

# Characterization of Poly(L-lactic acid) Fibers Produced by Melt Spinning

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Received 21 June 2000; accepted 3 December 2000

**ABSTRACT:** Biodegradable poly(L-lactic acid) (PLLA) fibers were processed by a two-step melt-spinning method (melt extrusion and hot draw) from PLLA with three different viscosity-average molecular weights (494,600, 304,700, and 262,800). Before spinning, the polymer flakes were first milled into powders and dried under vacuum. Viscosity-average molecular weight of PLLA following the fabrication process was monitored. Tensile properties of as-spun and hot-drawn fibers were investigated. Morphology of the PLLA fibers was viewed under a scanning electron microscope. Crystallinity of these fibers was assessed by thermogram analysis of differential scanning calorimetry. Results showed that the extent of decrease in the viscosity-average molecular weight of PLLA dropped sharply by 13.1–19.5% during pulverization and by 39.0–69.0% during melt-extrusion. The hot-draw process in this study had a little effect on the viscosity-average molecular weight of PLLA. Smoother fibers could be obtained for the die temperature at least 230°C for raw materials with higher crystallinity (more than 75%) and at least 220°C for raw materials with lower crystallinity (about 60%). The as-spun fibers showed crystallinity of 16.5–22.8% and the value increased to 50.3–63.7% after hot draw. Tensile moduli of the as-spun fibers were in the range of 1.2–2.4 GPa, which were raised to 3.6–5.4 GPa after hot draw. The final PLLA fibers with 110–160  $\mu\text{m}$  diameters showed tensile strengths of 300–600 MPa. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 251–260, 2001

**Key words:** poly(L-lactic acid); biodegradable fibers; melt spinning; viscosity-average molecular weight; tensile properties

## INTRODUCTION

As a major kind of biodegradable poly( $\alpha$ -hydroxy acids), Poly(L-lactic acid) (PLLA) has been widely studied for its applications in treatment of mus-

culoskeletal injuries,<sup>1</sup> tissue engineering,<sup>2,3</sup> and controlled release systems<sup>4</sup> because of its good processability, good biocompatibility, and suitable mechanical properties.

PLLA fibers can be prepared by means of melt spinning<sup>5–8</sup> or solution spinning (dry spinning)<sup>5,9–15</sup> to be used for ligament reconstruction,<sup>16</sup> suture,<sup>17,18</sup> and in self-reinforced composite.<sup>19,20</sup> Pennings et al.<sup>5</sup> obtained PLLA fibers

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*Journal of Applied Polymer Science*, Vol. 81, 251–260 (2001)  
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**Table I Physical Parameters of the Raw Materials Obtained**

Raw Materials	$\bar{M}_\eta$ <sup>a</sup>	Specific Rotation <sup>a</sup> (°) (Chloroform, 20°C)	Melting Range <sup>a</sup> (°C) (DSC, 10°C/min)	Heat of Fusion <sup>a</sup> (J/g) (DSC, 10°C/min)	Crystallinity <sup>b</sup> (%)
PLLA-a	494,600	-158.9	179.8–192.0	74.3	79.9
PLLA-b	304,700	-159.8	174.4–186.9	55.1	59.2
PLLA-c	262,800	-159.1	177.6–192.2	70.4	75.7

<sup>a</sup> Given by the supplier.<sup>b</sup> With respect to 93 J/g, the melt enthalpy of 100% crystalline PLLA.

with tensile strengths of 0.5 and 1.0 GPa by melt spinning and solution spinning, respectively. They have investigated the drawing behavior of PLLA and the influences of extrusion conditions by solution spinning in details.<sup>5,21–23</sup> Fambri et al.<sup>8</sup> have studied the effects of collecting rate and draw ratio on the tensile properties of PLLA fibers prepared by melt spinning. A tensile strength of 0.87 MPa and a tensile modulus of 9.2 GPa were reported by them. More recently, some investigators have reported a high-speed melt-spinning method to produce PLLA fibers.<sup>24,25</sup>

To obtain optimal biodegradable fibers for three-dimensional braided composites for tissue engineering, PLLA fibers were prepared by melt spinning from PLLA with three different molecular weights in our laboratory. The effects of the molecular weights of the raw materials and the fiber preparation conditions, especially the extrusion temperatures, on the properties of PLLA fibers were studied. Characterizations in terms of the viscosity-average molecular weight, SEM morphology, thermal behavior, and the tensile properties of the PLLA fibers formed following the preparation process are discussed in this article.

## EXPERIMENTAL

### Materials

PLLA with three viscosity-average molecular weights (494,600, 304,700, and 262,800) from *PU-RAC*, The Netherlands were used, and the three batches were designated as “PLLA-a,” “PLLA-b,” and “PLLA-c,” respectively, in this article. Parameters of the purchased PLLA were shown in Table I. Before melt spinning, the obtained polymer flakes were first pulverized using a mill in liquid nitrogen into powders and then dried in a vacuum oven at 50°C for at least 48 h.

### Melt Spinning

PLLA fibers were prepared by a two-step melt-spinning process, i.e., melt extrusion and hot draw. At the first step, the dried PLLA powders were extruded in air using a laboratory single screw extruder (RANDCASTLE Microtruder) with a  $\phi 6.35$ -mm screw and a  $\phi 1.0$ -mm die hole. Three heating bands were located along the screw and one on the die. The extrusion was carried out at a constant screw speed of 9.5 rpm at different temperatures along the screw and the die temperature ranging from 200 to 240°C. The as-spun fibers were collected at a rate of 3.20 m/min on a sandblasted glass drum, and subsequently drawn in nitrogen at 120°C in a self-constructed hot-draw apparatus at a feed velocity of 0.26 m/min and a take-up velocity of 1.09 m/min (the second step). Another 10 min of heat treatment was conducted additionally in nitrogen at 120°C to get the final hot-drawn fibers. The PLLA fibers so obtained were stored in a desiccator for further uses.

### Molecular Weight

Molecular weight was measured by the viscosity method in a diluted polymer/chloroform solution (0.1 g/dL) using an Ubbelohde viscometer (Type 0c) at 25°C. The viscosity-average molecular weight,  $\bar{M}_\eta$ , was then calculated from the intrinsic viscosity  $[\eta]$  by using the following equation<sup>26</sup>:

$$[\eta] = 5.45 \times 10^{-4} \bar{M}_\eta^{0.73} \quad (1)$$

The extent of decrease in the viscosity-average molecular weight was defined by the difference of the viscosity-average molecular weights of PLLA before and after a processing step, i.e.,

$$\text{Extent of decrease} = \frac{\bar{M}_{\eta 2} - \bar{M}_{\eta 1}}{\bar{M}_{\eta 1}} \times 100\% \quad (2)$$

where  $\bar{M}_{\eta_1}$  and  $\bar{M}_{\eta_2}$  were the viscosity-average molecular weight of PLLA before and after the processing step respectively.

### Morphology

Morphology of PLLA fibers was observed under a LEICA scanning electron microscope (SEM) (Model Stereoscan 440) after gold coating.

### Thermal Analysis

Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer DSC 7 calorimeter from 0 to 240°C with a heating rate of 10°C/min by flushing nitrogen. Samples consisted of approximately 10 mg of fibers that had been cut into pieces of 3–4 mm long for as-spun fibers, and specimens of about 1 mm long for hot-drawn fibers. They were carefully put into the aluminum pans. For the as-spun fibers, the glass transition temperature,  $T_g$ , was determined by the temperature at the middle point between the baseline and the plateau near the inflection of the thermogram. The lower and the higher crystallization temperatures,  $T_{c1}$  and  $T_{c2}$ , denoted the minimum values of the detected lower and higher crystallization exothermic peaks. The melting temperature,  $T_m$ , was the temperature at the maximum value of melting peak.  $C_1$ ,  $C_2$ , and  $C_m$  were the corresponding energies (J/g) (peak areas below the baseline for  $C_1$ ,  $C_2$ , and above the baseline for  $C_m$ ) at  $T_{c1}$ ,  $T_{c2}$ , and  $T_m$ , respectively. The melting energy of the specimens was referred to the difference between  $C_m$  and the sum of  $C_1$  and  $C_2$ . The crystallinity of the PLLA fibers was then determined by rating the melting energy of the specimens to 93 J/g, the melting enthalpy of 100% crystalline PLLA in the reference,<sup>27</sup> i.e.,

$$\text{Crystallinity} = 100 \times (C_m - C_1 - C_2)/93 \quad (3)$$

### Tensile Properties

An Instron tensile tester (Model Instron 4466) equipped with a 500 N load cell was used to measure the tensile properties of as-spun PLLA fibers and a number of the hot-drawn fibers. A Hounsfield tensile tester (Model H10KM/03) with a 100 N load cell was used to investigate the others of the hot-drawn fibers. All of them were conducted at room temperature at a crosshead speed of 12 mm/min. Specimens with a gauge length of 25 mm were carefully mounted. All the reported tensile properties and diameters repre-

sented average values of four to six tests. The diameter was measured using a micrometer, and the draw ratio was defined by rating the cross-sectional areas of the as-spun fibers to the final fibers.

## RESULTS AND DISCUSSION

### Molecular Weight

As a biodegradable polymer, PLLA can degrade *in vivo* or in humid environments by hydrolysis via ester linkage scission. Such degradation is also sensitive to elevated temperatures. Degradation reactions were also thought to involve the ester bond on the backbone, including thermohydrolysis, depolymerization, and cyclic oligomerization, intermolecular, and intramolecular transesterifications.<sup>28</sup> In our experiments, as shown in Table II, every step during the fiber preparation had an effect on the molecular weight of PLLA. The viscosity-average molecular weight of PLLA dropped sharply to a lower level after pulverization and melt extrusion, but decreased gently after hot draw. The extent of decrease during melt extrusion was about 39.0–69.0% far more than those during pulverization (about 13.1–19.5%) and hot draw (~9.1%).

Pulverization of the flake-like particles of raw polymers was a mechanical process. Polymers could suffer from the heat and shear forces generated by the mill friction, which could have an adverse effect on the molecular weight of PLLA. Although liquid nitrogen was used to freeze and protect PLLA, degradation reaction in chemical structure could still happen. Because PLLA-a and PLLA-c had higher crystallinity than PLLA-b when obtained (Table I), they were more rigid and need more energy to pulverize. Therefore, PLLA-a and PLLA-c degraded to a higher extent than PLLA-b did.

It was necessary to extrude a polymer at an elevated temperature higher than its melting range. To reduce the extent of decrease in molecular weight during melt extrusion, PLLA was dried completely in a vacuum oven before extrusion to eliminate water and low molecular weight compounds that could cause PLLA degradation. Melt extrusion was carried out in dry air environments at different die temperatures for each molecular weight of PLLA. The viscosity-average molecular weight of PLLA in the as-spun fibers was measured for every die temperature. Results

**Table II Viscosity-Average Molecular Weights of PLLA and Their Decrease During the Fiber Preparation Process**

Samples	Raw Materials	Powder Materials		As-Spun Fibers		Hot-Drawn Fibers		Die Temperature (°C)
	$\bar{M}_\eta$	$\bar{M}_\eta$	Extent of Decrease (%)	$\bar{M}_\eta$	Extent of Decrease (%)	$\bar{M}_\eta$	Extent of Decrease (%)	
PLLA-a	494,600	398,400	19.5	216,500	45.7	196,800	9.1	220
				146,600	63.2	137,900	5.9	230
				123,600	69.0	113,000	8.6	240
PLLA-b	304,700	264,700	13.1	161,400	39.0	166,200	-3.0	210
				157,300	40.6	143,800	8.6	220
				112,200	57.6	118,600	-5.7	230
PLLA-c	262,800	221,400	15.8	109,700	50.5	110,500	-0.7	210
				106,800	51.8	107,100	-0.3	220
				105,900	52.2	112,900	-6.6	230

showed that the viscosity-average molecular weight could vary significantly in different extrusion period due to the stability of the processing. The viscosity-average molecular weight of PLLA in the fibers at the beginning and at the end of extrusion was significantly lower (about a half) than that at the middle of the extrusion period. In general, for this study, the central sections of extruded fibers were selected for further hot-draw and characterization.

The viscosity-average molecular weight of as-spun PLLA fibers extruded at lower die temperature was generally higher than those obtained at higher die temperature. This phenomenon happened most obviously when PLLA had the highest original molecular weight, i.e., PLLA-a. In other words, the higher the original molecular weight of PLLA, the bigger the extent of decrease in molecular weight during melt extrusion.

The extent of decrease in the viscosity-average molecular weight during hot draw was less than 10%. Because hot draw was carried out with nitrogen flushing at 120°C, which was lower than the extrusion temperatures, the viscosity-average molecular weight dropped only slightly during this step. Some data showing a small increase in viscosity-average molecular weight after hot draw were probably caused by the variation of viscosity-average molecular weight in different process sections of the fibers.

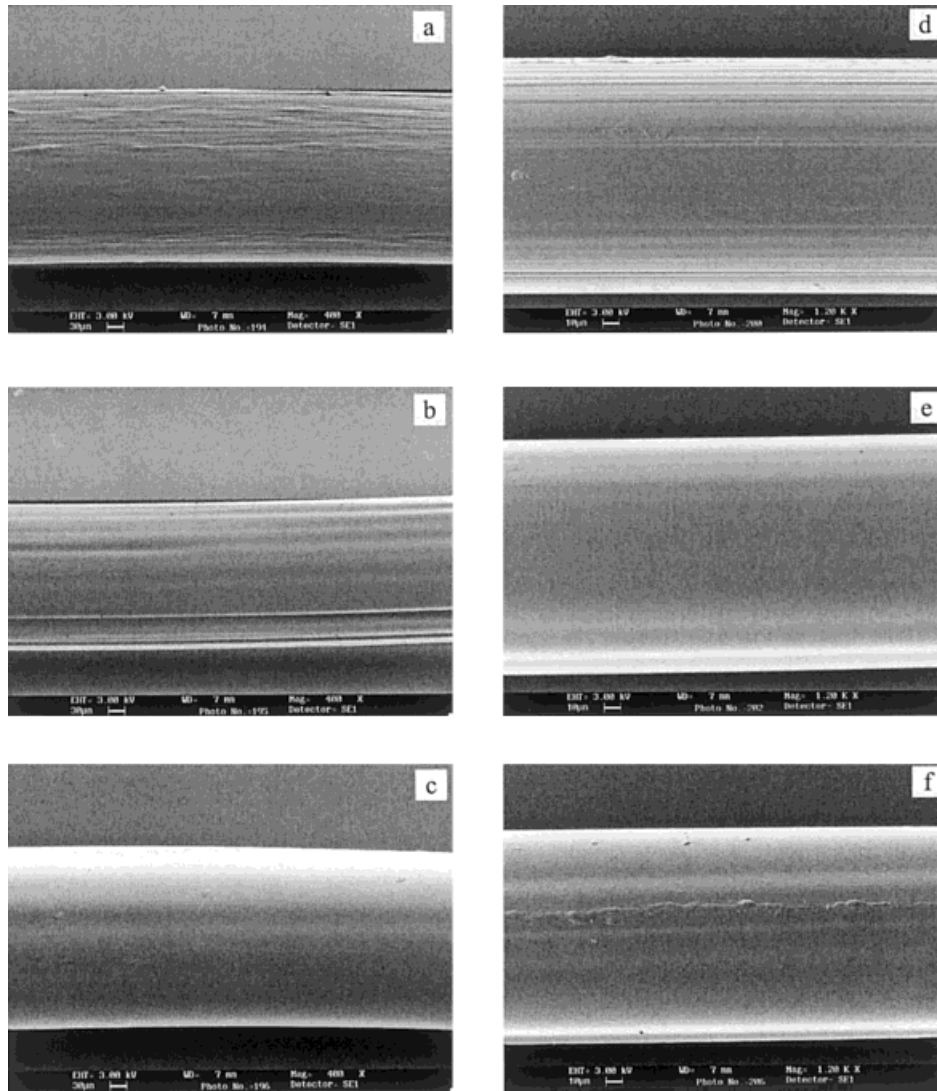
### Morphology

Surface morphology of PLLA fibers was observed under SEM. Pictures were shown in Figures 1–3.

From the SEM pictures in Figure 1, the as-spun fiber of PLLA-a formed at 240°C die temperature (a240) [Fig. 1(c)] appeared to be quite smooth. Extruding lines could be seen on the surface of the as-spun fiber formed at 230°C die temperature (a230) [Fig. 1(b)]. The surface of the as-spun fiber formed at 220°C die temperature (a220) [Fig. 1(a)] were quite rough, and some particles were observed on the surface, which were probably incompletely melting polymer particles caused by nonuniform melt-mixing during extrusion. After hot draw, the surface of the hot-drawn fibers became quite smooth. Some fibril lines could be seen from the SEM pictures [Fig. 1(d)–(f)].

Similar results were obtained in PLLA-b and PLLA-c fibers. For the as-spun fibers of PLLA-b obtained at the die temperature of 210, 220, and 230°C, respectively (b210, b220, and b230) [Fig. 2(a)–(c)], the surfaces were very similar to those of a220, a230, and a240 fibers, respectively [Fig. 1(a)–(c)]. Apparently some polymer particles existed on the surface of b210 [Fig. 2(a)]. The structures of hot-drawn fibers of b210 (b210hd), b220as (b220hd), and b230 (b230hd) were also shown in Figure 2.

PLLA-c when obtained was of higher crystallinity, similar to PLLA-a as shown in Table I. Although its molecular weight was the lowest, it was extruded with more difficulty compared to PLLA-b. The as-spun PLLA-c fiber extruded at three different die temperature of 210°C (c210), 220°C (c220), and 230°C (c230) were smooth, as observed from their lateral surface SEM pictures



**Figure 1** SEM micrographs of PLLA-a fibers. (a) As-spun fiber at 220°C die temperature (a220); (b) as-spun fiber at 230°C die temperature (a230); (c) as-spun fiber at 240°C die temperature (a240); (d) hot-drawn fiber of a220 (a220hd); (e) hot-drawn fiber of a230 (a230hd); (f) hot-drawn fiber of a240 (a240hd). The draw ratios for a220hd, a230hd, and a240hd were 4.71, 4.75, and 4.77, respectively. Original magnification for as-spun fibers: 400 $\times$ ; for hot-drawn fibers: 1200 $\times$ .

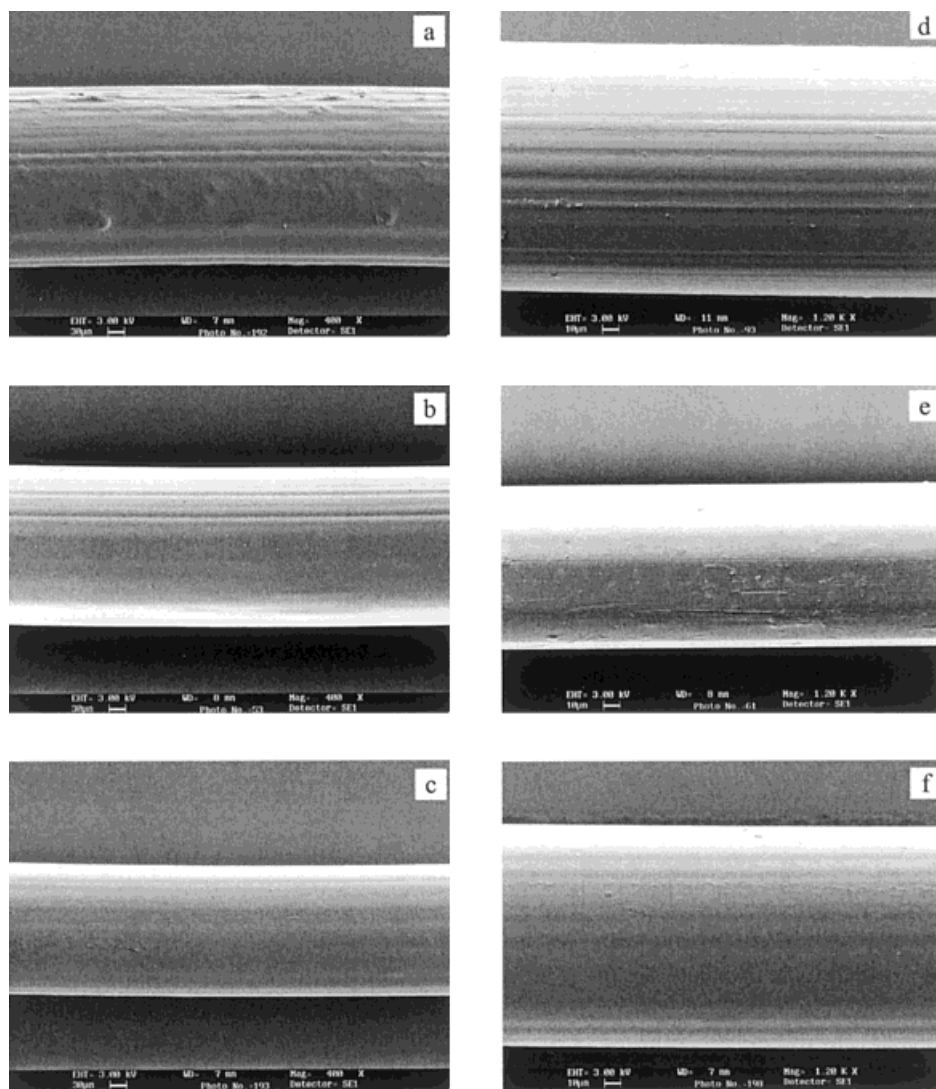
[Fig. 3(a)–(c)]. However, visual observations suggested that there were some bigger particles apparently existing on the surfaces of c210 and c220 fibers. From the SEM pictures of the hot-drawn PLLA-c fibers, some linear scratches could be seen on the hot-drawn fibers of c210 (c210hd) [Fig. 3(d)]. The same was not observed for the hot-drawn fibers of c220 (c220hd) and c230 (c230hd) [Fig. 3(e) and (f)].

In summary, the extruding temperature played an important role in the structure of the final fibers. It was suggested that melt extrusion

of PLLA of these three different molecular weights should be carried out at a die temperature higher than 230°C for PLLA-a and PLLA-c, and 220°C for PLLA-b. Low crystallinity of raw materials would be preferable.

#### Thermal Behavior and Crystallinity

The thermal behavior and crystallinities of the as-spun fibers and the hot-drawn fibers were studied using DSC. The results were shown in Table III as well as in Figures 4 and 5. The as-



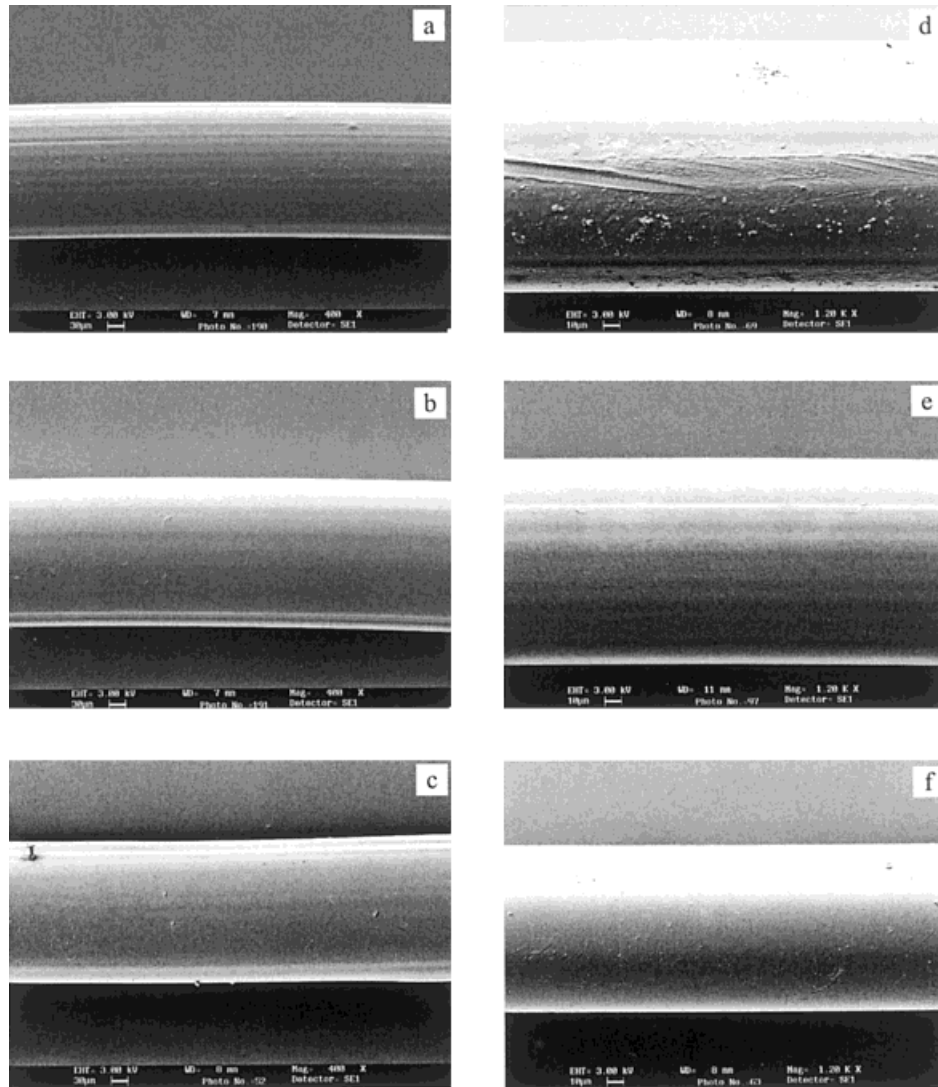
**Figure 2** SEM micrographs of PLLA-b fibers. (a) As-spun fiber at 210°C die temperature (b210); (b) as-spun fiber at 220°C die temperature (b220); (c) as-spun fiber at 230°C die temperature (b230); (d) hot-drawn fiber of b210 (b210hd); (e) hot-drawn fiber of b220 (b220hd); (f) hot-drawn fiber of b230 (b230hd). The draw ratios for b210hd, b220hd, and b230hd were 5.50, 4.66, and 5.35, respectively. Original magnification for as-spun fibers: 400 $\times$ ; for hot-drawn fibers: 1200 $\times$ .

spun PLLA fibers in this article were prepared at a definite extrusion speed and a definite collection rate, and subsequently hot drawn at 120°C at definite feed and take-up velocities. The different properties of such fibers were presumably dependent on their raw material properties and extrusion temperatures.

The glass transition and the lower and the higher crystallization exothermic peaks were detected in the DSC thermograms of the as-spun fibers (Fig. 4), but only the melting peaks appeared in those of the hot-drawn fibers (Fig. 5).

The  $T_g$ ,  $T_{c1}$  and  $T_{c2}$  values of the as-spun fibers were 61.9–66.4, 87.8–99.3, and 157.2–159.7°C, respectively. The melting temperature of the as-spun and the hot-drawn fibers were 176.2–177.7 and 168.0–172.7°C, respectively. The as-spun fibers showed low crystallinity of 16.5–22.8%, but the hot-drawn fibers exhibited higher crystallinity of 50.3–63.7%.

It was expected that  $T_m$  values could be affected by the specimen size. The as-spun fibers were thicker and easier to handle than the hot-drawn fibers. The sizes of the specimens in the



**Figure 3** SEM micrographs of PLLA-c fibers. (a) As-spun fiber at 210°C die temperature (c210); (b) as-spun fiber at 220°C die temperature (c220); (c) as-spun fiber at 230°C die temperature (c230); (d) hot-drawn fiber of c210 (c210hd); (e) hot-drawn fiber of c220 (c220hd); (f) hot-drawn fiber of c230 (c230hd). The draw ratios for c210hd, c220hd, and c230hd were 5.18, 5.11, and 5.89, respectively. Original magnification for as-spun fibers: 400 $\times$ ; for hot-drawn fibers: 1200 $\times$ .

aluminum pans were different for these fibers. The length and thickness of the as-spun fibers were obviously bigger than those of the hot-drawn fibers. This difference in specimen size might lead to the different ranges of  $T_m$  for the as-spun and the hot-drawn fibers.

Because of their low crystallinity, the as-spun fibers could recrystallize as they were heated up during the measurement process. Two crystallization exothermic peaks,  $T_{c1}$  and  $T_{c2}$ , were clearly shown in their thermograms (Fig. 4). These two crystallization peaks were not detected

in these thermograms of the hot-drawn fibers (Fig. 5) apparently because the fibers were already of rather high crystallinity. The hot-draw process could enhance the molecular orientation along the drawing direction. The crystallinity of PLLA fibers could, therefore, be improved by this process.

Because the as-spun fibers were cooled relatively quickly when they were extruded at a higher die temperature, they showed lower crystallinities and higher  $T_{c1}$  values with die temperature decreasing (Table III, Fig. 5). The low crys-

**Table III** DSC Analysis of the As-Spun and the Hot-Drawn PLLA Fibers

Samples	Die Temperature (°C)	As-Spun Fibers								Hot-Drawn Fibers			
		$T_g$ (°C)	$T_{c1}$ (°C)	$T_{c2}$ (°C)	$T_m$ (°C)	$C_1$ (J/g)	$C_2$ (J/g)	$C_m$ (J/g)	Crystallinity (%)	$T_m$ (°C)	$C_m$ (J/g)	Crystallinity (%)	Draw Ratio
PLLA-a	220	64.2	87.8	157.2	176.2	15.6	5.44	42.4	22.9	172.7	57.6	61.9	4.71
	230	63.0	93.9	159.3	177.2	20.2	6.91	44.3	18.6	171.0	59.7	64.2	4.75
	240	63.2	97.1	159.7	176.8	22.4	6.81	44.6	16.6	169.1	57.4	61.8	4.77
PLLA-b	210	65.7	90.8	159.1	176.8	18.6	5.93	43.5	20.4	172.3	59.1	63.6	5.50
	220	64.4	92.5	158.8	176.5	20.0	6.08	44.3	19.6	171.0	56.2	60.4	4.66
PLLA-c	230	61.9	95.7	159.2	177.7	21.7	5.97	45.2	18.9	168.7	57.4	61.7	5.35
	210	66.4	95.7	159.7	177.0	20.7	7.24	44.7	18.0	168.0	47.1	50.6	5.18
	220	65.9	93.9	159.2	176.5	21.4	7.55	45.1	17.3	168.2	48.2	51.9	5.11
	230	64.1	99.3	159.6	176.5	23.3	6.55	45.9	17.3	169.4	56.7	61.0	5.89

tallinities of PLLA-c hot-drawn fibers obtained at 210 and 220°C die temperatures might be caused by the nonuniform melt mixing during extrusion although PLLA-c had higher crystallinity before use. Big polymer particles existing in the as-spun fibers might have hindered the process of molecular orientation in the hot-drawn fibers.

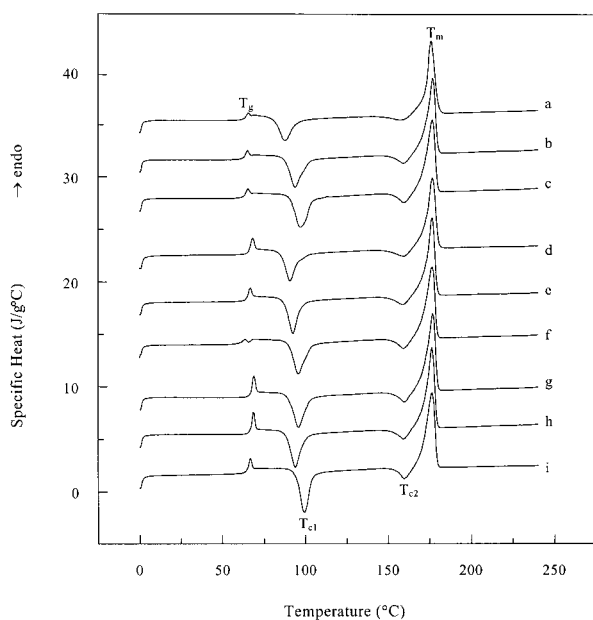
### Tensile Properties

Tensile properties of PLLA fibers were dependent on their preparation conditions.<sup>5,8,21–23</sup> In this article, the as-spun and hot-drawn fibers were all

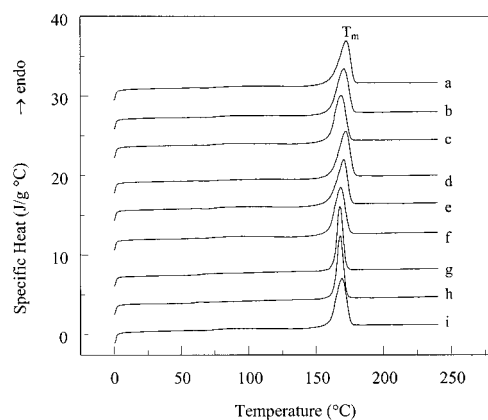
prepared in similar melt-extrusion and hot-draw conditions. The effects of the molecular weight of the raw materials and the melt-extrusion temperature on the tensile properties of fibers were studied. Results were shown in Table IV and V.

The diameters of the as-spun PLLA fibers were in the range of 250–360  $\mu\text{m}$  (Table IV). The variation was probably caused by the variation of the extrusion conditions. The diameter of the hot-drawn fibers was about 110–160  $\mu\text{m}$  (Table V).

The tensile moduli of the as-spun PLLA fibers were in the range of 1.2–2.4 GPa (Table IV), and these moduli were raised to 3.6–5.4 GPa (Table V) after hot draw. The differences of the tensile moduli among the as-spun fibers were relatively small ( $p = 0.02\text{--}1.00$ ), and the differences among the hot-drawn fibers were a



**Figure 4** DSC thermograms of the as-spun PLLA fibers. (a) a220; (b) a230; (c) a240; (d) b210; (e) b220; (f) b230; (g) c210; (h) c220; (i) c230.



**Figure 5** DSC thermograms of the hot-drawn PLLA fibers. (a) a220hd; (b) a230hd; (c) a240hd; (d) b210hd; (e) b220hd; (f) b230hd; (g) c210hd; (h) c220hd; (i) c230hd.



**Table IV Tensile Properties of the As-Spun PLLA Fibers**

Samples	Die Temperature (°C)	Diameter (μm)	Tensile Modulus (GPa)	Ultimate Strength (MPa)	Ultimate Elongation (%)	Yield Strength (MPa)	Strain at Yield (%)
PLLA-a	220	319 ± 19	2.15 ± 0.22	95.4 ± 7.9	395 ± 40	68.5 ± 4.5	3.52 ± 0.55
	230	290 ± 18	2.32 ± 0.15	79.3 ± 8.5	435 ± 54	67.9 ± 3.5	3.32 ± 0.66
	240	319 ± 21	1.76 ± 0.56	60.9 ± 17.1	4.19 ± 0.45	— <sup>a</sup>	— <sup>a</sup>
PLLA-b	210	340 ± 23	2.04 ± 0.15	60.7 ± 2.3	293 ± 85	62.9 ± 3.6	3.65 ± 0.57
	220	298 ± 40	2.24 ± 0.24	71.9 ± 9.3	440 ± 54	62.5 ± 5.8	3.60 ± 0.99
	230	310 ± 6	2.02 ± 0.26	66.0 ± 7.0	105 ± 163	69.5 ± 3.3	3.96 ± 0.17
PLLA-c	210	339 ± 36	1.81 ± 0.29	50.6 ± 4.9	8.96 ± 4.43	55.7 ± 5.0	3.90 ± 0.39
	220	269 ± 22	2.15 ± 0.18	50.8 ± 8.5	74.8 ± 91.5	58.3 ± 7.1	3.59 ± 0.68
	230	335 ± 13	2.19 ± 0.08	53.2 ± 11.2	33.4 ± 39.6	61.2 ± 5.9	2.96 ± 0.44

<sup>a</sup> Samples of a240 broke before or near the yield point.

little more significant ( $p = 0.00$ – $0.95$ ). There was a tendency that the tensile modulus was higher when the original molecular weight was higher or when the extrusion temperature was lower. The ultimate strengths of the as-spun fibers were in the range of 42–103 MPa. After hot draw, the values were raised dramatically to 300–600 MPa.

Most of the as-spun fibers showed a plastic deformation in their tensile behavior, but their toughnesses were quite different. As-spun fibers of a220, a230, b210, and b220 showed significantly higher elongation of 210–480% compared to others. For all the as-spun fibers, yielding often happened at 3–4% elongation with the tensile yield strengths of about 50–72 MPa.

Because the as-spun and the hot-drawn fibers were all prepared in the similar extrusion and

hot-draw conditions, their draw ratios as well as their crystallinity were very similar (Table III). The molecular orientation was assumed to reach a similar extent for the as-spun and hot-drawn fibers. Hence, the tensile properties of the as-spun and the hot-drawn fibers tended to be quite similar. The effects of molecular orientation on the tensile properties of the fibers will be investigated in the further studies.

In summary, the a220hd fibers with the highest molecular weight had the highest tensile modulus of 5.22 GPa and the highest ultimate strength of 535 MPa. This tensile modulus value was significantly higher ( $p < 0.01$ ) than those of the others except b210hd ( $p = 0.24$ ). The ultimate strength of the a220hd fibers was significantly higher ( $p < 0.01$ ) than those of a240hd, b230hd, c210hd, c220hd, and c230hd.

**Table V Tensile Properties of the Hot-Drawn PLLA Fibers**

Samples	Die Temperature (°C)	Diameter (μm)	Draw Ratio	Tensile Modulus (GPa)	Ultimate Strength (MPa)	Ultimate Elongation (%)	Yield Strength (MPa)	Strain at Yield (%)
PLLA-a	220 <sup>a</sup>	147 ± 7	4.71	5.22 ± 0.24	535 ± 70	39.2 ± 3.3	— <sup>b</sup>	— <sup>b</sup>
	230	151 ± 9	4.75	4.74 ± 0.25	488 ± 57	55.6 ± 7.7	148 ± 7	3.98 ± 0.24
	240	146 ± 11	4.77	4.58 ± 0.14	412 ± 27	65.4 ± 9.3	127 ± 7	3.07 ± 0.16
PLLA-b	210 <sup>a</sup>	145 ± 10	5.50	4.96 ± 0.43	484 ± 86	40.8 ± 6.6	— <sup>b</sup>	— <sup>b</sup>
	220	138 ± 13	4.66	4.47 ± 0.31	480 ± 84	51.3 ± 7.2	139 ± 13	4.00 ± 0.61
	230	134 ± 8	5.35	3.88 ± 0.27	332 ± 34	57.8 ± 7.9	116 ± 3	3.65 ± 0.43
PLLA-c	210	149 ± 10	5.18	4.46 ± 0.11	365 ± 40	66.8 ± 10.3	117 ± 4	3.12 ± 0.29
	220	119 ± 9	5.11	4.12 ± 0.36	400 ± 55	73.6 ± 13.1	112 ± 10	2.96 ± 0.15
	230	138 ± 8	5.89	4.43 ± 0.53	415 ± 50	67.3 ± 7.8	121 ± 11	3.23 ± 0.37

<sup>a</sup> Samples of a220hd and b210hd were tested in the Instron tester.

<sup>b</sup> Samples of a220hd and b210hd showed no significant yield points.

## CONCLUSIONS

PLLA with viscosity-average molecular weights of 494,600, 304,700, or 262,800 can be fabricated as fibers by a two-step melt-spinning method, i.e., melt extrusion and hot draw. Melt extrusion should be carried out at a die temperature higher than 230°C for raw materials with higher crystallinity, such as PLLA-a and PLLA-c, and higher than 220°C for PLLA-b with lower crystallinity. Tensile moduli of 1.2–2.4 GPa for the as-spun PLLA fibers and 3.6–5.4 GPa for the hot-drawn PLLA fibers were obtained by this method. The hot-draw process could increase the fiber ultimate strengths to 300–600 MPa and crystallinity to 50.3–63.7%.

The authors would like to thank Prof. C. L. Choy, Dr. Y. W. Wong, and Dr. Z. H. Liu at the Department of Applied Physics of The Hong Kong Polytechnic University (PolyU) for their help in melt extrusion; thanks also to Mr. M. N. Yeung at Materials Research Centre of PolyU for SEM and DSC services, thanks to Prof. X. M. Tao and Mr. Y. H. Siu at the Institute of Textiles & Clothing of PolyU for the use of the Instron tensile tester.

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