High-Strength Poly(L-Lactide) Fibers by a Dry-Spinning/Hot-Drawing Process. I. Influence of the Ambient Temperature on the Dry-Spinning Process

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Synopsis

In this paper the influence of the ambient temperature of the spinline during dry spinning of PLLA solutions has been discussed. Variation of this ambient temperature induced variation of the extrudate swell of the spinline, affected by the rate of solidification of the PLLA. By way of phase separation, porous filaments were achieved in which the morphology depended on the applied ambient temperature. Hot drawing of these filaments led to tensile strengths varying between 1.1 and 2.2 GPa. An optimal tensile strength of 2.2 GPa was achieved by hot drawing of a filament which was spun into a surrounding of 25°C.

INTRODUCTION

During the last decade much attention has been given to polylactides, which are biocompatible and biodegradable materials. The production of fibers for general medical applications[1] has found renewed interest.[2-7] High-strength poly(L-lactide) (PLLA) fibers could be prepared by a dry-spinning/hot-drawing process. The ultimate fiber properties were found to be affected by, for instance, PLLA concentration in the spinning solution, solvent composition, drawing temperature, drawing rate, molecular weight, molecular weight distribution, and fiber diameter.[6,7] PLLA fibers having a tenacity of 2.3 GPa and a Young's modulus of 16 GPa were produced by dry spinning of solutions of PLLA in mixtures of a good (chloroform) and a poor solvent (toluene), near the θ conditions. The as-spun filaments exhibited a porous texture, which could be easily hot-drawn to high draw ratios, giving fibers with high strengths. This porous texture was to be attributed to a rapid phase separation in the presence of a poor solvent, when the chloroform evaporates during spinning. From this point of view it is expected that the rate of chloroform evaporation should influence the morphology of the as-spun fiber and thus the ultimate fiber properties after hot drawing. The rate of chloroform evaporation depends on the ambient temperature of the spinline. The

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purpose of Part I of this study of the preparation of high-strength PLLA fibers was to investigate the influence of the ambient temperature during dry spinning on the ultimate fiber properties after hot drawing. Part II of this study will be concerned with the influences of extrusion speed and winding speed on the ultimate tensile properties of the PLLA fibers.

EXPERIMENTAL

In this study poly(L-lactide) was used with $M_v = 9.1 \times 10^5$ ($\Delta H_m = 52.2$ J/g, $T_m = 189.5$°C). The preparation of the polymer and of the spinning solutions have been published elsewhere.[7]

In a piston-cylinder apparatus a 4% (m/v) PLLA solution in a chloroform/toluene (40/60) mixture was conditioned at 70°C. After 3 h the solutions were extruded at 60°C through a stainless-steel, conical die (entrance angle 43°C, length 23 mm, and exit diameter 0.25 mm) into a Helios electro oven (type 284520). The temperature of the oven could be varied within 1°C. The extrudate was collected on a sand-blasted glass bobbin, without applying additional stress. The distance between die and bobbin (air gap) was 6.5 cm. The extrusion rate was 3 m/min. After collecting the filaments on the bobbins, the temperature of the oven was maintained at the initial temperature for another 10 min. At that moment the fiber was completely solidified. Further drying of the fibers occurred at room temperature until constant weight was reached (usually about 40 h). Ambient temperatures below room temperature were achieved by placing the spinning apparatus in a cold-storage room. The as-spun filaments were drawn to the maximum draw ratio in a heated, double-walled, glass tube as described previously[7] at 190°C, in a nitrogen atmosphere, applying an entrance velocity of 0.625 cm/min.

Mechanical properties of the fibers were determined at room temperature using an Instron (4301) tensile tester, equipped with a 10 N load cell, at a crosshead speed of 12 mm/min. The gauge length was 25 mm. Cross sections of the filaments were calculated from the fiber weight and length, assuming a value of 1290 kg/m^3 for the density of the fiber.[8] All the tensile properties to be presented are the average of at least five tests.

Scanning electron micrographs were taken using an ISI-DS130 microscope operating at 20 kV from gold-covered samples.

Thermal analysis of the samples was performed by means of a Perkin Elmer DSC-7, calibrated with indium and operated at a scan speed of 10°C/min.

RESULTS AND DISCUSSION

Solutions of poly(L-lactide) in mixtures of chloroform and toluene (40/60) were spun at various ambient temperatures, in the range from 9 to 60°C. The extrudate swell of the filaments, defined as the measured weight of the fiber per unit length divided by the weight of the fiber per unit length as calculated from the spinneret dimensions and the polymer concentration without extrudate swell, appeared to be affected by the temperature of the surrounding of the spinline (Fig. 1). At low temperatures ($T < 22$°C) and at high tempera-

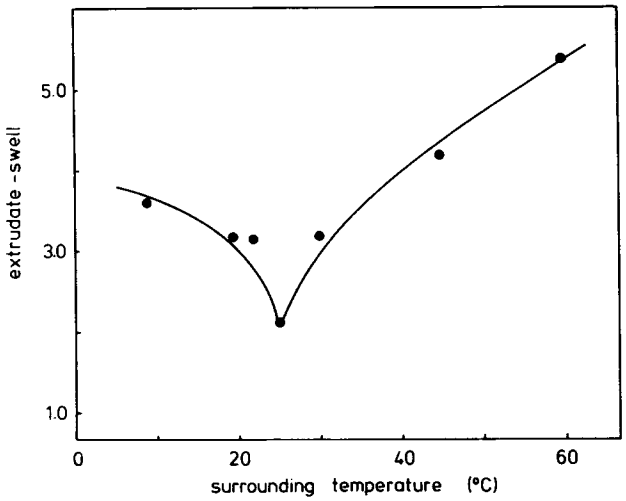

Fig. 1. Extrudate swell of PLLA filaments, spun from 4 wt % solutions of PLLA in chloroform/toluene (40/60) mixtures as a function of the ambient temperature of the spinline.

tures ($T > 30°C$) the extrudate swell appeared greater than 3.0. A minimum degree of extrudate swell of 2.1 was found at 25°C.

After hot drawing of the different as-spun fibers the ultimate tensile strength also appeared to be dependent on the ambient temperature applied during spinning. A maximum strength of 2.2 GPa was achieved after hot-drawing filaments which were spun in a surrounding with a temperature of 25°C (Fig. 2). At lower and higher ambient temperatures the ultimate tensile strength decreased drastically.

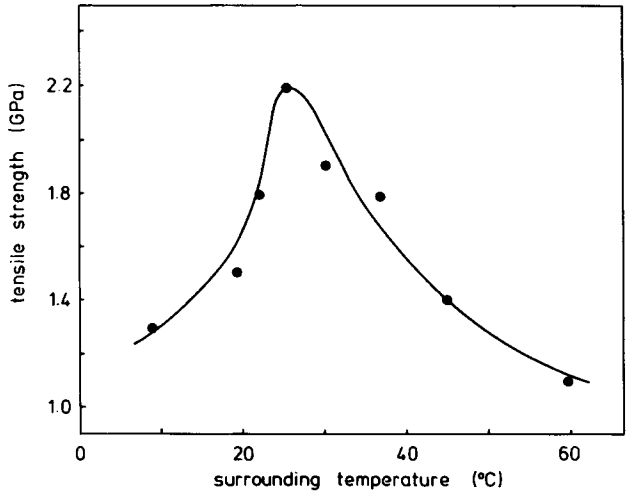

Fig. 2. Tensile strengths of PLLA filaments after hot drawing to the maximum draw ratio as a function of the applied ambient temperature during dry spinning.

As is evident from Figures 1 and 2, the strongest PLLA fibers were obtained by hot drawing of as-spun filaments, which exhibited a minimal degree of extrudate swell. This phenomenon was also observed in a previous study[6] on the influence of the solvent composition in the dry-spinning process of PLLA on the ultimate fiber properties.

TABLE I
Heat of Fusion of the As-Spun Fibers, Maximum Draw Ratio, Diameter of the Drawn Fiber and Tensile Strength of the PLLA Filaments, Spun from 4 Wt % Solutions in Chloroform/Toluene (40/60) into a Surrounding with Various Temperatures

Ambient temperature (°C)	Heat of fusion (J/g)	Draw ratio	Fiber diameter (μm)	Tensile strength (GPa)
9	48.8	12	27	1.3
20	44.6	14	23	1.5
22	41.2	13	21	1.8
25	54.8	13	17	2.2
30	45.6	14	22	1.9
37	53.5	13	19	1.8
45	34.9	12	26	1.4
60	49.3	13	28	1.1

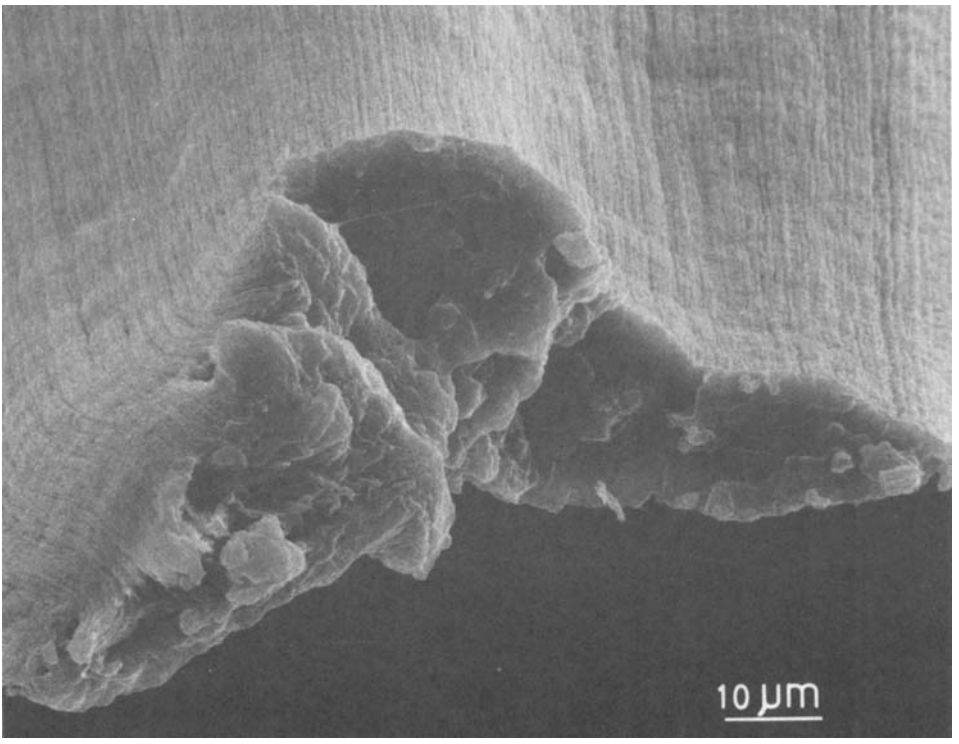

Fig. 3. SEM micrograph of a cross-sectional surface of a PLLA filament, spun into a surrounding of 37°C, showing morphologies of fiber skin and core.

Extrudate swell originates from the orientation of molecules (or parts of molecules) in the die, which (on emerging in the atmosphere) tend to recoil, leading to a contraction in the direction of the flow being offset by lateral expansion.[9] A higher mobility of the chains will reduce the extrudate swell, because chains (or parts of chains) will slip along each other and will diminish the contraction of the filament in the direction of the flow.[10] Phase separation followed by precipitation/crystallization of the polymer will impede this sliding of chain parts, resulting in large extrudate swells. This has also been found for melt-spinning of nylon 6.[11] Under conditions where solidification in the spinline was suppressed, a minimum degree of extrudate-swell was attained.

In dry-spinning processes[11] the solvent is removed by:

a. flash vaporization,
b. diffusion within the spinline,
c. convective mass transfer from the spinline surface to the surrounding medium.

The flash vaporization of the solvent takes place at the spinneret orifice as a result of decompression of the polymer solution. Rapid vaporization is then followed by a rapid cooling of the system caused by the removal of the heat of vaporization of the system. By using a mixture of a good (chloroform) and a

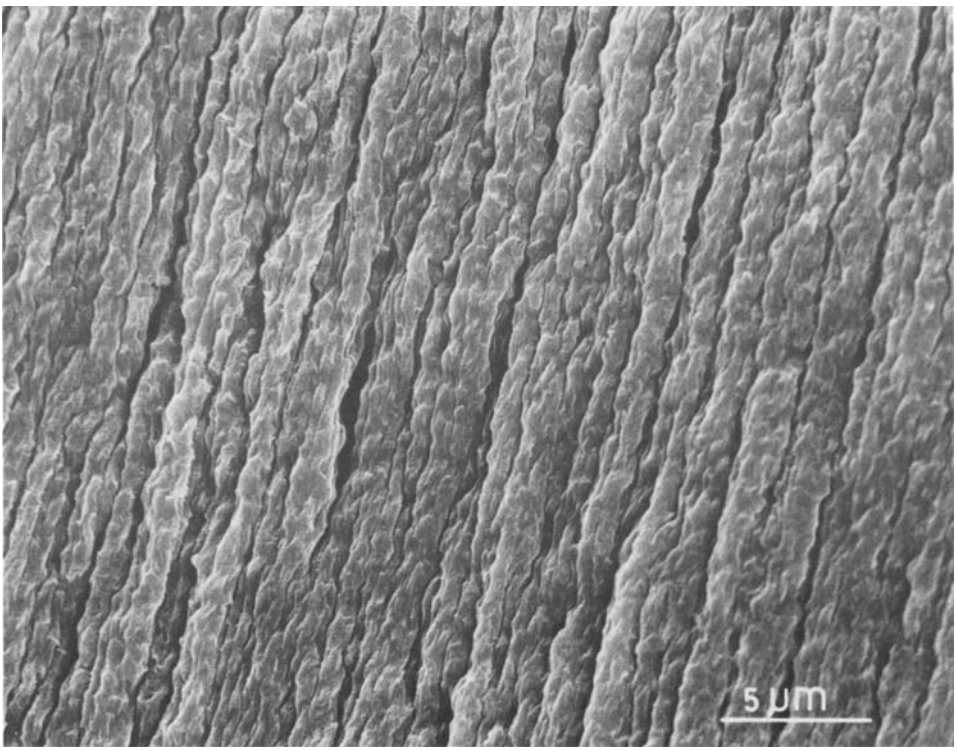

Fig. 4. SEM micrograph of the surface texture of a PLLA filament, spun into a surrounding of 37°C, showing long bundlelike structures

poor solvent (toluene), near the θ conditions of the polymer,[6] the dry-spinning process becomes more complicated. Evaporation of the chloroform results in an increasing PLLA concentration and a decreasing solvent power. The diffusion process of chloroform out of the fiber may induce a thermodynamically unstable composition in the solution,[12] i.e., a solution which can decrease its free energy of mixing by splitting up into two phases with different compositions (liquid–liquid phase separation). This generates a polymer-poor and a polymer-rich phase. The existence of a polymer rich phase may induce rapid solidification, generating porous fiber structures (e.g., Refs. 12–14). At high surrounding temperatures the flash vaporization of chloroform becomes very fast, leading to cooling of the spinline and reduction of the solvent power (higher content of poor solvent). Rapid solidification of the polymer will hamper sliding of chain parts along each other, resulting in a very elastic network containing many physical crosslinks. In this case a high degree of extrudate swell will appear. Applying low ambient temperatures results in a decreasing temperature in the spinline and thus a decreasing solvent power, resulting in phase separation (thermal precipitation). This process is intensified by a higher rate of crystallization.[15] In this case too, rapid solidification will give rise to a high degree of extrudate swell. Between these two extremes a temperature (25°C) exists where the solidification is delayed long enough, so that parts of chains can slip off, thereby reducing the number of topological

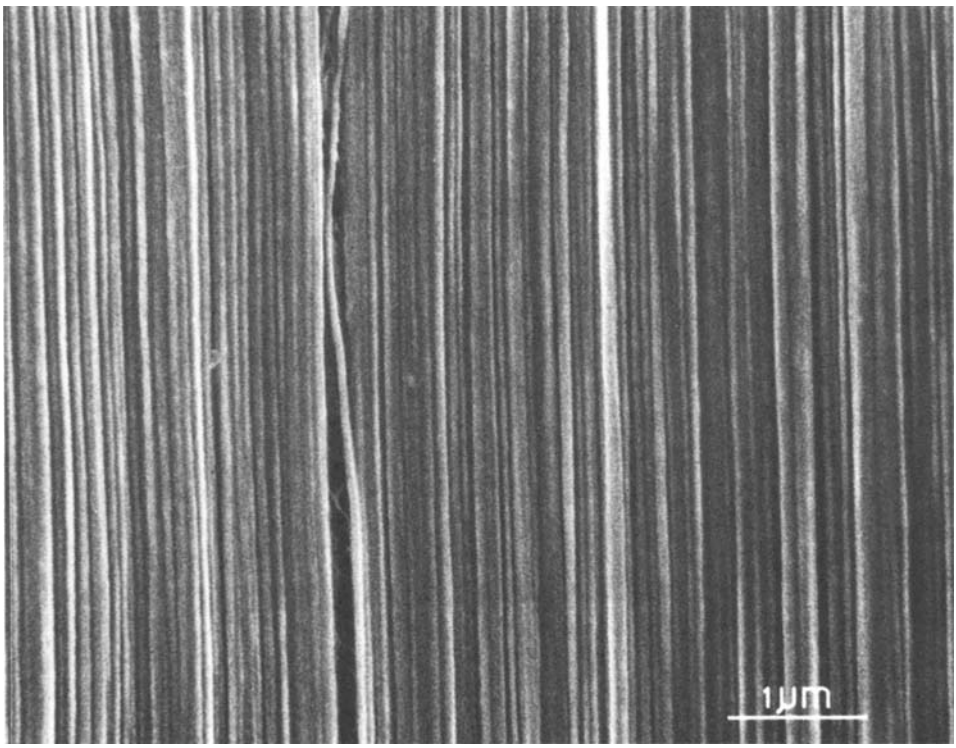

Fig. 5. SEM micrograph of the surface structure of a PLLA filament, spun into a surrounding of 37°C and subsequently hot-drawn at 190°C to a draw ratio of 13. Note an extensive fibrillation.

defects, giving rise to a low elasticity of the spinline. Hot drawing of these as-spun fibers resulted in optimum fiber properties. The rate of solidification did not influence the overall crystallinity of the filaments (Table I). Measurements of the crystallinity by means of DSC revealed heats of fusion between 34.9 and 54.8 J/g, without any correlation with the ultimate tensile strength. This was also found for the cold-drawing behavior of the as-spun filaments in relation to the ultimate tensile strength. In the hot-drawing process the maximum draw ratio appeared to be constant in all cases (Table I). Because both the heats of fusion (crystallinity) and the maximum draw ratios were found to be constant for all fibers, large differences in entanglement concentration cannot be the basic cause for the differences in the ultimate tensile strength.

In a previous study on the drawing process of PLLA fibers,[7] it was found that weak fibers were formed under conditions which led to inhomogeneities. These conditions were affected by the deformation rate of the fiber in the tube drawing process. The strengths of the filaments spun at low and high ambient temperatures were not affected by the deformation rate in the tube drawing process. On the other hand, a large effect of the deformation rate was found for the filaments spun at 25°C. The results indicate that during spinning in surroundings of low and high temperatures heterogeneous filaments are formed (possibly due to rapid phase separation[16,17]), which lead to weak fibers after hot drawing.

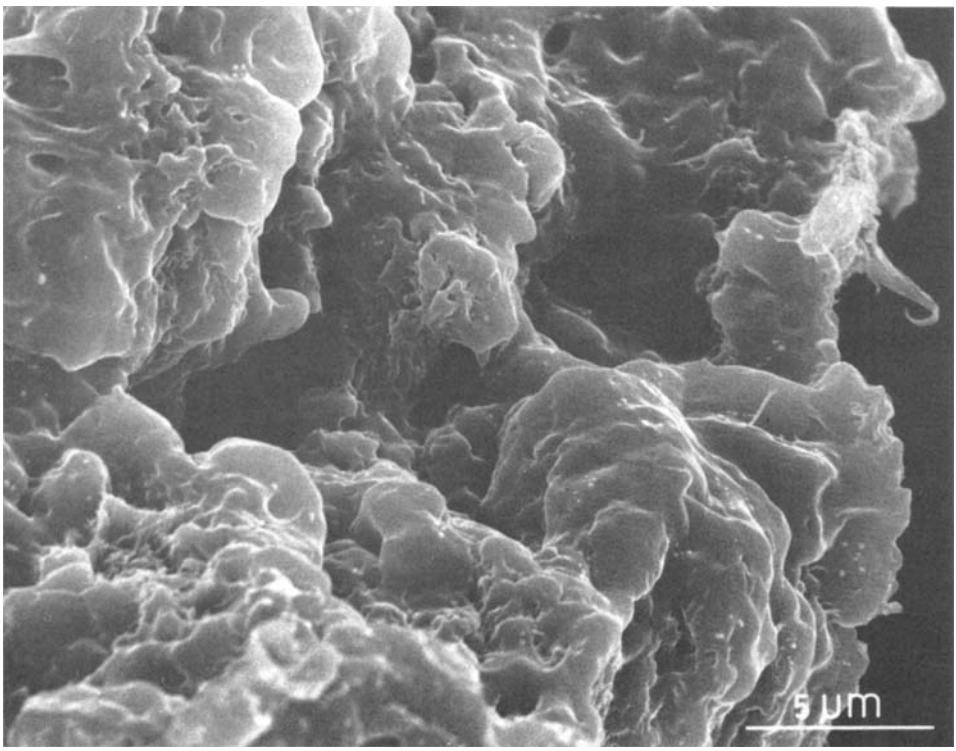

Fig. 6. SEM micrograph of the core texture of a PLLA filament, spun into a surrounding of 37°C, showing heterogeneous structures and large voids.

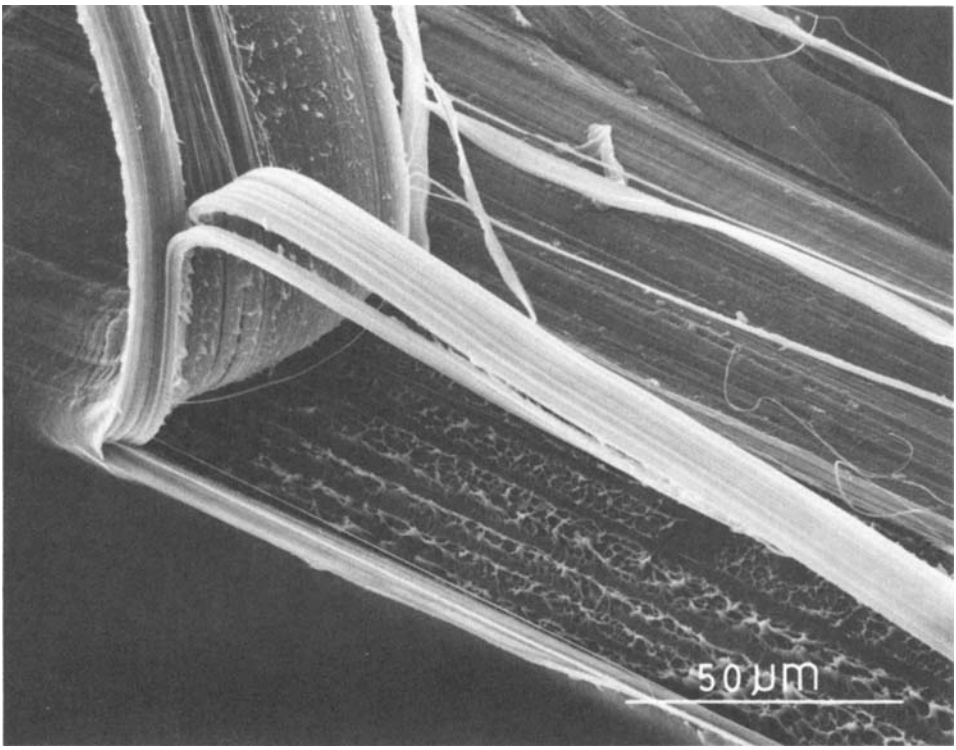

Fig. 7. SEM micrograph of a peeled PLLA filament, spun into a surrounding of 45°C and subsequently hot-drawn to the maximum draw ratio.

Evaporation of the good solvent from the upper layer of the filament brings about a polymer distribution that is nonuniform over the cross section. This distribution is determined by the evaporation step and results in a different morphology of the fiber skin and core.[13] This is illustrated by a SEM micrograph of the fiber cross section (Fig. 3) showing different structures of the fiber skin and core. All the filaments, spun at different temperatures of the surrounding, displayed the same surface textures (Fig. 4). The surface exists of long macrofibrillar structures, which probably originate from the shearing of flow units[18] along the wall of the die. In the hot-drawing process these macrofibrils are converted into fibrillar structures[19] (Fig. 5). Measurements of the magnitude of the fibrils (diameter ≈ 0.3 μm) indicate that every fibril originates from one particular macrofibril in the as-spun fiber. The scanning electron micrograph of the as-spun fiber core (Fig. 6) shows a rather rough heterogeneous structure. This structure of the core was more heterogeneous in those fibers, which were spun into a surrounding with a low (< 20°C) or a high (> 30°C) temperature. The heterogeneous network structures may give rise to defects in the fiber. Figure 7 presents a peeled PLLA fiber,[20] spun into a surrounding of 45°C and subsequently hot-drawn. Next to the highly fibrillated structures it also shows nonfibrillar regions. This indicates the lack of coherence in these heterogeneous fibers. In addition to the many large voids, which reduces the fiber coherence, these heterogeneous networks often

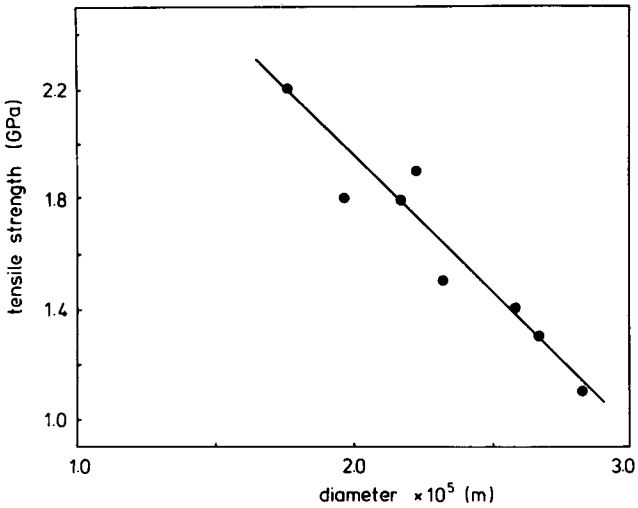

Fig. 8. Tensile strengths of PLLA filaments (Fig. 2) vs. their diameter.

contain many topological defects, leading to tight knots by stretching[21] and lowering the tensile strength.

The maximum draw ratio of the various filaments appeared in all cases between 13 and 15. Consequently, fibers with minimum extrudate swell had minimum diameter after hot drawing to the ultimate draw ratio. The tensile properties of polymeric fibers have found to be affected by the concentration of surface flaws and thus by the surface area of the fiber. Thinner filaments usually yield higher values of the breaking strength.[6,18,22-24] Figure 8 presents the ultimate tensile strength of the various filaments as a function of their diameter. The filaments with the smallest diameter yielded the highest tensile strength. In this case not only do surface flaws affect the ultimate properties (according to the Griffith theory[25]) but more importantly the amount of residual topological defects, which were embedded during the spinning process, do also.

CONCLUSIONS

From this study of the influence of the ambient temperature on the spinline during dry spinning of PLLA solutions as reflected in the ultimate tensile strengths, the following conclusions may be drawn:

Variation of the temperature of the surrounding of the spinline during spinning of PLLA solutions leads to ultimate tensile strengths after hot drawing varying between 1.1 and 2.2 GPa.

Phase separation, followed by rapid crystallization, preserving the entanglement network, led to large extrudate swells and to heterogeneous filaments, having poorer tensile properties after hot drawing.

Minimum extrudate swell was achieved by suppressing the phase separation and crystallization so that slippage of chains led to homogeneous filaments which could be hot-drawn to filaments with a tensile strength of 2.2 GPa.

Scanning electron micrographs showed different fiber morphologies of the fiber skin and core. The surface texture exists of long macrofibrillar structures, which are converted into fibrils in the hot-drawing process.

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