Resorbable Materials of Poly(L-lactide). V. Influence of Secondary Structure on the Mechanical Properties and Hydrolyzability of Poly(L-lactide) Fibers Produced by a Dry-Spinning Method

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Synopsis

Fibers of poly(L-lactide) (PLLA) with a loosened fibrillar structure were produced by solution spinning from a good solvent (chloroform) in the presence of various additives (camphor, polyurethanes). No decrease in mechanical properties was observed as compared with PLLA fibers spun from a good solvent only. *In vitro* degradation studies showed that the rate of degradation of PLLA fibers with the loosened fibrillar structure was increased approaching that found for fibers composed of the homopolymer of glycolide or copolymers of glycolide and L-lactide. Helices on the fiber surface caused by melt fracture during spinning of the fibers leads to higher knot strengths of the hot-drawn PLLA fiber up to 70% of the tensile strength.

INTRODUCTION

Preparation of polylactide fibers for general medical application[1,2] has found recently a renewed interest.[3-5] Poly(L-lactide) (PLLA) fibers with a tensile strength at break in the range of 1–1.2 GPa and modulus up to 15 GPa were produced upon hot drawing of fibers spun, respectively, from poor[3] and good solvents.[4] PLLA fibers with a structurized surface were found to have knot strengths that were two times higher than that of fibers with the same tensile strength, but with a smooth surface.[4] It is claimed that PLLA fibers show an insufficient rate of resorption,[6-8] which make them rather undesirable for use in surgery.

However, it has recently been found that hot drawing of PLLA fibers spun in the presence of a small amount of polyurethane leads to the fibers with a highly loosened fibrillar structure.[9] This type of structure enhances the diffusion of body fluids into the fiber, thereby speeding up the resorption, which takes place at a rate comparable to that of commercially produced sutures. Highly fibrillated PLLA fibers can be also produced upon hot drawing of porous materials obtained by crystallization of polylactide in presence of low molecular weight additives from solution in good solvents.[10] This paper provides detailed information on the preparation of these polylactide

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fibers and the relationship between the processing conditions and the various secondary structures.

EXPERIMENTAL

Materials and Techniques. Poly(L-lactide) with the viscosity-average molecular weight in the range 1–5.5 × 10^5 was synthesized according to the procedure described previously.[3] The intrinsic viscosities were measured in chloroform at 25°C. The viscosity-average molecular weight of PLLA was calculated using the formula[11] $[\eta] = 5.45 \times 10^{-4} \overline{M}_v^{0.73}$. Zinc 2-ethyl hexanoate was prepared and used as a catalyst for the polymerization of lactides. A polyurethane was synthesized by reaction of 4,4′-diphenylmethane diisocyanate (MDI) with a copolymer prepared from PLLA ($\overline{M}_n$ = 1000) and diethylene glycol (DEG), using 1,4-butane diol as a chain extender. The polymerization was carried out according to standard procedures.[12] The medical-grade polyesterurethane used in the present study was purified by three times precipitation from solution in *N,N*-dimethylformamide (DMF) and tetrahydrofuran (THF).[9] Camphor (Merck) was used as supplied. All solvents were purified prior use according to routine procedures.

Spinning of the Fibers. Fibers of PLLA with a viscosity-average molecular weight ($\overline{M}_v$) in the range 1.6–4.6 × 10^5 were produced by a dry spinning method, as reported elsewhere.[4] To obtain some idea about the role played by adsorption, in addition to the untreated glass extruder, a silanized glass extruder and a stainless-steel cylinder having a capillary die with diameter 0.25 mm and length 10 mm were also used for spinning of the fibers.

The polymer solutions were extruded at room temperature. Chloroform was used as a solvent. Concentrations of the polymer were in the range 10–18% (w/v). Toluene, camphor, a copolymer—poly(L-lactide)—polyurethane, and a commercial, medical-grade polyesterurethane were used as additives with concentrations, respectively, of 30% (v/v), 20% (w/w), and 5% (w/w) for both polyurethanes. No orientation or degradation was introduced during the low-speed spinning of the fibers.

Hot Drawing. Hot-drawing experiments were carried out in an electric tube furnace, 300 mm in length. Details concerning temperature regulation are given elsewhere.[3,4] The velocity of the fiber at the entrance of the tube was about 2 cm · min^{-1}. The fiber was collected on the takeup bobbin at a speed in the range of 12–60 cm · min^{-1}.

Characteristics of the Fibers. The mechanical properties of the fibers were measured at room temperature using a Zwick tensile tester at a crosshead speed of 12 mm · min^{-1}. The length of the specimen was 28 mm. The cross-sectional areas of the fibers were calculated from the fiber weight and length, assuming a value of 1290 kg · m^{-3} for the density of the fiber. All the tensile properties, given in this paper, represent average values of five or six tests. An ISI-DS 130 scanning electron microscope was used for observation of the fiber surfaces.

Hydrolysis. *In vitro* degradation of hot-drawn PLLA fibers was studied by submerging the fibers in a 0.09% (w/v) aqueous solution of NaCl containing a 0.2M phosphate buffer of pH 7[13] (saline solution). The degradation was carried out in a thermostatically controlled oil bath at 37 ± 1°C.

RESULTS AND DISCUSSION

Polymerization of Poly(L-lactide)

Figure 1 illustrates the effect of polymerization temperature and polymerization time on $\overline{M}_v$ of poly(L-lactide). It can be seen that the viscosity-average molecular weight of PLLA samples obtained at a given temperature depends greatly on polymerization time. After 17 and 21 h of polymerization at 130°C using stannous 2-ethyl hexanoate as a catalyst the samples with $\overline{M}_v$, respectively, 4.6×10^5 and 5.5×10^5 can be produced. For each polymerization temperature the value of $\overline{M}_v$ levels off after a certain optimum period. This observation is in a good agreement with data given elsewhere.[3,5,13] It was found that for the temperature range under investigation (130–160°C), lowering of the polymerization temperature leads to higher values of the optimal molecular weight, $\overline{M}_v$ max.

It has frequently been suggested that stannous compounds might be potentially toxic when present as residues in implanted polymeric devices. Therefore, an effort has been made to develop a more compatible catalyst for synthesis of polylactides. A zinc 2-ethyl hexanoate synthesized at present study was used for synthesis of poly(L-lactide). Preliminary results show that the use of this catalyst leads to PLLA with the high molecular weight. Further work on the polymerization is in progress and will be reported soon.

Fibers with Various Secondary Structures

Fibers of PLLA ($\overline{M}_v = 4.6 \times 10^5$) were extruded at different speeds (1–16 cm · min^{-1}) from a (18% w/v) solution of the polymer in a solvent-poor

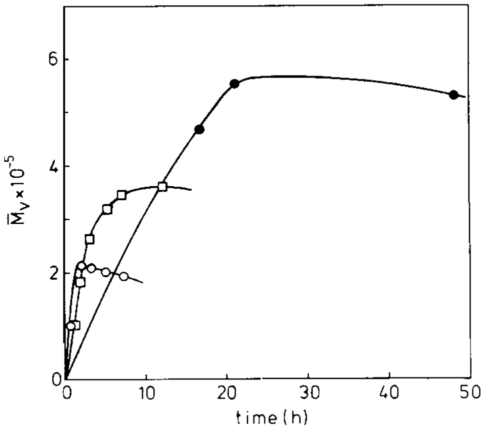

Fig. 1. Effect of polymerization time on the viscosity-average molecular weight $\overline{M}_v$ of PLLA samples polymerized at various temperatures: (●) 130°C; (□) 140°C; (○) 160°C [140°C and 160°C].[5]

solvent mixture [chloroform 70/toluene 30% (v/v)]. Figure 2 shows scanning electron micrographs of the as-spun fibers extruded at various spinning rates. The fibers appeared to have a regular structure, due to melt fracture.[4] This phenomenon was also observed for other polymers[14,15] and is caused by elastic turbulences of the polymeric flow occurring above a certain critical shear rate. This can lead to a regular "spiralling" distortion of the extrudate. In the present study this secondary structure of the as-spun PLLA fibers does not seem to be strongly affected by adsorption effects since a stainless-steel cylinder, a silanized glass, and untreated glass vessel yielded the same structure of the fibers.

Figure 3 presents the values of the helical pitch formed on the as-spun PLLA fibers as a function of the spinning rate. Increasing the spinning rate, i.e., the pressure applied to the polymer solution, increases also the pitch of the helical distortion on the fiber. It was found that there is a linear relation between the pitch and the spinning rate. An extrapolation of the spinning rate to zero leads to a value representing the thickness of the "helical band" on the fiber surface (20–30 μm). Fibers made of biodegradable polymers can be considered as a potential material for several medical applications such as sutures[1,3,4,16,17] or reinforcing elements for implants in the field of orthopedic surgery.[18] It was recently reported that "structurized" PLLA fibers had a higher knot strength then those of smooth ones.[4] As the knot strength is an important property of medical suture materials, it was essential to investigate the effect of the "secondary surface structure" of PLLA fibers on their mechanical properties. In the present study the strength was determined of square knots,[19] in which the throws are joined in a parallel way. The force in tensile testing is applied to two

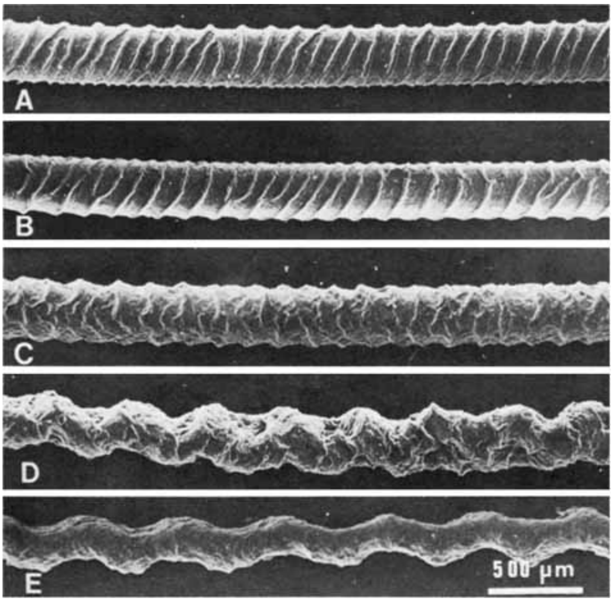

Fig. 2. Scanning electron micrograph of PLLA fibers. The micrograph illustrates the effect of extrusion speed on the surface morphology of as-spun fibers: (A) 1 cm · min^{-1}; (B) 2 cm · min^{-1}; (C) 3.5 cm · min^{-1}; (D) 9 cm · min^{-1}; (E) 12 cm · min^{-1}.

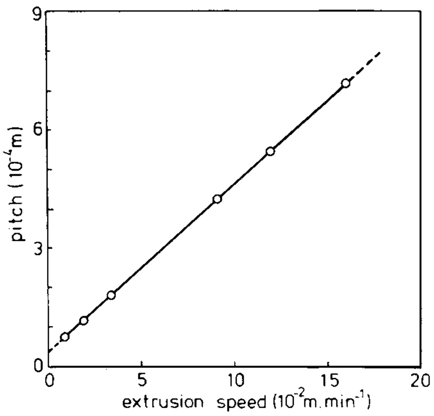

Fig. 3. Effect of the spinning rate on the helical pitch of the as-spun PLLA fibers.

free ends of the fiber and fracture always occurred in the knot because it forms the weakest spot as a result of severe bending. Other types of knots were found to have the same strength.

The PLLA fibers were hot drawn at 200°C, the optimal drawing temperature,[3,4] to $\lambda = 10$. The typical mechanical properties of the hot-drawn fibers are summarized in Table I. Unpublished results of work on solution spinning of PLLA fibers, using a sample with $\overline{M}_v = 1.7 \times 10^5$, showed that hot-drawn PLLA fibers spun from a good solvent-poor solvent mixture [chloroform 70/toluene 30% v/v] had a higher initial modulus (up to 14.5 GPa) than fibers spun from a good solvent (only 6–9 GPa).[20] It appeared that this effect on the initial modulus could not be observed when using a sample of PLLA with $\overline{M}_v = 5.5 \times 10^5$ and the PLLA used in the present study ($\overline{M}_v = 4.6 \times 10^5$). Figure 4 presents the ratio of the square knot strength (KS) to the tensile strength (TS) of the hot-drawn PLLA fibers as a function of the helical pitch formed on the as-spun fibers. It was found that differences in surface structure affects the knot strength of the hot-drawn PLLA fibers. More irregularities on the fiber surface, introduced during spinning, seem to increase the knot strength up to about 70% of the tensile strength. This may be explained by the fact that elastic turbulences of the polymeric flow during extrusion will give rise to a locally more disordered network

TABLE I

Mechanical Properties of PLLA Fibers $\overline{M}_v = 4.6 \times 10^5$) Hot Drawn at 200°C to $\lambda = 10$[a]

Spinning rate ($m^{-2} \cdot min^{-1}$)	TS (GPa)	KS (GPa)	Initial modulus (GPa)	ϵ (%)
1	0.56	0.35	9.6	12
2	0.54	0.35	9.3	13
3.5	0.54	0.36	9.7	13
9	0.55	0.37	11.4	13
12	0.52	0.32	8.9	14
16	0.47	0.25	7.7	14

[a] The fibers were spun from an 18% solution (w/v) of a mixture of a good and poor solvent [chloroform 70/toluene 30% (v/v)] at different spinning rates.

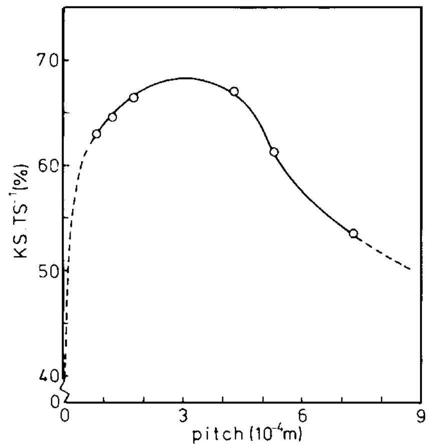

Fig. 4. The ratio of square knot strength to tensile strength (%) of hot-drawn PLLA fibers as a function of the helical pitch on the as-spun fibers.

of PLLA chains on the fiber surface, which upon hot drawing will not disappear completely. Natural fibers also show a less oriented surface layer, which makes them more resistant against mechanical deformation, e.g., bending. Since several surgical knots are known, it is difficult to compare data given in literature about the knot strength. Therefore, the strength of a similar knot in a commercial Vicryl suture was measured and appeared to be 50% of the tensile strength of the straight fiber.

In a previous paper of the series[10] it was shown that crystallization of PLLA in presence of a low molecular weight additive from a solution of the polymer and additive in chloroform leads to a porous material. The pore size was in the range 5–300 μm, depending on the amount and sort of additive used. Additives were removed from the polymer by extraction or evaporation. Based on this observation, porous fibers of PLLA were produced by spinning the fibers from a solution of the polymer ($\bar{M}_v = 4.6 \times 10^5$) in chloroform (10 % w/v) in the presence of camphor [PLLA 80/camphor 20% w/w].

Figure 5 presents scanning electron micrographs of PLLA fibers, as spun at different magnification and the same fiber cold drawn to $\lambda = 2$. It was found that the as-spun fibers exhibit a regular structurized surface [Fig. 5(A)]. The pores, with a size in the range 5–15 μm, are uniformly distributed in the fiber and interconnected [Fig. 5(B),(C)].

Figure 6 shows scanning electron micrographs of the fibers hot drawn at different temperatures to λ_{max}. The porosity of the as-spun fibers could be utilized to produce hot-drawn PLLA fibers with a more loosened fibrillar structure [Fig. 6(A),(B)]. However, it appeared that hot drawing above 170°C leads to PLLA fibers with a compact fibrillar structure [Fig. 6(C)]. The mechanical properties of the hot-drawn fibers are collected in Table II.

Figure 7 presents the tensile strength at λ_{max} vs. drawing temperature of PLLA fibers spun from chloroform in presence of camphor and PLLA fibers spun from toluene.[3] The presence of camphor in the polymer causes a depression of the melting temperature; therefore, the curve is shifted

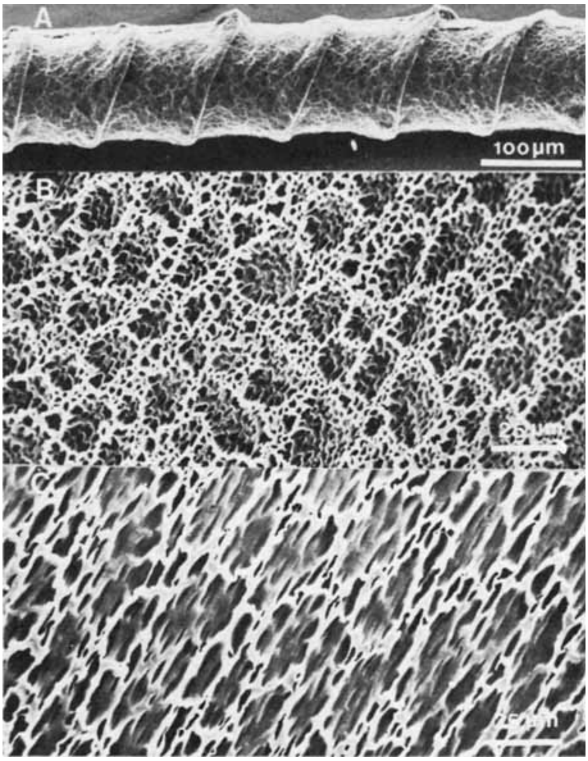

Fig. 5. Scanning electron micrograph of PLLA fibers spun in the presence of camphor (PLLA 80 wt %/camphor 20 wt %): (A) general view; (B) higher magnification of the fiber surface; (C) the same fiber drawn at room temperature to $\lambda = 2$.

towards lower temperatures. As in previous studies,[3,4] again two maxima in the tensile strength vs. drawing temperature were observed.

Figure 8 shows the λ_{max} of the hot-drawn fibers as a function of the drawing temperature. It was found that the drop in tensile strength after reaching both maxima is also accompanied by a decrease of the draw ratio. The character of both curves (Figs. 7 and 8) may be due to the fact that after passing the melting point of the polymer at the first maximum, the fraction of shorter chains present in the polymer become so mobile that molecular relaxation of these chains dominates and reduces the drawability of the fiber which leads to lower tensile strength. Further increase in draw temperature increases the mobility of the longer chains resulting in thermal motions which lead to a second maximum in the curve. Beyond this maximum drawing temperature the mechanical properties are again decreasing due to molecular relaxation of the longer chains. The difference in shape of both curves (Fig. 7) may be explained by the fact that the sample of PLLA used in the present study was fractionated prior to use. As is described in a previous paper, the drawability of PLLA fibers is influenced by the amount of lower molecular weight PLLA present in the sample.[4]

Decreasing of the chain end concentration of the polymer sample by fractionation leads to a lower value of the maximum draw ratio, namely, $\lambda_{max} = 11$, as compared with values found for a nonfractionated sample,

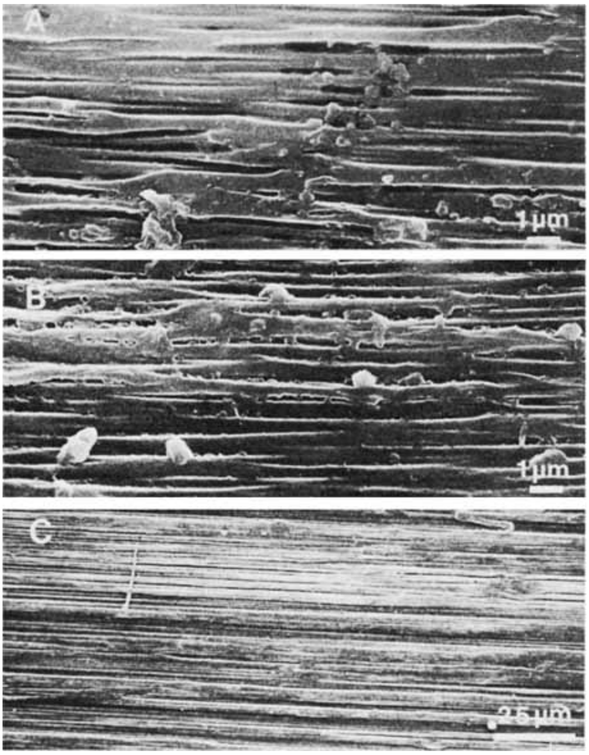

Fig. 6. Scanning electron micrograph of PLLA fibers spun in the presence of camphor (PLLA 80 wt %/camphor 20 wt %) and hot drawn at various temperatures to λ_{max}: (A) 140°C; (B) 160°C; (C) 190°C.

λ_{max} up to 20.[4] Similar results were obtained in the present study (Tables I and II). The drop in mechanical properties after reaching the first maximum is less dramatic when a fractionated sample of PLLA is used. This observation indicates that the occurrence of a minimum in the curve of tensile strength vs. drawing temperature is caused by a fraction of PLLA with a low molecular weight present in the sample.

TABLE II
Mechanical Properties of PLLA Fibers ($\bar{M}_v = 4.6 \times 10^5$) Spun from Chloroform (10 % w/v) in the Presence of Camphor (PLLA 80 wt %/Camphor 20 Wt %)[a]

Drawing temp (°C)	TS (GPa)	KS (GPa)	Initial modulus (GPa)	Draw ratio
95	0.40	0.30	6.0	5.0
140	0.45	0.30	7.5	7.0
150	0.55	0.30	8.5	7.5
160	0.78	0.45	9.0	10.8
170	0.85	0.45	9.5	11.8
178	0.75	0.45	9.0	10.2
180	0.65	0.35	8.5	9.8
190	0.85	0.50	8.0	11.5
200	0.65	0.40	8.5	9.0

[a] The fibers were hot drawn at different temperatures to λ_{max}.

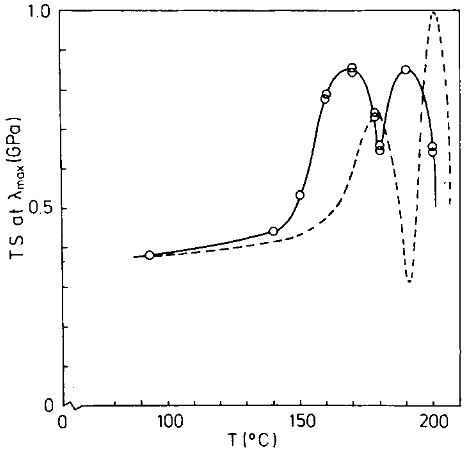

Fig. 7. Effect of drawing temperature on the tensile strength of PLLA fibers: (——) fibers spun from a good solvent (chloroform) in the presence of camphor (PLLA 80 wt %/camphor 20 wt %); (– – –) fibers spun from a poor solvent (toluene).

Figure 9 shows the initial modulus plotted against the tensile strength of PLLA fibers spun from chloroform in presence of camphor and drawn at different temperatures to λ_{max}. It was found that a higher value of the tensile strength always is accompanied by a higher initial modulus. The dependence of the tensile strength on the modulus changes when the region of hot drawing, above the melting point of the polymer, is reached. Regularly structurized fibers of PLLA spun from chloroform in presence of camphor [Fig. 5(A)] had the knot strength up to 70% of the tensile strength. It is claimed that materials made of PLLA are stiff[9]; therefore, sutures prepared from high molecular weight poly(L-lactide) may have some disadvantages as compared with more flexible suture material. However, flexible fibers of PLLA were produced by spinning fibers from chloroform (10 % w/v) in the presence of a copolymer of PLLA and a polyurethane [PLLA 95/copolymer 5% w/w]. Only at higher spinning rates regular melt fracture could be observed. The additive acted as a plasticizer which suppressed the

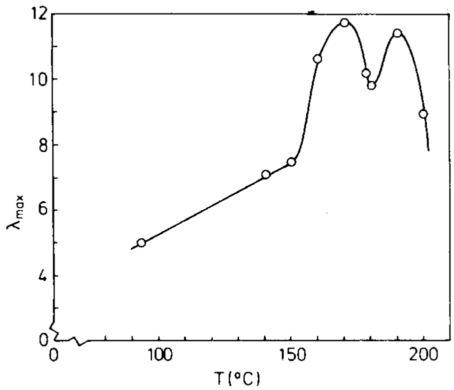

Fig. 8. Effect of drawing-temperature on the λ_{max} for PLLA fibers spun from chloroform in the presence of camphor (PLLA 80 wt %/camphor 20 wt %).

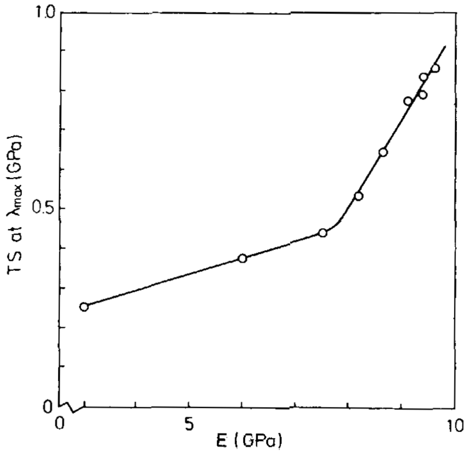

Fig. 9. Tensile strength at λ_{max} (GPa) as a function of the initial modulus (GPa) for PLLA fibers spun from chloroform in the presence of camphor (PLLA 80 wt %/camphor 20 wt %).

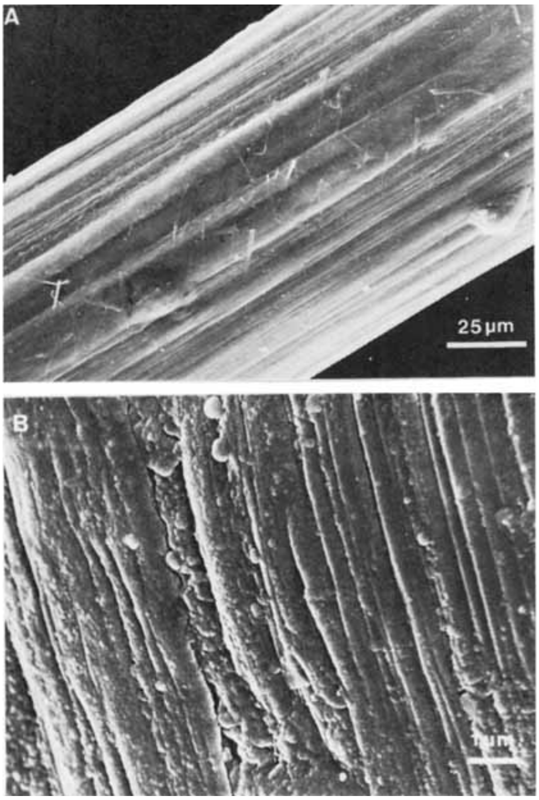

Fig. 10. Scanning electron micrograph of a PLLA fiber spun from chloroform in the presence of a low molecular weight copolymer of poly(L-lactide) and polyurethane (PLLA 95 wt %/copolymer 5 wt %): (A) fiber hot-drawn at 200°C to λ_{max}; (B) the same fiber treated with a saline solution for 5 weeks at 37°C.

occurrence of melt fracture. After hot drawing of the fibers at different temperatures only a densely packed fibrillar structure was found which is illustrated by a scanning electron micrograph [Fig. 10(A)]. During hot drawing, the copolymer was squeezed out of the fiber and formed a layer on the fiber surface, which is probably the cause of the flexibility of the fiber. These fibers had a knot strength up to 75% of the tensile strength. The typical mechanical properties of the hot-drawn fibers like tensile strength (up to 0.85 GPa) and initial modulus (up to 9.5 GPa) were similar to those found for the fibers spun in presence of camphor.

As described in a previous paper, PLLA fibers with a loosened fibrillar structure can be produced by spinning PLLA fibers in the presence of a segmented polyesterurethane.[9]

Figure 11 shows a scanning electron micrograph of the fiber as-spun [Fig. 11(A)] and the fiber hot drawn at 165°C to λ_{max} [Fig. 11(B)]. Details concerning spinning and hot drawing are given elsewhere.[9] The fibers had a tensile strength at break up to 0.7 GPa and modulus up to 10 GPa.

In vitro Degradation

Figure 13 presents the remaining tensile strength of PLLA fibers with various secondary structures vs. the time of *in vitro* degradation. In order

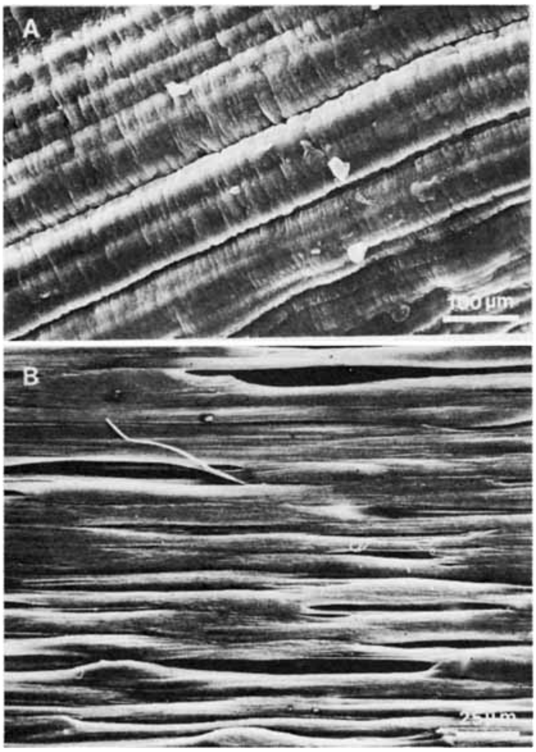

Fig. 11. Scanning electron micrograph of PLLA fibers spun in the presence of a segmented polyesterurethane (PLLA 95 wt %/polyesterurethane 5 wt %): (A) as-spun fiber; (B) fiber hot drawn at 165°C to λ_{max}.

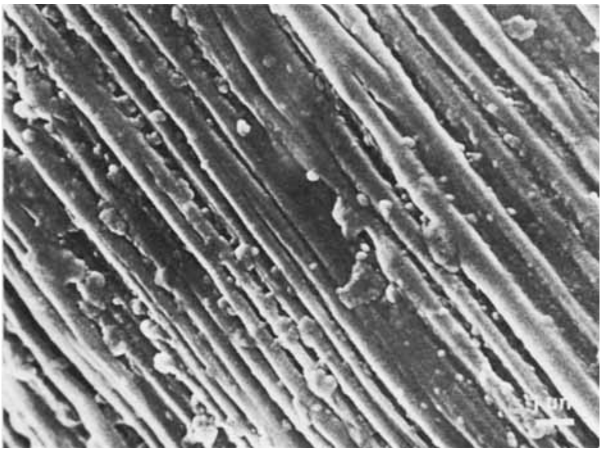

Fig. 12. Scanning electron micrograph of a PLLA fiber spun from chloroform in the presence of camphor (PLLA 80 wt %/camphor 20 wt %) and hot drawn at 160°C to λ_{max}. The fiber was treated with a saline solution for 3 weeks at 37°C.

to evaluate these results, data concerning the *in vitro* degradation of a commercial polyglycolic acid surgical suture (Dexon) are also included in the figure.[8] It was found that a more loosened fibrillar structure of the PLLA fibers increases the rate of degradation. This is in agreement with the assumption that the rate of degradation can be influenced by making the polymer more or less accessible for the degradation medium. The scanning electron micrographs presented in Figures 6,10(A), and 11(B) illustrate the differences in fibrillar structure of the PLLA fibers due to spinning in presence of various additives. Figures 10(B) and 12 show scanning electron micrographs of PLLA fibers spun in the presence of, respectively, a copoly-

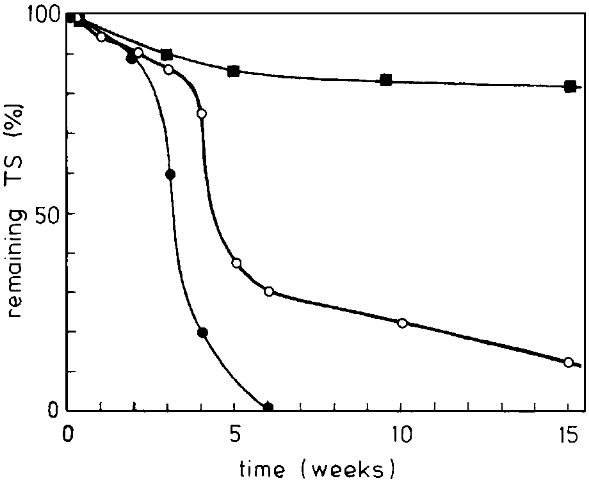

Fig. 13. The remaining tensile strength of hot-drawn PLLA fibers (%) vs. the *in vitro* degradation time in a saline solution at 37°C: (■) PLLA fiber spun from chloroform; (○) PLLA fiber spun from chloroform in the presence of camphor (PLLA 80 wt %/camphor 20 wt %); (●) '30' Dexon 's' suture.

mer of PLLA and polyurethane and in the presence of camphor. The fibers were treated with a saline solution at 37°C for 3 weeks [Fig. 10(B)] and 5 weeks (Fig. 12). PLLA fibers spun in the presence of toluene having a compact fibrillar structure as observed before[3,4] lost 20% of their tensile strength after 70 days of *in vitro* degradation which is in agreement with data described elsewhere.[8] No mass loss was observed. PLLA fibers containing an amount of a copolymer of PLLA and polyurethane showed only a small increase in the rate of degradation. The tensile strength dropped to 60% of the original value after 70 days of *in vitro* degradation. During this period no mass loss was observed. PLLA fibers spun in the presence of camphor showed a strong increase in the rate of degradation. The fibers lost 50% of their tensile strength after 32 days. This is comparable with the values found for a commercial Dexon suture, namely, 24 days. The mass loss after 70 days of *in vitro* degradation was in the range 5–10%. PLLA fibers produced in the presence of a polyesterurethane lost 10–50% of their fiber diameter in 40–60 days by exposing them to a saline solution at 37 ± 1°C. These data are comparable with those found for a commercial Vicryl surgical suture (copolymer of glycolide and L-lactide, molar ratio 90/10).

CONCLUSIONS

Preliminary experiments showed that zinc 2-ethyl hexanoate is a suitable catalyst for preparing the high molecular weight poly(L-lactide). More irregularities formed on the fiber surface during solution spinning of PLLA fibers, due to the melt fracture, lead to higher knot strengths up to 70% of the original tensile strength. This observation is of importance with regard to surgical and other applications of PLLA fibers. PLLA fibers with a loosened fibrillar structure produced by spinning the fibers from a solution of the polymer in a good solvent in the presence of various additives show similar mechanical properties to PLLA fibers spun from good solvents only.

Results of *in vitro* degradation of these fibers are in some cases comparable with those found for commercial sutures composed of the homopolymer of glycolide or copolymers of glycolide and L-lactide. The concept of making resorbable fibers which are more accessible for the degradation medium introduces a new possibility to regulate the rate of degradation of resorbable biomaterials.

References

1. A. K. Schneider, U. S. Pat. 3,636,956 (1971); *Chem. Abstr.*, **67**, 116596m (1967).
2. R. L. Kronenthal, Z. Over, and E. Martin, Eds., *Polymer Science and Technology*, Plenum, New York, 1975.
3. B. Eling, S. Gogolewski, and A. J. Pennings, *Polymer*, **23**, 1587 (1982).
4. S. Gogolewski and A. J. Pennings, *J. Appl. Polym. Sci.*, **28**, 1045 (1983).
5. S.-H. Hyon, K. Jamshidi, and Y. Ikada, *Polym. Prep.*, **24**(1), 6 (1983).
6. A. R. Katz and R. J. Turner, *Surg. Gynecol.*, **131**, 701 (1970).
7. A. S. Hoffmann, *J. Appl. Polym. Sci., Polym. Symp.*, **31**, 313 (1977).
8. A. M. Reed and D. K. Gilding, *Polymer*, **22**, 494 (1981).
9. S. Gogolewski and A. J. Pennings, *Macromol. Chem., Rapid Commun.*, **3**, 839 (1982).
10. S. Gogolewski and A. J. Pennings, *Colloid Polym. Sci.*, **261**, 477 (1983).
11. T. Tsuruta, K. Matsura, and S. Inoue, *Makromol. Chem.*, **75**, 211 (1964).
12. S. Gogolewski and A. J. Pennings, to appear.

13. D. K. Gilding and A. M. Reed, *Polymer,* **20**, 1459 (1979).
14. J. J. Benbow and P. Lamb, *Soc. Plast. Eng. Trans.,* **7** (Jan), (1963).
15. Y. Oyanagi, *J. Appl. Polym. Sci., Appl. Polym. Symp.,* **20**, 123 (1973).
16. R. K. Kulkarni, K. C. Pani, C. Neuman, and F. Leonard, *Arch. Surg.,* **93**, 839 (1966).
17. R. K. Kulkarni, E. G. Moore, A. E. Hageyli, and F. Leonard, *J. Biomed. Mater. Res.,* **5**, 169 (1971).
18. M. Vert, F. Chabot, J. Leray, and P. Christel, *Makromol. Chem. Supply.,* **5**, 30 (1981).
19. H. Tera and C. Åberg, *Acta. Chir. Scand.,* **142**, 1 (1976).
20. J. W. Leenslag, S. Gogolewski, and A. J. Pennings, unpublished data.

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