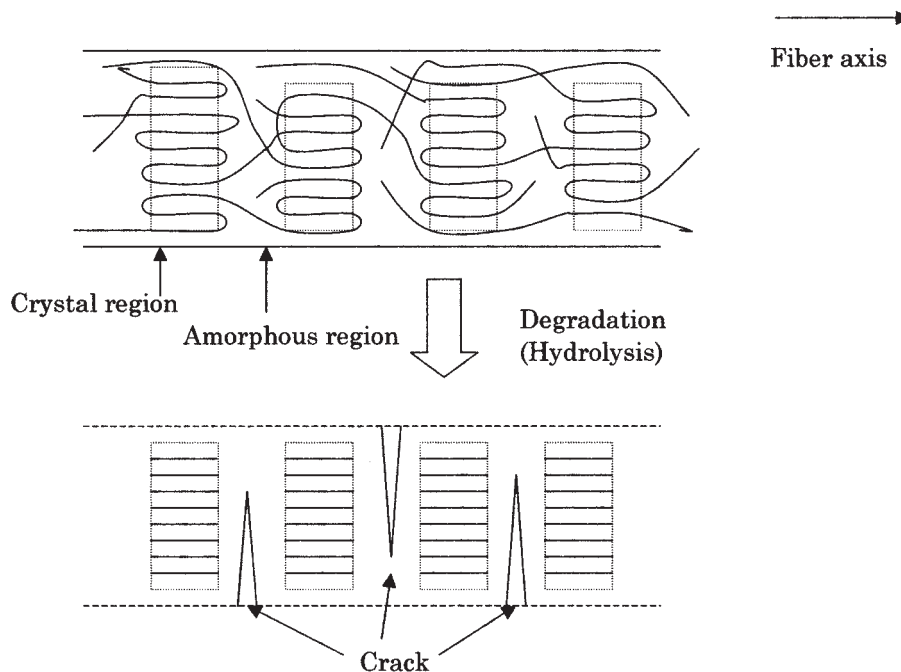
Figure 7 Speculative structure and degradation mechanism for the PLLA fiber.

in Figure 7. The drawn PLLA fiber in this work apparently has a highly ordered structure in which crystalline and amorphous regions are rather regularly arranged along the axis direction of the fiber.

Figure 8 shows the change in the tensile strength of the PLLA fiber as a function of the dipping time in a phosphate buffer solution. The PLLA fiber could be readily hydrolyzed at more than 60°C in contrast to 37°C, at which the fiber could not be hydrolyzed in the buffer solution even after 1 month. Figure 4(c) presents an SEM picture of the sample 5 after hydrolysis at 80°C for 48 h. Regular cracks along the vertical direction of the fiber axis can be observed similarly in the rapid degradation under the composting conditions. This temperature dependence on the rate of hydrolysis of the PLLA fiber suggests that T_g might
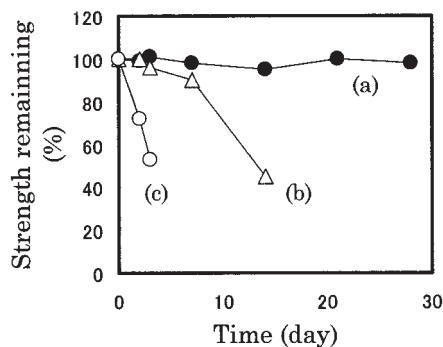

Figure 8 Tensile strength as a function of the dipping time in a phosphate buffer solution at (a) 37, (b) 60, and (c) 80°C.

play a very important role in determining the degradation rate.

CONCLUSIONS

A PLLA fiber with a tensile strength of 0.81 GPa was successfully prepared through melt spinning and two consecutive drawings at a draw ratio of 18 in hot water. The fiber had good enough tensile properties for common engineering use. When the as-spun fiber was drawn only once on the first drawing machine, it changed from being transparent to being white and opaque. However, its tensile strength and density were low because of the many microcracks generated in the fiber in the course of drawing.

The PLLA fiber was readily degraded under controlled composting conditions at 70°C within 1 week. The SEM observations of the fiber revealed a regular pattern of cracks running along the vertical direction to the fiber axis. This suggested that our PLLA fiber build up a highly ordered structure arranged along the direction of the fiber axis. The surface of the PLLA fiber buried in a test field was still smooth after 1 year, and no reduction of the tensile strength was observed. On the other hand, the PLLA fiber could be hydrolyzed rapidly at more than 60°C. It was suggested that the rate of degradation (hydrolysis) of PLLA was correlated with its T_g. For the hydrolysis of the fiber at 80°C for 48 h, a regular crack along the vertical direction to the fiber axis was observed, and it was very similar to the case of decomposition under the composting conditions.

References

1. Eling, B.; Gogolewski, S.; Pennings, A. J. Polymer 1982, 23, 1587.
2. Penning, J. P.; Dijkstra, H.; Pennings, A. J. Polymer 1993, 34, 942.
3. Cicero, J. A.; Dorgan, J. R.; Garrett, J.; Runt, J.; Lin, J. S. J Appl Polym Sci 2002, 86, 2839.
4. Tsuji, H.; Ikada, Y.; Hyon, S.; Kimura, Y.; Kitao, T. J Appl Polym Sci 1994, 51, 3371.
5. Gogolewski, S.; Pennings, A. J. J Appl Polym Sci 1983, 28, 1045.
6. Leeslag, L. W.; Pennings, A. J. Polymer 1987, 28, 1965.
7. Kondo, Y. Soc Fiber Sci Technol Jpn 1996, 49, 484.
8. Reeve, M. S.; McCarthy, S. P.; Downey, M. J.; Gross, R. A. Macromolecules 1994, 27, 825.
9. Iwata, T.; Doi, Y. Macromolecules 1998, 31, 2461.
10. Tuji, H.; Miyauchi, S. Polymer 2001, 42, 4463.
11. Tuji, H.; Muramatu, H. Polym Degrad Stab 2001, 71, 403.
12. Tsuji, H.; Ikada, Y. J Polym Sci Part A: Polym Chem 1998, 36, 59.
13. Tsuji, H.; Mizuno, A.; Ikada, Y. J Appl Polym Sci 2000, 77, 1452.
14. Tuji, H.; Ikada, Y. Polym Degrad Stab 2000, 67, 179.
15. Hyon, S. Soc Fiber Sci Technol Jpn 1998, 54, 527.
16. Fischer, E. W.; Sterzel, H. J.; Wegner, G. Kolloid-Z Z Polym 1972, 251, 980.