

Effect of Hot Drawing on Properties of Wet-Spun Poly(L,D-Lactide) Copolymer Multifilament Fibers

Marja Rissanen,¹ Arja Puolakka,¹ Terttu Hukka,² Ville Ellä,³ Minna Kellomäki,³ Pertti Nousiainen¹

¹Department of Materials Science, Tampere University of Technology, Tampere, Finland

²Department of Chemistry and Bioengineering, Tampere University of Technology, Tampere, Finland

³Department of Biomedical Engineering, Tampere University of Technology, Tampere, Finland

Received 9 April 2009; accepted 23 June 2009

DOI 10.1002/app.31015

Published online 8 September 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Polylactide stereocopolymer multifilament fibers were prepared by wet spinning and subsequent hot drawing. The stereocopolymers were poly-(L,D-lactide) [P(L,D)LA], L/D ratio 96/4, and poly-(L,DL-lactide) [P(L,DL)LA], L/DL ratio 70/30. They were dissolved in dichloromethane and coagulated in a spin bath containing ethanol. The hot-drawing temperature was 65°C. The draw ratios (DR) were up to 4.5 to the P(L,D)LA 96/4 filaments and up to 3 to the P(L,DL)LA 70/30 filaments. Wet spinning decreased crystallinities of both copolymers. Hot drawing increased the crystallinity of the P(L,D)LA 96/4 filament but not to the level of the original copolymer, whereas the as-spun and the hot-drawn P(L,DL)LA 70/30

filaments were amorphous. The filament diameter, tenacity, Young's modulus, and elongation at break were dependent on the DR. The maximum tenacity (285 MPa) and Young's modulus (2.0 GPa) were achieved with the P(L,D)LA 96/4 filament at the DR of 4.5. Respectively, the maximum tenacity of the hot-drawn P(L,DL)LA 70/30 filament was 175 MPa and Young's modulus 1.3 GPa at the DR of 3. Hot drawing slowed down *in vitro* degradation rate of both stereocopolymer filaments. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 608–615, 2010

Key words: biopolymers; crystallization; degradation; fibers; mechanical properties

INTRODUCTION

Polylactide is a bioresorbable and biocompatible polymer which is used in medical applications,^{1,2} and also in high-value packaging.³ In addition, polylactide fibers are used for apparel, nonwovens, and furnishing.⁴ Polylactide is produced by a ring-opening polymerization of lactide into high-molar-mass polymers. Lactide is the cyclic dimer of lactic acid and it exists in three stereoisomeric forms as follows: D,D cyclic dimer (D-lactide), L,L-cyclic dimer (L-lactide), and D, L-cyclic dimer (mesolactide). The copolymerization of L-lactide with a different ratio to D-lactide or DL-lactide decreases the degree of crystallinity, and thus shortens the degradation time of polymer. The complete degradation time of enantiomerically pure polylactide could be many years.⁵ Such a long degradation time is not necessary in many medical applications, as tissue engineering, and then it is possible to use poly(L,D-lactide) [P(L,D)LA] copolymers.

Polylactide filaments are normally produced by melt spinning but also solution spinning (both wet spinning and dry spinning) has been studied.⁶ Dur-

ing melt spinning, polymer is prone to thermal degradation, which can cause molecular weight decrease and thus affects the mechanical properties of polymer. During solution spinning, the polymer is not exposed to as high temperatures as during melt spinning, and thus the decrease of molecular weight is lower or nonexistent.

Wet spinning of polylactide filaments has been known for several years.⁷ The drawback of wet-spun filaments is their low mechanical strength. Nelson et al.⁸ have studied the wet spinning of poly(L-lactide) [P(L)LA], and the ultimate stress values of filaments have been between 30 and 120 MPa.

The mechanical strength of filament can be increased by hot drawing. The drawing process orientates long molecules into alignment along the longitudinal axis of the filament. The higher alignment of molecules increases the intermolecular bonds which causes higher mechanical strength. The orientation can also increase the crystallinity of filament. For normal textile filaments, the optimum drawing temperature is around or just below the glass transition temperature (T_g) of polymer.⁹

Penning and coworkers^{10,11} have increased the mechanical strength of their P(L)LA ($M_v = 910,000$) filaments remarkably by using hot-drawing temperatures near the melting temperature (T_m) of polymer. The tenacity value of filament was as high as 2.3 GPa

Correspondence to: M. Rissanen (marja.rissanen@tut.fi).

and Young's modulus of 16 GPa. The degree of crystallinity was about 53%. The filament has been extruded from chloroform/toluene solution at 60°C and subsequent hot-drawn at the temperature range from 190 to 200°C. The maximum tensile strength was attained at very low entrance velocity (0.625 cm/min). The solution-spun filaments were able to hot-draw using high-draw-ratios because of the low number of entanglements in the solution, and thus the low number of entanglements in the formed filament. The use of high-drawing-temperature increased the molecular mobility which also enabled high-draw ratios, and furthermore high-mechanical-strength values.¹² Fambri et al.¹³ have also reported the dry spinning and subsequent hot drawing of P(L)LA ($M_v = 660,000$) filament. The filament was extruded from chloroform solution at room temperature and hot-drawn at temperature of 200°C. The maximum tensile strength was 1.1 GPa, Young's modulus was 9.6 GPa, and the degree of crystallinity was about 20%.

Gupta et al.¹⁴ have utilized lower drawing temperature (90°C) to their dry-jet-wet-spun P(L)LA ($M_v = 150,000$) filament. They have extruded the filament from chloroform solution through an air gap into a methanol-containing spin bath, and the filament was hot-drawn at 90°C. The maximum tensile strength of filament was 0.6 GPa, Young's modulus was 8.2 GPa, and the degree of crystallinity was about 40%.

The hot drawing of solution-spun polylactide stereocopolymers has not studied as widely as the hot drawing of enantiomerically pure polylactide. Penning et al.¹⁵ have studied dry spinning and subsequent hot drawing of P(L,D)LA 95/5 copolymer filaments. The filaments were extruded from chloroform/toluene solution at 60°C and the optimum drawing temperature was 145°C. The tensile strength of filaments was 0.95 GPa, Young's modulus was 9.2 GPa, and the degree of crystallinity was about 20%.

The previous solution spinning and hot-drawing studies have been focused on dry-spun or dry-jet-wet-spun monofilament fibers. However, we wanted to study the hot drawing of wet-spun P(L,D)LA copolymer multifilament fibers. In our earlier study, we have prepared poly(L,D-lactide) multifilament fibers by wet spinning using different spin draw ratios between the spinneret and the take-up bobbin.¹⁶ The tenacity values were upto 150 MPa and Young's modulus values were upto 1.7 GPa. Now, we studied the effect of hot drawing on the mechanical and degradation properties of P(L,D)LA multifilament fibers.

EXPERIMENTAL

Materials

The two tested medical grade polylactide stereocopolymers were supplied from Purac Biochem by

TABLE I
The Tested Copolymers, Their IVs, Molecular Weights, and Spin Dopes

| Copolymer | IV (dL/g) | M_v (g/mol) | Spin dope concentration (%) | Spin dope viscosity (cP) |
|-----------------|-----------|---------------|-----------------------------|--------------------------|
| P(L,D)LA 96/4 | 2.2 | 93,700 | 15 | 1720 |
| P(L,DL)LA 70/30 | 3.1 | 167,200 | 10 | 1660 |

(Gorinchem, The Netherlands). The polymers were P(L,D)LA, L/D ratio 96/4, and poly-(L,DL-lactide) [P(L,DL)LA], L/DL ratio 70/30, as shown in Table I. The intrinsic viscosities (IVs) were given by the polymer supplier, and the viscosity-average molecular weight (M_v) values were determined by gel permeation chromatography.¹⁷

Spin dope preparation, wet spinning, and hot drawing

The polymer was dissolved in dichloromethane (analytical grade) in a conical flask covered by a glass stopper at room temperature. Magnetic stirrer was used for the dissolution until the dissolution was clear. The spin dope concentrations were calculated from the volume of solvent. Viscosity was measured by Brookfield viscometer. The spin dope concentrations and viscosities are given in Table I.

The polymer solution was pumped by Zenith gear pump (Allweiler AG, Radolfzell, Germany) through the spinneret (20 holes, hole diameter 0.1 mm; Enka Technica GmbH, Heinsberg, Germany) into a spin bath containing ethanol (analytical grade). The filaments were reeled to a bobbin (diameter 87 mm). The extrusion velocity was 7 m/min and the reeling velocity was 10 m/min. The coagulation time of filaments was 5.6 s. The schematic drawing of wet spinning equipment is shown in Figure 1.

The filaments were evacuated in a vacuum oven at 40°C overnight to eliminate the chemical residues. The filaments were stored in a desiccator until their hot drawing and testing to avoid their moisture intake.

The separate hot drawing was carried out in an electric tube furnace, 900 mm in length. The utilized hot-drawing temperature was 65°C and the draw ratios (DR) were upto 3 to P(L,DL)LA 70/30 and upto 4.5 to P(L,D)LA 96/4. The draw ratios were calculated from the ratio of final velocity (reeling velocity) and initial velocity (entrance velocity). The entrance velocity was 4 m/min.

Filament characterization

A scanning electron microscope (Jeol JSM-T100, Jeol, Tokyo, Japan) was used to characterize the filament

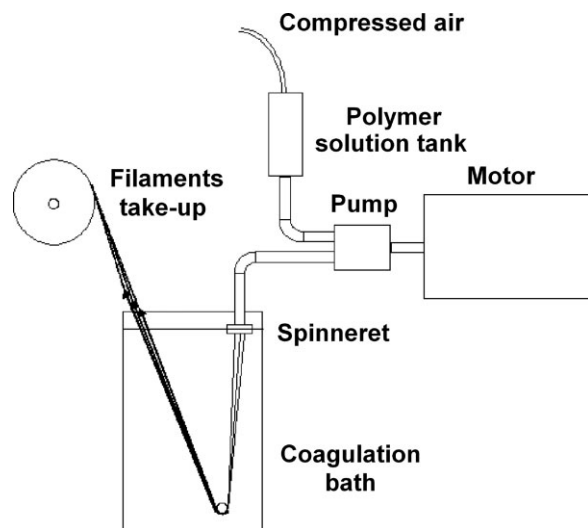


Figure 1 Schematic drawing of wet spinning equipment.

surface. An optical microscope was used to determine the mean value of filament diameter from 50 individual filaments.

A heat-flux type differential scanning calorimeter (DSC) 821TM from Mettler Toledo (Columbus, OH) was used for measurements of thermal behavior of the copolymer granulates, as-spun and hot-drawn filaments. The glass transition temperatures (T_g), the peak melting temperatures (T_m), the crystallization enthalpies (ΔH_c), and the melting enthalpies (ΔH_m) were measured at a heating rate of 10 K min^{-1} . The value of 93.6 J/g was used as H_m for the totally crystalline P(L)LA crystal.¹⁸

The breaking force, the Young's modulus, and the elongation at break of 50 individual filaments were tested using the tensile testing machine (Vibrodyn by Lenzing AG, Lenzing, Austria), having the gauge length of 20 mm, the testing velocity of 20 mm/min, and the maximum force of cell load of 100 cN. Because the diameters of filaments were differed from each other, the breaking force was converted to the tenacity.

For *in vitro* degradation tests, the filament bundles were placed in test tubes and the tubes were filled (about 10 mL) with soaking solution (phosphate buffer solution).¹⁹ The filled test tubes were kept at constant temperature ($37^\circ\text{C} \pm 1^\circ\text{C}$). The soaking solution was changed during the testing to maintain a pH of 7.4 ± 0.2 . At each data point, the filaments were taken out from the test tube, and the breaking forces of 20 individual wet filaments were measured. The data points were 0, 2, 4, 6, 8, 12, 16, 20, and 24 weeks.

RESULTS AND DISCUSSION

Hot drawing

Both copolymers were possible to draw at the temperature of 65°C . At this temperature, the maximum

DR was 4.5 to the P(L,D)LA 96/4 filaments and 3 to the P(L,DL)LA 70/30 filaments. We also tried higher drawing temperatures ($>70^\circ\text{C}$), but the filaments shrank and broke [P(L,DL)LA 70/30] or they melted together in the yarn [P(L,D)LA 96/4] during hot drawing at higher temperatures.

In the earlier studies, much higher draw temperatures has been used to dry-spun P(L)LA filament.^{10–13} In their studies, the optimum hot-drawing temperature was as high as 200°C , which is near the T_m of P(L)LA. However, their use of thick monofilament enabled the high-draw temperature, whereas we used thin multifilament yarn.

Filament surface structure

The cross section of as-spun P(L,D)LA 96/4 was collapsed and serrated as shown in Figure 2(a,b). It was also observed distinct skin on the surface and porous structure inside the filament. The skin-core structure was formed during the coagulation process and it is typical for wet-spun filaments.²⁰ The surface of filament was solidified immediately when immersed to the spin bath and thereby the skin was formed first.^{16,21} Because the skin was solidified immediately, the solvent and nonsolvent were trapped inside the filament. The porous structure was formed when solvent and nonsolvent were evaporated from the filament during drying. The similar porous structure was observed also in the previous studies of wet-spun filaments.^{14,22,23} The collapsed, serrated cross section was formed when the solidified outer skin was rigid and more solvent left the filament than nonsolvent entered.²⁰ After hot drawing, the filament structure was smoother, but the original serrated structure still existed as shown in Figure 2(c,d).

The surface structures of P(L,DL)LA 70/30 filaments were partly serrated and partly smooth as shown in Figure 3. The P(L,DL)LA 70/30 polymer did not solidified as rapidly as P(L,D)LA 96/4 in the spin bath and the skin of filament was softer and more deformable.^{16,21} The cross section of filament became more circular. In the cross section of filaments was not distinct porous structure which was caused by the slow solidification process. The hot-drawn filaments had smaller diameter but the appearance was similar as the as-spun filaments.

Thermal behavior and crystallinity

T_g and T_m values of copolymer granulates, as-spun filaments, and hot-drawn filaments are given in Table II. According to the DSC measurements, the T_g of P(L,D)LA 96/4 copolymer granulates was in the range of $65.1\text{--}67.9^\circ\text{C}$ and the T_m was 157.3°C . The T_g of the as-spun P(L,D)LA 96/4 filaments remained

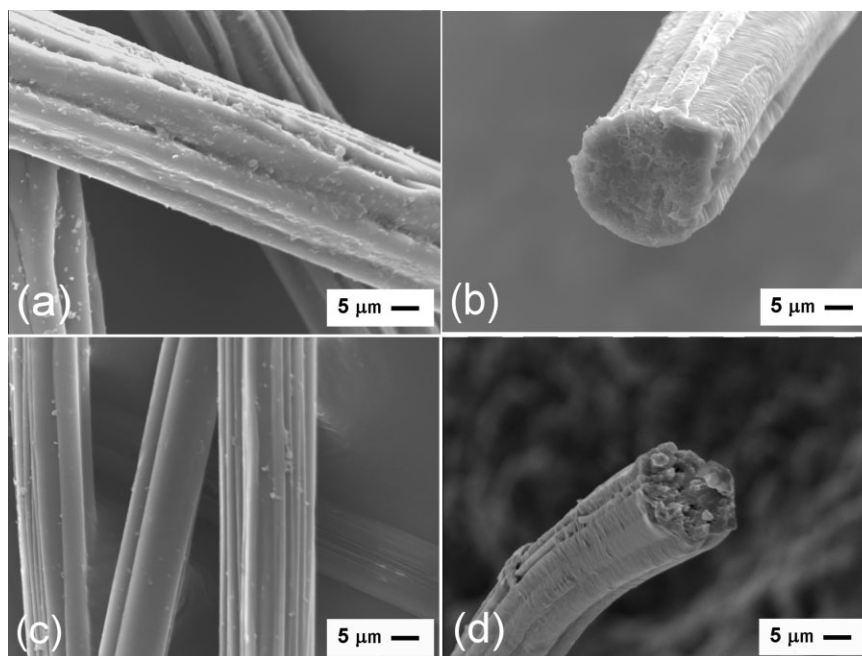


Figure 2 SEM-images of P(L,D)LA 96/4 filaments: (a and b) as-spun and (c and d) hot-drawn at DR 4.5.

practically unchanged ($T_g = 66.3^\circ\text{C}$) compared with the copolymer granulates. The increase of the T_g value was observed with the hot-drawn filaments. The T_g value was determined at 77.6°C but the cold-crystallization peak was overlapped with the glass transition, see Figure 4 (curve 3).

The P(L,DL)LA 70/30 copolymer granulates had a lower T_g ($59.6\text{--}61.7^\circ\text{C}$) and T_m (121.5°C) compared

with P(L,D)LA 96/4 copolymer. The T_g value of the as-spun P(L,DL)LA 70/30 filaments remained also practically unchanged (62.0°C). The T_g value of hot-drawn filaments was 60.3°C , as shown in Table II and Figure 5.

The crystallinity values of granulates, as-spun, and hot-drawn filaments are given in Table II. The P(L,D)LA 96/4 granulates were partially crystalline

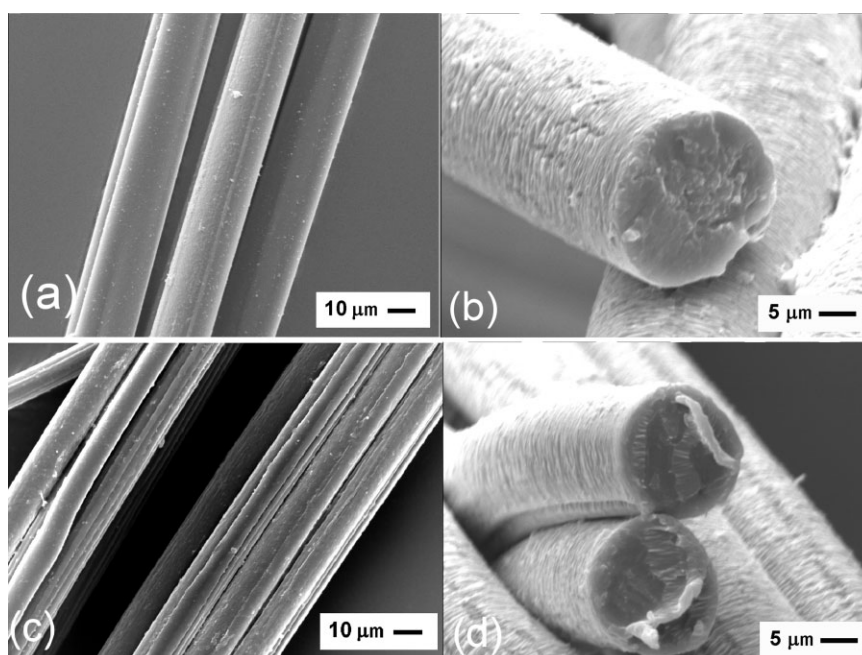


Figure 3 SEM-images of P(L,DL)LA 70/30 filaments: (a and b) as-spun and (c and d) hot-drawn at DR 3.

TABLE II
 T_g and T_m Values and Crystallinities of the Granulates, As-Spun, and Hot-Drawn Filaments

| Material | T_g (°C) | T_m (°C) | X (%) |
|------------------------------|-------------------------|-------------|------------|
| P(L,D)LA 96/4 | | | |
| Granulates | 65.1–67.9 | 157.3 | 40.0 ± 0.0 |
| As-spun filaments | 66.3 ± 0.1 | 155.4 ± 0.0 | 3.2 ± 0.2 |
| Hot-drawn filaments (DR 4.5) | 76.6 ± 0.3 ^a | 158.0 ± 0.3 | 29.6 ± 0.2 |
| P(L,DL)LA 70/30 | | | |
| Granulates | 59.6–61.7 | 121.5 | 14.0 ± 0.0 |
| As-spun filaments | 62.0 ± 0.1 | – | 0.1 ± 0.0 |
| Hot-drawn filaments (DR 3) | 60.3 ± 0.0 | – | 0.9 ± 0.1 |

^a The cold-crystallization peak was overlapped with the glass transition.

having the degree of crystallinity of 40%. The crystallinity of as-spun filaments was lower compared with polymer granulates. In the DSC curves of as-spun P(L,D)LA 96/4 filaments have been found post-crystallization, that is to say cold-crystallization (X_{cc})^{8,24,25} in the temperature range approximately from 75 to 120°C with the peak at 91°C, see Figure 4, curve 2. The initial degree of crystallinity (X) of 3.2% was calculated by subtracting the crystallinities (X_{cc}) gained during the postcrystallization from the total crystallinities (X_c) of the melting endotherms ($X = X_c - X_{cc}$). Hot drawing decreased the cold-crystallization temperature and the cold-crystallization enthalpy, see Figure 4, curve 3.²⁵ The crystallinity of hot-drawn filaments was higher ($X = 29.6\%$) than that of as-spun filaments, but it was not in the level of the original copolymer granulate. Compared with the melt-spun filaments²⁶ our hot-drawn wet-spun P(L,D)LA 96/4 filament had similar crystallinity. Hot drawing led to the higher degree of crystallinity than spin drawing of filaments in our previous study.¹⁶

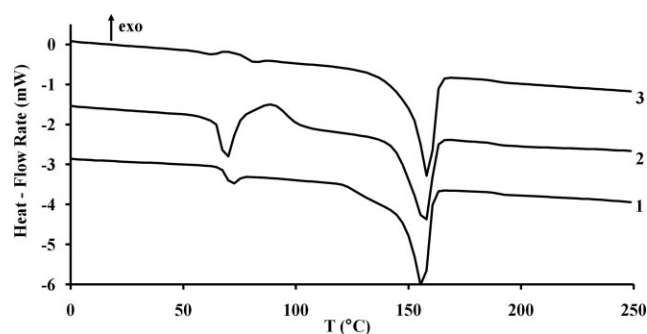


Figure 4 DSC curves of P(L,D)LA 96/4 copolymer: (1) granulate; (2) as-spun filament; and (3) hot-drawn filament at DR 4.5. The curves have been shifted by an arbitrary amount for clarity.

The P(L,DL)LA 70/30 copolymer granulates were partially crystalline having the degree of crystallinity of 14%. There was no cold-crystallization during the heating process in the DSC, see Figure 5. The crystallinity was lost during wet spinning and the wet-spun P(L,D)LA 70/30 filaments were amorphous ($X = 0.1\%$). The hot-drawn P(L,DL)LA 70/30 filaments were also amorphous ($X = 0.9\%$), as the spin-drawn P(L,DL)LA 70/30 filaments in our previous study.¹⁶ Compared with the melt-spun P(L,DL)LA 70/30 filaments our wet-spun hot-drawn filaments had lower crystallinity.²⁷

The drawing ability of as-spun filaments can be explained by the thermal behavior of filaments. The better hot-drawing ability of as-spun P(L,D)LA 96/4 filaments was caused by its higher T_g and T_m values. The as-spun P(L,DL)LA 70/30 filaments were amorphous and the shrinkability of filaments was very high. This high shrinkability resisted the stretching of filament yarn.

Mechanical properties

The diameters of as-spun and hot-drawn filaments are in Table III. Hot drawing stretched the filaments and they became thinner. The diameter of as-spun P(L,D)LA 96/4 filament was 26 μm , whereas the diameter of hot-drawn filament was as low as 14 μm at the DR of 4.5. Respectively, the diameter of as-spun P(L,DL)LA 70/30 filament was 27 μm and that of hot-drawn filament was 15 μm at the DR of 3. The diameters of hot-drawn filaments were at the same level as the filaments prepared by high spin draw ratio in our earlier study.¹⁶

Compared with the other wet spinning studies, our hot-drawn filaments are relatively fine (14–15 μm). In the earlier studies, filaments having diameters in the range from 28 to 550 μm have been prepared.^{8,14}

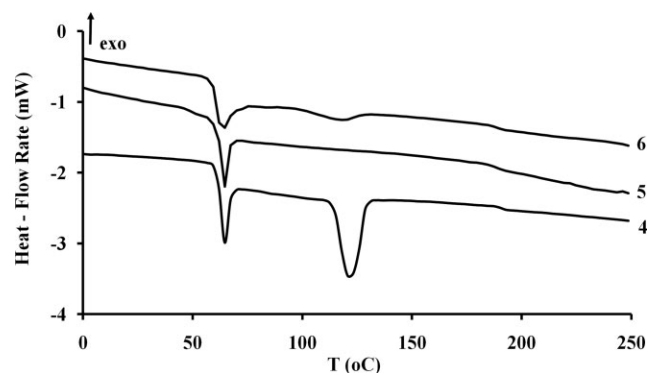


Figure 5 DSC curves of P(L,DL)LA 70/30 copolymer: (4) granulate; (5) as-spun filament; and (6) hot-drawn filament at DR 3. The curves have been shifted by an arbitrary amount for clarity.

TABLE III
Diameters and Mechanical Properties of As-Spun and Hot-Drawn Filaments

| Draw ratio | Diameter (μm) | Tenacity (MPa) | Young's modulus (GPa) | Elongation (%) |
|-----------------|----------------------------|----------------|-----------------------|----------------|
| P(L,D)LA 96/4 | | | | |
| As-spun | 26 \pm 3 | 78 \pm 7 | 1.2 \pm 0.1 | 235 \pm 15 |
| 2.5 | 20 \pm 2 | 108 \pm 14 | 1.2 \pm 0.2 | 97 \pm 19 |
| 3 | 17 \pm 1 | 154 \pm 22 | 1.9 \pm 0.2 | 75 \pm 15 |
| 4.5 | 14 \pm 1 | 285 \pm 34 | 2.0 \pm 0.2 | 30 \pm 2 |
| P(L,DL)LA 70/30 | | | | |
| As-spun | 27 \pm 3 | 52 \pm 5 | 0.9 \pm 0.1 | 260 \pm 21 |
| 2 | 17 \pm 2 | 130 \pm 20 | 1.5 \pm 0.2 | 69 \pm 11 |
| 3 | 15 \pm 2 | 175 \pm 24 | 1.3 \pm 0.2 | 44 \pm 4 |

The tenacity and Young's modulus values of as-spun and hot-drawn filaments are also shown in Table III. The maximum tenacity of P(L,D)LA 96/4 filaments (285 MPa) and Young's modulus (2.0 GPa) were achieved with the DR of 4.5. The tenacity of as-spun filament was as low as 78 MPa, so the increase of tenacity was significant. The maximum tenacity value of P(L,DL)LA 70/30 filament was 175 MPa at the DR of 3. At this DR, the Young's modulus value was 1.3 GPa. Compared with the tenacities achieved in our earlier wet spinning study, hot-drawing increased especially the tenacity values of P(L,D)LA 96/4 filaments.¹⁶

The elongation at break decreased as the function of the DR as shown in Table III. The elongation at break of P(L,D)LA 96/4 filament decreased from about 250% to 30% and that of P(L,DL)LA 70/30 to 44%.

The stress-strain curves of P(L,D)LA 96/4 filaments are presented in Figure 6 and those of P(L,DL)LA 70/30 filaments in Figure 7. In the beginning of curves was a linear Hookean region, where the molecular chains started to stretch and the molecules straightened in the amorphous region of the filament, and the intermolecular bonds strained. The yield stress of as-spun P(L,DL)LA 70/30 was lower

than that of as-spun P(L,D)LA 96/4 filament, and therefore, the chain molecules and intermolecular bonds in as-spun P(L,DL)LA 70/30 filament were easier to strain compared with P(L,D)LA 96/4 as-spun filaments. The yield stresses of hot-drawn filaments (DR 2–DR 3) were similar with both copolymers. After the Hookean region came a region of easier extension. This region was very long with as-spun filaments, whereas it was practically disappeared with hot-drawn filaments (DR 4.5 in Fig. 6 and DR 3 in Fig. 7). In this easy extension region, the highly strained bonds in the amorphous region broke because they could not withstand the force applied to them. The molecules straightened further, and the load of the other bonds increased. Therefore, the extension became easier. After this region came the region of increasing slope. In this region, some of the molecules were fully straightened, and further extension became more difficult. The increasing strain affected on the bonds and molecules, and finally the filament broke.²⁸

In vitro degradation

The *in vitro* hydrolytic degradation results of as-spun and hot-drawn filaments are presented in

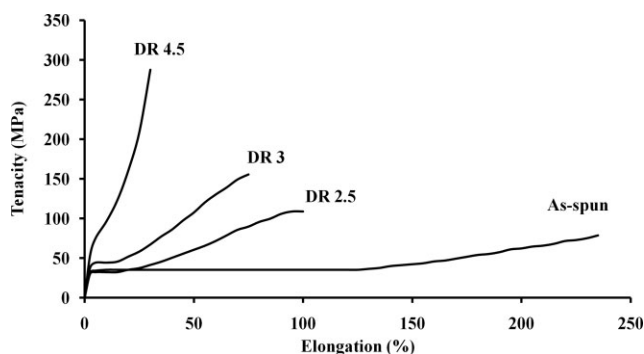


Figure 6 Tenacity-elongation curves of as-spun and hot-drawn P(L,D)LA 96/4 filaments.

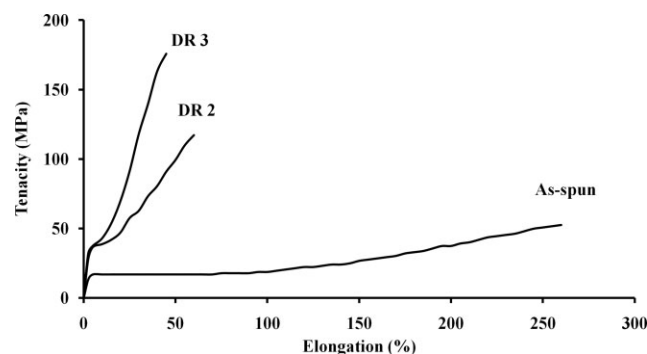


Figure 7 Tenacity-elongation curves of as-spun and hot-drawn P(L,DL)LA 70/30 filaments.

Figures 8 and 9. Hot drawing had an effect on the degradation rate of both copolymers. The decrease of tenacity was about 40% for the as-spun $P_{(L,D)}$ LA 96/4 filaments and only about 10–20% for the hot-drawn filaments after 24 weeks. Hot drawing increased the crystallinity of $P_{(L,D)}$ LA 96/4 filaments, and thus had an effect on the degradation rate of filaments. During the hydrolytic degradation, water first diffuses into the amorphous regions of the polymer, and it causes the breakage of the ester bonds. After amorphous regions, the hydrolytic degradation happens in the crystalline regions.²⁹ Paakinaho et al.³⁰ have studied the hydrolytic degradation of melt-spun filaments made from the same copolymer as used in this study, and the tenacity loss of their filaments has been about 11% after 24 weeks. Their filaments have been γ -irradiated (25 kGy) for sterility, and that is why the results are not fully comparable.

Because the $P_{(L,D)}$ LA 70/30 filaments were amorphous, their degradation rate was faster than that of semicrystalline $P_{(L,D)}$ LA 96/4. The tenacity loss of as-spun $P_{(L,DL)}$ LA 70/30 filament was about 70% after 16 weeks. After this period, the mechanical strength of as-spun filaments was so low that the filaments broke already before the mechanical testing. Hot drawing declined the degradation rate, and the decrease of tenacity was only about 30–40% for the hot-drawn $P_{(L,D)}$ LA 70/30 filaments after 24 weeks. The differences in the degree of crystallinity do not explain the decrease of degradation rate because both the as-spun and hot-drawn filaments were amorphous. It seems that the orientation of polymer has also effect on its degradation properties.

CONCLUSIONS

Poly lactide copolymer multifilaments [$P_{(L,D)}$ LA 96/4 and $P_{(L,DL)}$ LA 70/30] were prepared by wet spinning and subsequent hot drawing. The drawability of the partially crystalline $P_{(L,D)}$ LA 96/4 multifilaments was better compared with the amorphous

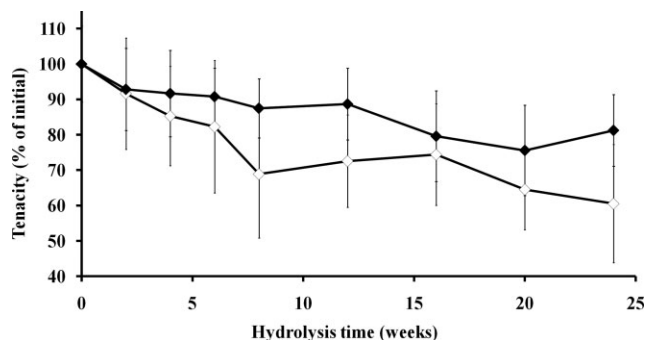


Figure 8 Retention of the tenacity *in vitro* for $P_{(L,D)}$ LA 96/4 filaments: (\diamond) as-spun and (\blacklozenge) hot-drawn at DR 4.5.

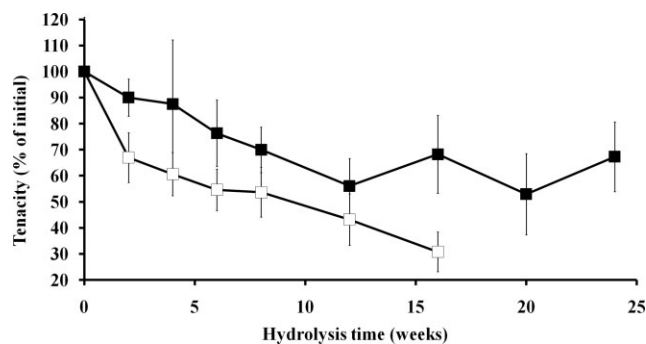


Figure 9 Retention of the tenacity *in vitro* for $P_{(L,DL)}$ LA 70/30 filaments: (\square) as-spun; (\blacksquare) hot-drawn at DR 3.

$P_{(L,DL)}$ LA 70/30 filaments. Hot drawing increased the mechanical strength of filaments. The maximum tenacity of the $P_{(L,D)}$ LA 96/4 filaments was 285 MPa and Young's modulus was 2.0 GPa. Respectively, the values of the $P_{(L,DL)}$ LA 70/30 filaments were 175 MPa and 1.3 GPa. Hot drawing extended the degradation time of filaments. In the possible end-uses of filaments, the deceleration of degradation rate caused by hot drawing should be taken into account.

References

- Eppley, B. L. *Operat Tech Plast Reconstr Surg* 2003, 9, 36.
- Maurus, P. B.; Kaeding, C. C. *Oper Tech Sports Med* 2004, 12, 158.
- Auras, R.; Harte, B.; Selke, S. *Macromol Biosci* 2004, 4, 835.
- Vink, E. T. H.; Rábago, K. R.; Glassner, D. A.; Springs, B.; O'connor, R. P.; Kolstad, J.; Gruber, P. R. *Macromol Biosci* 2004, 4, 551.
- Suuronen, R.; Pohjonen, T.; Hietanen, J.; Lindqvist, C. *J Oral Maxillofac Surg* 1998, 56, 604.
- Linneman, B.; Sri Harwoko, M.; Gries, T. *Chem Fibers Int* 2003, 53, 426.
- Kulkarni, R. K.; Pani, K. C.; Neuman, C.; Leonard, F. *Arch Surg* 1966, 93, 839.
- Nelson, K. D.; Romero, A.; Waggoner, P.; Crow, B.; Borneman, A.; Smith, G. M. *Tissue Eng* 2003, 9, 1323.
- Fourne, F. *Synthetic Fibers—Machines and Equipment Manufacture, Properties*; Hanser: Munich, 1999.
- Leenslag, J. W.; Pennings, A. J. *Polymer* 1987, 28, 1695.
- Postema, A. R.; Pennings, A. J. *J Appl Polym Sci* 1989, 37, 2351.
- Eling, B.; Gogolewski, S.; Pennings, A. J. *Polymer* 1982, 23, 1587.
- Fambri, L.; Pegoretti, A.; Mazzurana, M.; Migliaresi, C. *J Mater Sci Mater Med* 1994, 15, 679.
- Gupta, B.; Revagade, N.; Anjum, N.; Atthoff, B.; Hilborn, J. *J Appl Polym Sci* 2006, 100, 1239.
- Pennings, J. P.; Dijkstra, H.; Pennings, A. J. *Polymer* 1993, 34, 942.
- Rissanen, M.; Puolakka, A.; Hukka, T.; Ellä, V.; Nousiainen, P.; Kellomäki, M. *J Appl Polym Sci* 2009, 113, 2683.
- Ellä, V.; Kellomäki, M.; Törmälä, P. *J Mater Sci Mater Med* 2005, 16, 655.
- Fischer, E. W.; Sterzel, H. J.; Wegner, G.; *Kolloid, Z. Z Polym* 1973, 251, 980.
- Shah, S. S.; Chay, Y.; Pitt, C. G. *J Control Release* 1992, 18, 261.

20. Frushour, B. G.; Knorr, R. S. In *Handbook of Fiber Chemistry*; Lewin, M., Ed.; CRC: Boca Raton, FL, 2007; Chapter 12.
21. Rissanen, M.; Puolakka, A.; Nousiainen, P.; Kellomäki, M.; Ellä, V. *J Appl Polym Sci* 2008, 110, 2399.
22. Gupta, B.; Revagade, N.; Anjum, N.; Atthoff, B.; Hilborn, J. *J Appl Polym Sci* 2006, 101, 3774.
23. Gao, H.; Gu, Y.; Ping, Q. *J Control Release* 2007, 118, 325.
24. Cao, X.; Mohamed, A.; Gordon, S. H.; Willet, J. L.; Sessa, D. J. *Thermochim Acta* 2003, 406, 115.
25. Solarski, S.; Ferreira, M.; Devaux, E. *Polymer* 2005, 46, 11187.
26. Ellä, V.; Gomes, M. E.; Reis, R. L.; Törmälä, P.; Kellomäki, M. *J Mater Sci Mater Med* 2007, 18, 1253.
27. Fambri, L.; Bragagna, S.; Migliaresi, C. *Macromol Symp* 2006, 234, 20.
28. Morton, W. E.; Hearle, J. W. S. *Physical Properties of Textile Fibres*; Textile Institute: Manchester, 1997.
29. Vert, M.; Li, S. M.; Spenlehauer, G.; Guerin, P. *J Mater Sci Mater Med* 1992, 3, 432.
30. Paakinaho, K.; Ellä, V.; Syrjälä, S.; Kellomäki, M. *Polym Degrad Stab* 2009, 94, 438.