Polylactide. I. Continuous Dry Spinning–Hot Drawing Preparation of Fibers

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SYNOPSIS

The mechanical properties and *in vitro* degradability of gamma-rays sterilized and nonsterilized PLLA fibers prepared by a continuous dry spinning–hot drawing process were studied in relation to the spinning solution composition. Chloroform/cyclohexane mixtures of different volume ratios were used for dissolution either purified or as polymerized (with a residual monomer) PLLA. The fibers obtained had average or poor mechanical properties and a porous structure with a pointed outer skin. No increase of the degradation rate was observed except for the fibers formed from pure chloroform with a residual monomer at a drawing temperature of 110°C. At chloroform/cyclohexane volume ratio of 6 : 4 the process resulted in nearly hollow fiber formation. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Because of its biocompatibility, poly(L-lactide) (PLLA) has been widely studied for biomedical application such as body absorbable sutures.[1-4] Special attention has been given to the PLLA fiber preparation via the dry spinning–hot drawing process. This preparation method, using chloroform as a solvent, gave some interesting results, i.e., coil surface structured fibers with an improved knot tensile strength[5] or fibers with an increased degradability due to the camphor addition in the spinning solution.[6] This low molecular weight additive prevents a compacting of the polymer chains and causes a loosening of the structure. Using a combined theta-solvent ($CHCl_3$-toluene), high tenacity and high modulus (2.1 and 16 GPa, respectively) fibers were prepared,[7-10] which are suitable for microsurgery, ophthalmosurgery, or for use as a reinforcing material in implants. Despite improved degradability, the degradation rate is still too long for most suture surgical applications.

The mechanism of PLLA biodegradation is believed to be mainly plain hydrolysis. Many studies showed no major effect of body enzymes in the seventies.[11,12] The reaction of body fluids with a fiber is a heterogenous reaction; its rate depends on the reaction surface. Therefore, improving the degradation is directly related to the porous fiber preparation.

Considering the dry-spinning method, one possibility to prepare porous fibers is spinning from a solvent/nonsolvent mixture. If the solvent is more volatile than the nonsolvent, phase separation takes place in the very early stage of the fiber formation. The resulting fibers are usually porous, with a skin.

A combination of hot drawing and fast solvent evaporation could bring interesting structure/degradation related results. Therefore, this study of the continuous dry spinning/hot drawing PLLA fiber preparation was made.

EXPERIMENTAL

Sample

L-lactide was prepared according to the procedure described by Kulkarni et al.[13] and recrystallized 5 times from ethyl acetate. Ethyl acetate was dried 48 h over 3A-molecular sieves prior to use.

Poly(L-lactide) with a viscosity–average molecular weight of 3.5×10^5 was obtained by polymer-

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ization of L-lactide at 130°C in the presence of $SnCl_2 \cdot 2\ H_2O$ as a catalyst for 33 h. The $SnCl_2 \cdot 2\ H_2O$ was used in the amount of 10^{-4} mol per mol L-lactide. A part of the polymer was purified from residual lactide by dissolution in chloroform and subsequent precipitation with methanol.

The intrinsic viscosity of the polymer was measured in trichloromethane at 25°C. The viscosity–average molecular weight of PLLA was calculated according to the formula[14]

$$(\eta) = 5.45 \times 10^{-4}\ M_v^{0.73}$$

Continuous Dry Spinning–Hot Drawing Process

The polymer was dissolved by stirring for 16 h at 50°C. After cooling to 33°C (2 h), the solution was spun at lab temperature through an orifice (0.5 × 7 mm) with an extrusion speed of 6.5 cm · min^{-1}. The filament was continuously led via 3 threads on a steel drum in a 1 × 30 cm drawing tube, and the hot, drawn fiber was collected on the other drum. The fiber length between the orifice and the tube was 200 cm. The drawing tube was built in a bath circulator, which allowed precise temperature control.

Sterilization and *In Vitro* Degradation

Fibers (in dry argon atmosphere) were subjected to a Co^{60} gamma-irradiation dose of 25 kGy (Bioster s.p., Veverská Bítýška, Czech Republic). *In vitro* degradation was performed by the fibers' submersion into McIlvaine buffer (pH 7) for the required time at 37°C.

Characterization of the Fibers

The mechanical properties of PLLA fibers were measured at room temperature using an Instron 1122 tensile tester at a crosshead speed of 4 mm · min^{-1}. The length of the specimen was 8 mm.

Table I Composition of Spinning Systems

System No.	PLLA (g)	$CHCl_3$ (mL)	Cyclohexane (mL)
1	2.3	15	—
2	2.3	12	3
3	2.3	9	6
4	2.1[a]	15	—
5	2.1[a]	12	3

[a] As-polymerized PLLA containing 10% of the residual monomer.

Table II Spinning Speed Ratios

System No.	v_1 (cm · min^{-1})	v_1/v_0
1	4.3	0.66
2	4.3	0.66
3	4.3	0.66
4	4.5	0.69
5	3.9	0.60

v_0: Extrusion speed.
v_1: Entrance speed into the drawing tube.

The fiber diameters were measured on a light microscope and represent an average value of 15 measurements. Microphotographs were obtained using a Tesla BS 340 electron microscope. Samples were cut or broken in liquid nitrogen.

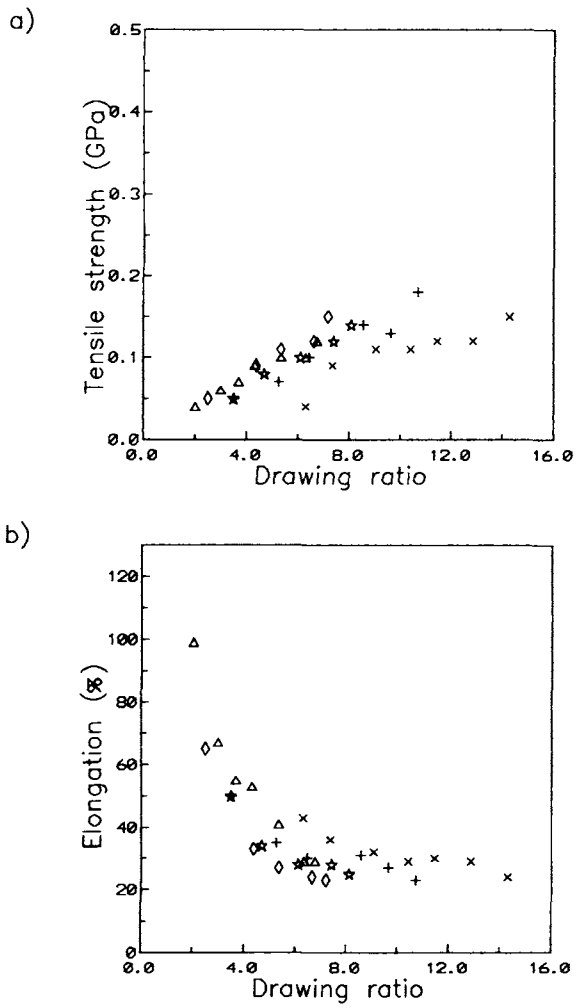

Figure 1 Mechanical properties of PLLA fibers, system 3. (△) 110°C; (◇) 130°C; (☆) 150°C; (+) 170°C; (×) 190°C.

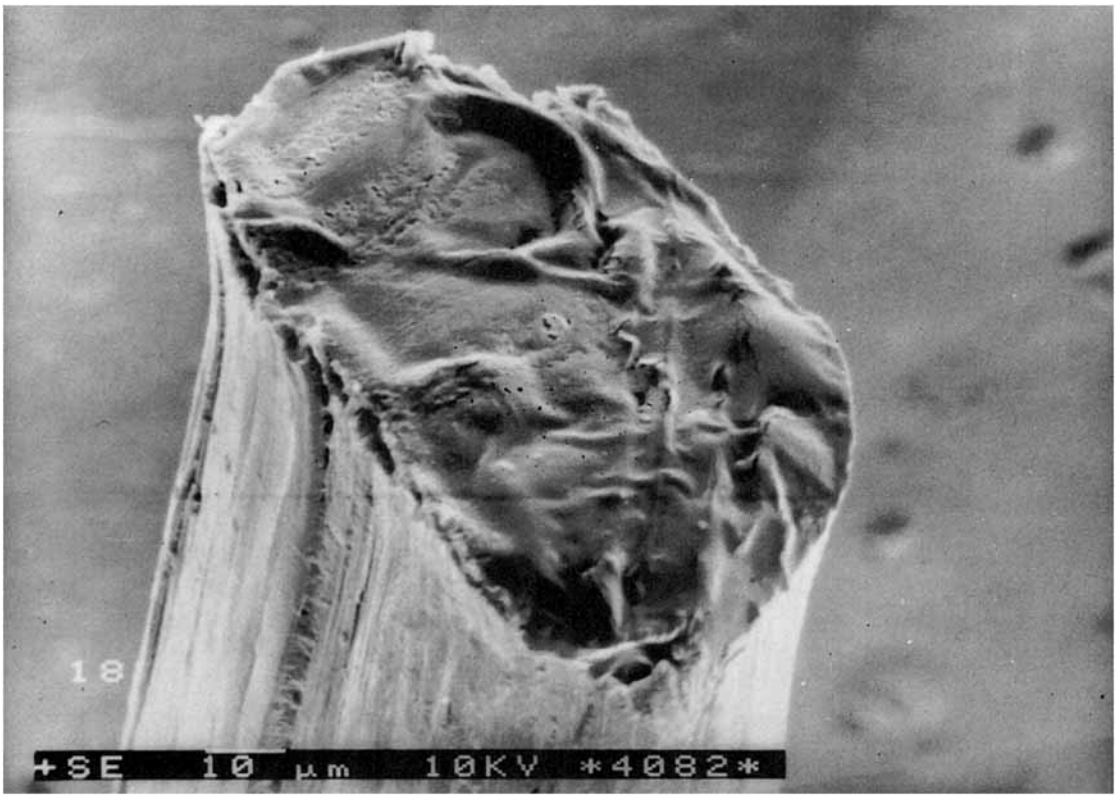

Figure 2 SEM of fiber, system 1: drawing temperature 180°C, maximum drawing ratio.

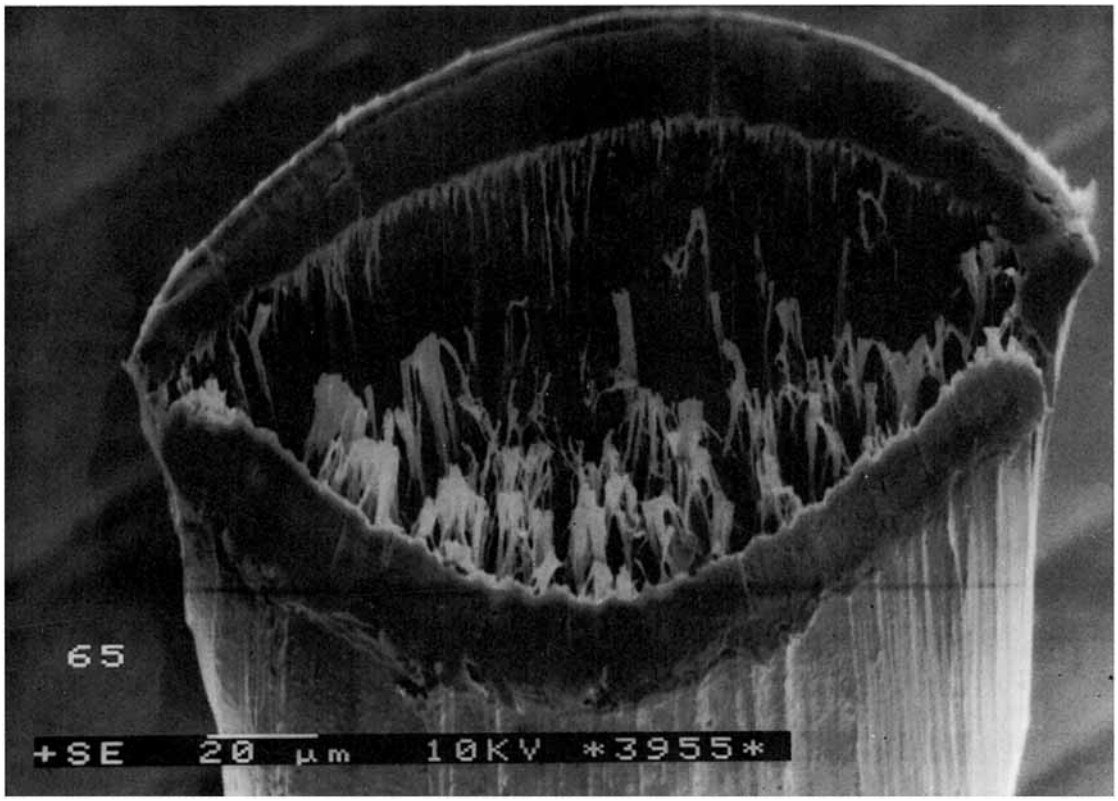

Figure 3 SEM of fiber, system 3: drawing temperature 170°C, maximum drawing ratio.

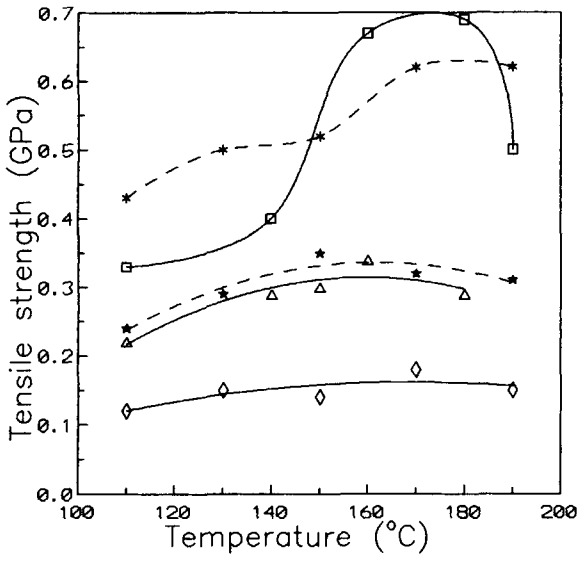

Figure 4 Tensile strength of PLLA fibers vs. the drawing temperature at maximum drawing ratio: (□) system 1; (△) system 2; (◇) system 3; (*) system 4; (★) system 5.

RESULTS AND DISCUSSION

Characterization of the Fibers

The spinning systems employed are characterized in Tables I and II.

Because of the presence of L-lactide in systems 4 and 5, the concentrations and the spinning speed ratios had to be adjusted to obtain regular fibers. A set of fibers was prepared for each system using different drawing temperatures and ratios. The maximum drawing ratio increases with increasing temperature within all systems. Mechanical properties of fibers always correspond to the drawing ratio regardless of the temperature (for example, Fig. 1), which is probably a consequence of filament plastification by the remaining solvent(s). An effect of the temperature on the relaxation time of the elastic deformation is overcome by the plastification effect.

The scatter of values in Figure 1 corresponding to higher temperatures and lower drawing ratios can be caused by the fast solvent(s) evaporation at a low drawing tension. This fast evaporation can result in mechanical damage of the fiber.

The spinning system solvent ratio substantially affects a fiber morphology. The greater the amount of cyclohexane in the solution, the faster the phase separation takes place. The same amount of the polymer must fill a greater volume. Thus, the fiber diameter increases with the content of nonsolvent in the spinning solution (Figs. 2 and 3).

This increase of the diameter is accompanied by a decline in the tensile strength because the tensile strength is calculated using the fiber cross-section area, which also includes voids (Fig. 4).

A lower steep of the tensile strength curves belonging to systems 2, 3, and 5 in comparison to those of systems 1 and 4 can also be noticed. Therefore, by the drawing process, the overall diameter of the porous fibers (systems 2, 3, and 5) does not decrease proportionally like that of the compact ones (systems 1 and 4). Via the drawing process, there is a reduction of the skin and of the elements of the inner structure, but the overall diameter changes less dramatically (Table III).

The maximum tensile strength for system 1 was found at about 180°C. This temperature is relatively low in comparison with that stated by Postema et al.[9] The difference is caused by the solvent presence in the fiber during the drawing process. The high temperature gradient between the solvent boiling point and the drawing temperature causes a sudden transition of the solvent in a vapor phase. The consequential inner press damages the fiber mechanically, which was observed microscopically. Of course, the drawing is accompanied by a next phase separation and a crystallization, which make this process even more complicated.

The presence of the residual monomer affects the tensile strength curve shape of only systems 1 and 4. The monomer acts as a plastificator and also as a heat shock-absorber. Therefore, at system 4, there are higher values of the strength at lower drawing temperatures, the maximum strength is lower, and there is no strength drop at 190°C. Microscopically, there was little difference between the fibers formed from system 1 (Fig. 2) and from system 4 (Fig. 5).

The fiber structures (and strength) of systems 2 and 5 are governed by the phase separation, which takes place because of the nonsolvent presence in the spinning solutions. During phase separation, the monomer remains soluted in the polymer-poor phase

Table III Fiber Diameters at Different Drawing Temperatures (Maximum Drawing Ratio)

System 1		System 2		System 3	
Drawing T (°C)	d (μm)	Drawing T (°C)	d (μm)	Drawing T (°C)	d (μm)
110	105	110	105	110	111
140	93	140	96	130	110
160	76	160	91	170	105

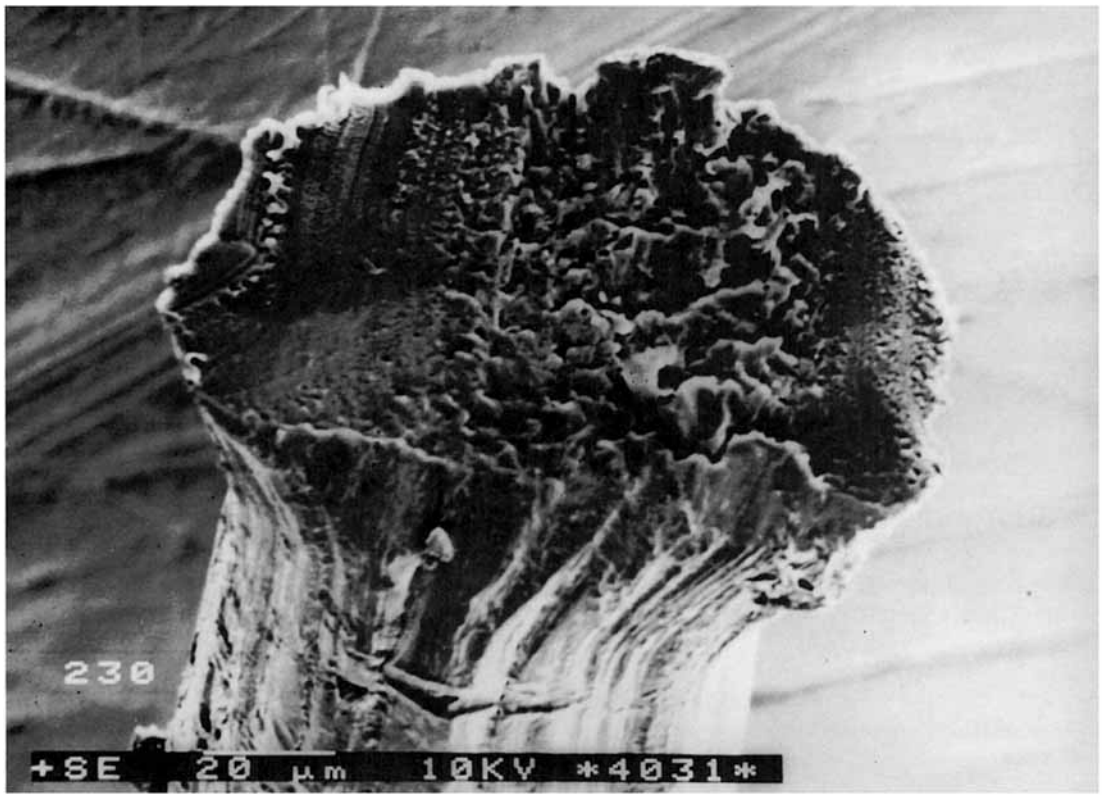

Figure 5 SEM of fiber, system 4: drawing temperature 170°C, maximum drawing ratio.

and therefore does not significantly affect the system 5 fiber strength.

Sterilization

The fibers drawn to the maximum drawing ratio at 110°C and at the maximum strength drawing temperature were chosen for sterilization and *in vitro* degradation. The fibers were subjected to a simple sterilization dose of 25 kGy. The resulting changes in mechanical properties are shown in Table IV.

Scission has been recognized as the main gamma-irradiation degradation mechanism of poly(L-lactide).[15] The chain scission frees some points of the amorphous entanglement network. Therefore, the irradiation sterilization of PLLA fibers usually results in a decline of the tensile strength and in an increase of the elongation.[16]

This statement is fully valid for systems 1 and 4, for fibers formed from chloroform solutions. In systems 2 and 3, it is necessary to consider different morphologies (skin formation) originating from phase separation during the drawing process. The entanglement network density is probably lower (lower solution power), and the orientation is higher. Therefore, the ultimate elongation of the sterilized fibers is even lower than that of fibers before the sterilization. System 5 fiber formation is even more complicated due to the monomer presence in the spinning solution. The fiber morphology is probably more similar to that of system 1 than to that of system 2.

Table IV Changes in Mechanical Properties After Sterilization

System No.	Drawing T (°C)	Δ of Tensile Strength (%)	Δ of Elongation (%)
1	110	−6.1	31.3
1	180	−10.3	16.0
2	110	−23.0	−6.0
2	150	−3.3	−39.0
3	110	−8.3	−25.0
3	170	−2.4	−32.0
4	110	−1.4	54.7
4	170	−11.3	4.0
5	110	−12.5	25.8
5	170	−7.9	14.3

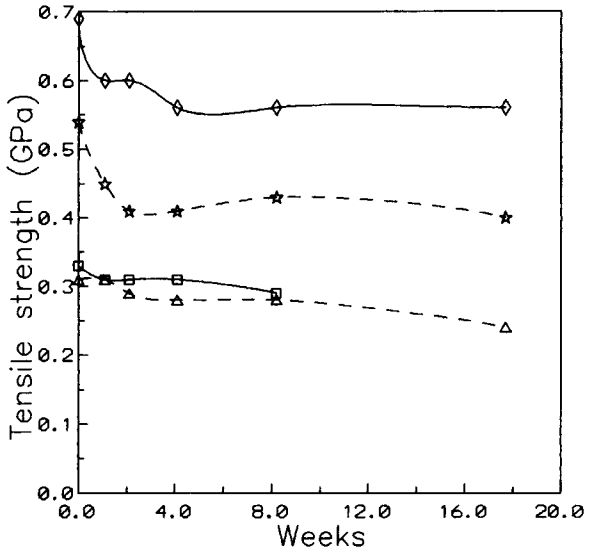

Figure 6 *In vitro* degradation of system 1 fibers: (□) 110°C, nonsterilized; (△) 110°C, sterilized; (◇) 180°C, nonsterilized; (☆) 180°C, sterilized.

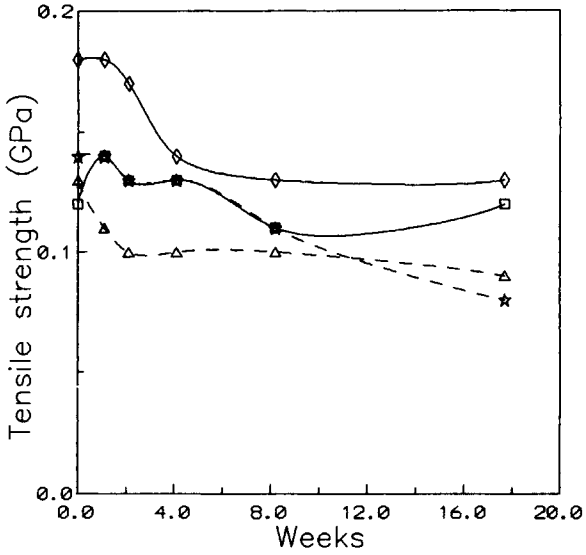

Figure 8 *In vitro* degradation of system 3 fibers: (□) 110°C, nonsterilized; (△) 110°C, sterilized; (◇) 170°C, nonsterilized; (☆) 170°C, sterilized.

In Vitro Degradation

Sterilized and nonsterilized fibers were used for *in vitro* degradation. The tensile strength was measured after 1, 2, 4, 8, and 18 wk degradation. The degradation courses are shown in Figures 6–10.

Considering systems 1–3 (Figs. 6–8), the rate of degradation is not affected by an addition of the nonsolvent in the spinning solution or by the drawing temperature. According to electron microphotographs (Fig. 3), the fibers appear to have a porous structure, but also a thick and compact skin. The skin thickness is even more pronounced due to the continuous fiber preparation. Therefore, from the degradability point of view, the porosity is irrelevant.

The residual monomer in the spinning dope consequently affects the degradation rate, but only at the low drawing temperature (Fig. 9). The degra-

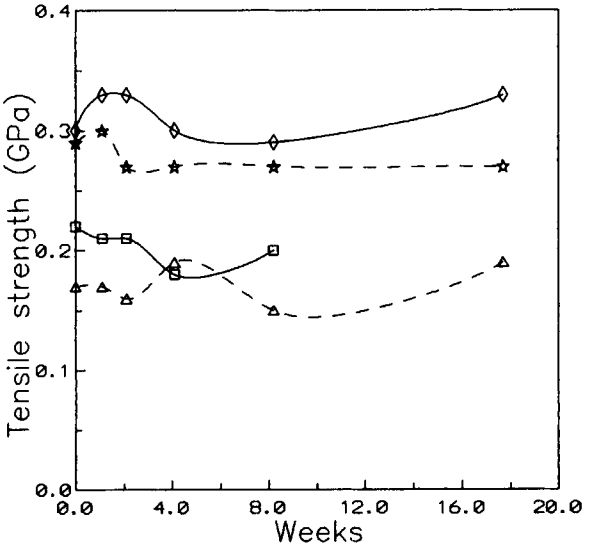

Figure 7 *In vitro* degradation of system 2 fibers: (□) 110°C, nonsterilized; (△) 110°C, sterilized; (◇) 150°C, nonsterilized; (☆) 150°C, sterilized.

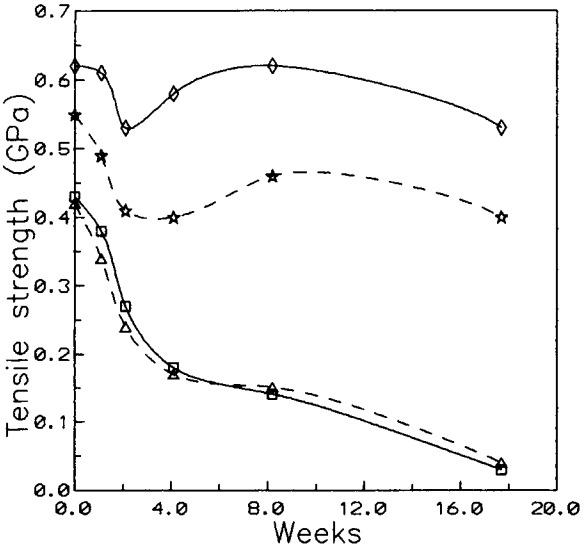

Figure 9 *In vitro* degradation of system 4 fibers: (□) 110°C, nonsterilized; (△) 110°C, sterilized; (◇) 170°C, nonsterilized; (☆) 170°C, sterilized.

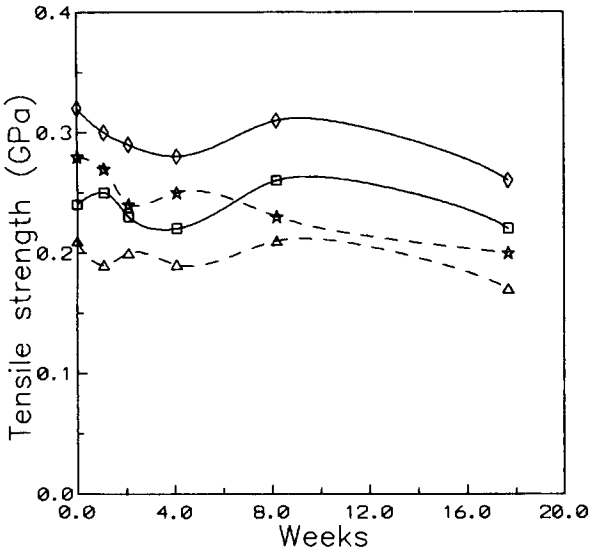

Figure 10 *In vitro* degradation of system 5 fibers: (□) 110°C, nonsterilized; (△) 110°C, sterilized; (◇) 170°C, nonsterilized; (☆) 170°C, sterilized.

dation course of the 110°C drawn fibers is very similar to that published by Leenslag et al.[6] At high drawing temperatures, the lactide is evaporated (condensation on the input and output surfaces of the drawing tube) and the loosened structure is probably tightened again.

In system 5 (Fig. 10), the influence of the nonsolvent prevails. The lactide is concentrated in the polymer-poor phase (pores); therefore, the skin structure and the degradation rate are unaffected. No change in the degradation rate was observed due to the gamma-irradiation sterilization.

CONCLUSIONS

An addition of cyclohexane in spinning solutions leads to skin porous fiber with lower mechanical properties and the same degradability as without this addition.

The residual monomer affects the fiber degradability only when they are formed from chloroform solutions. In the case of solvent mixtures, the monomer remains in the fiber pores and the skin morphology is unaffected.

The continuous dry spinning–hot drawing process may be a way to hollow PLLA fibers. When the 4 : 6 volume ratio of cyclohexane to chloroform is used, the polymer mass is concentrated mainly in the skin area.

The gamma-irradiation sterilization does not affect the degradation rate, and only causes a smooth decrease of the starting tensile strength.

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