High-strength poly(L-lactide) fibres by a dry-spinning/hot-drawing process

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High-strength poly(L-lactide) (PLLA) fibres (tenacity 2.1 GPa, Young's modulus 16 GPa) have been produced by dry spinning and subsequently hot drawing of PLLA ($\bar{M}_v = 9 \times 10^5$) from solutions in chloroform/toluene mixtures near the θ conditions where PLLA adopts an interrupted helical conformation. Ultimate fibre tenacity was dependent on drawability and final fibre cross section. Drawability improved with increasing heat of fusion, ΔH_m, of the as-spun filaments, and was affected by the solvent composition, PLLA concentration in the spinning solution and preparation conditions. PLLA can exhibit an α–β crystal transition upon hot drawing. The theoretical strength of PLLA should amount to about 8 GPa as deduced from the diameter dependence of the tensile strength.

(Keywords: poly(L-lactide) fibres; dry spinning; good/poor solvent mixtures; θ conditions; interrupted helix; hot drawing; α–β crystal transition; theoretical strength)

INTRODUCTION

For several decades biocompatible and resorbable synthetic polymers like poly(L-lactide) (PLLA) have been widely studied for biomedical applications such as body-absorbable sutures[1–8]. However, the preparation of high-strength fibres of the resorbable type (tenacity > 1 GPa) has only received little attention so far[3–7]. Strong filaments may find application as a small-sized suture in microsurgery or become useful in the field of composite materials[9–11].

In two previous papers it was shown that PLLA fibres ($\bar{M}_v = 5$–6×10^5) with a σ_b of 1–1.2 GPa could be produced by dry spinning/hot drawing from PLLA solutions in toluene (poor solvent) and chloroform (good solvent) respectively[4,5]. For the range of molecular weights investigated ($\bar{M}_v = 1.8$–6×10^5) the tensile properties of the fibres were found to improve with increasing $\bar{M}_v$. Recently it was observed that bulk polymerization of L-lactide at relatively low temperatures (100–110°C) yielded PLLA with an extremely high M_v up to 1×10^6 (ref. 12). Previous studies have indicated that for solution spinning of fibres the use of binary solvent mixtures may lead to filaments with improved tensile properties[13,14]. In the case of nylon-6 fibres the presence of a non-solvent in the spinning solution was found to facilitate the formation of a better drawable entanglement network[13].

Preliminary experiments revealed that hot-drawn PLLA fibres ($\bar{M}_v = 1.6 \times 10^5$) spun from a chloroform/toluene mixture exhibited a higher value for the Young's modulus (14.5 GPa) than usually observed ($E = 6$–9 GPa)[7]. Further exploration of good solvent/poor solvent mixtures for fibre preparation of PLLA with very high $\bar{M}_v$ may therefore lead to improvement of mechanical properties.

It will be shown how PLLA fibres ($\bar{M}_v = 9 \times 10^5$) with a σ_b of 2.1 GPa ($E = 16$ GPa) can be produced from a specific chloroform/toluene 40/60 (v/v) mixture. Several factors that were found to affect the ultimate fibre properties like PLLA concentration in the spinning solutions, solvent composition, drawing temperature, molecular weight (*MW*), *MW* distribution and fibre diameter will be discussed in detail.

EXPERIMENTAL

Materials

Samples of PLLA with $\bar{M}_v = 6.5 \times 10^5$ ($\Delta H_m = 55.3$ J g^{-1}, $T_m = 187.8$°C) and $\bar{M}_v = 9 \times 10^5$ ($\Delta H_m = 57.2$ J g^{-1}, $T_m = 188.6$°C) were synthesized at 130°C (24 h) and 110°C (112 h) respectively as reported elsewhere[4,5,12]. PLLA with $\bar{M}_v = 1 \times 10^6$ and $\bar{M}_v = 8 \times 10^5$ was obtained after fractionated precipitation of samples with $\bar{M}_v = 9 \times 10^5$ and $\bar{M}_v = 7.2 \times 10^5$ respectively as described in a previous paper[5]. Chloroform (Merck) and toluene (Merck, distilled from sodium) were used for dissolution of the polymer.

Intrinsic viscosity

An Ubbelohde viscometer (type Oa; ASTM D445) was used for the determination of the intrinsic viscosity $[\eta]$ of the polymer in chloroform and chloroform/toluene mixtures at 25°C and 60°C. The viscosity-average molecular weight ($\bar{M}_v$) of the samples was estimated from the $[\eta]$ in chloroform at 25°C according to the formula[4]:

$$[\eta] = 5.45 \times 10^{-4} \bar{M}_v^{0.73}$$

Optical rotation

The specific optical rotation $[\alpha]$ of PLLA ($\bar{M}_v = 1 \times 10^6$) in chloroform and chloroform/toluene mixtures (0.1 g dl^{-1}) was determined at 60°C and at a fixed wavelength (578 nm) using a Perkin–Elmer (241) polarimeter. The polymer solutions to be measured were prepared by dissolving PLLA in chloroform at room temperature (16 h) and subsequent addition of toluene (if

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required). The polymer solutions were conditioned in the polarimeter at 60°C for 14 h while the value for the rotation was recorded. Usually the optical rotation had reached a constant value after 7 h.

Dry-spinning, hot-drawing procedure

The spinning solutions (*Figure 1*, curves A–D) were prepared by dissolving PLLA in chloroform (16 h) and subsequent addition of toluene without mechanical stirring (4 days) (*Figure 1*, curves B–D, *Figures 3* and *13*). The PLLA/toluene solution (*Figure 1*, curve E) was obtained after distillation of chloroform from a 2% (w/v) PLLA solution in chloroform/toluene 50/50 (v/v) at 95°C. Before extrusion the PLLA solutions were conditioned in the piston–cylinder apparatus at 70°C (PLLA/toluene 90°C) for 3 h. The fibres were extruded at 60°C through a stainless-steel, conical die (entrance angle 20°, length 23 mm and exit diameter 0.25 mm) and collected on sandblasted glass bobbins (1.15–1.65 m min^{-1}) without applying additional stress to the extrudate. The distance between die and bobbin was 6.5 cm. The as-spun fibres were dried on the bobbins at room temperature until constant weight was reached (usually about 48 h). Hot-drawing experiments were carried out in a heated, double-walled glass tube (length 0.6 m) as described previously[4,5,7,13]. The entrance velocity of the fibres was 6.3 cm min^{-1}. The take-up speed was in the range of 25–170 cm min^{-1}. It was found that during fibre spinning and hot drawing no decrease in M_v of the polymer had taken place.

Characterization of the fibres

An ISI-DS-130 scanning electron microscope operated at 5–10 kV was used to study the microstructure of the various filaments of PLLA. Thermal analysis of the samples was performed by means of a Perkin–Elmer DSC-7, calibrated with ICTA (International Confederation for Thermal Analysis) certified reference materials and operated at a scan speed of 10°C min^{-1}.

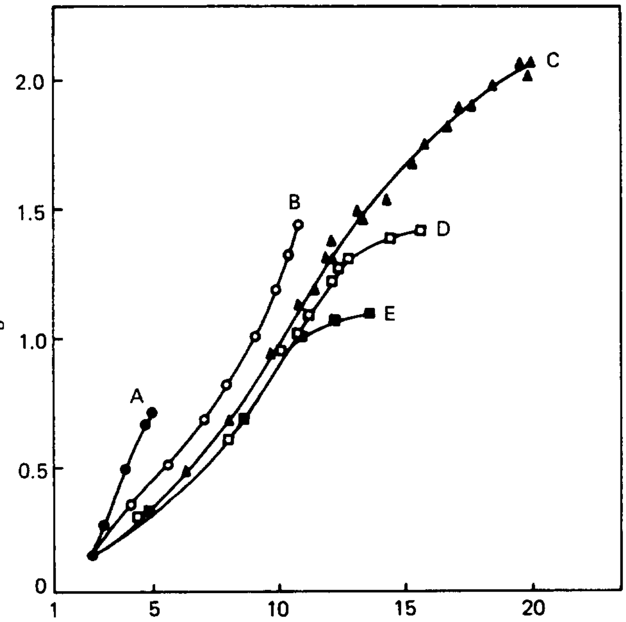

Figure 1 Effect of chloroform/toluene ratio in the PLLA ($\bar{M}_v = 9 \times 10^5$) spinning solution (4% w/v; 60°C) on the fibre drawability at 204°C and subsequent tensile strength of the filaments: curve A (●) $\phi = 0$ (chloroform); curve B (○) $\phi = 0.5$; curve C (▲) $\phi = 0.6$; curve D (□) $\phi = 0.7$; curve E (■) $\phi = 1$ (toluene)

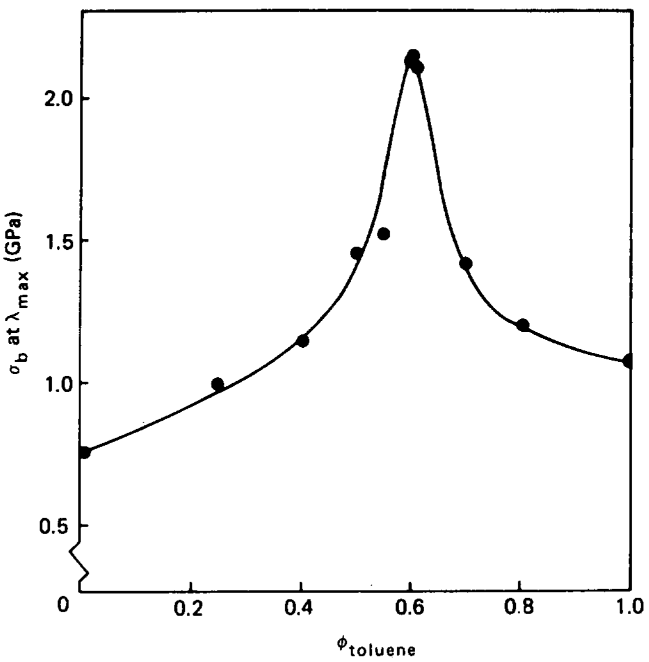

Figure 2 Effect of chloroform/toluene ratio in the spinning solution on the ultimate tensile strength of the PLLA filaments shown in *Figure 1*

Mechanical properties of the fibres 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^{-1}. The length of the specimen was 25 mm. Cross sections of the fibres were calculated from the fibre weight and length, assuming a value of 1290 kg m^{-3} as the density of the fibre[4,5,7,15]. All the tensile properties to be presented are the average values of five tests.

RESULTS AND DISCUSSION

The tenacity of PLLA fibres ($\bar{M}_v = 9 \times 10^5$) spun from 4% (w/v) polymer solutions in various chloroform/toluene mixtures at 60°C and subsequently hot drawn to different λ at 204°C are presented in *Figure 1*. All curves show the same feature, namely the increase in tensile strength with draw ratio, but its limiting value seems to depend on the solvent quality. *Figure 2* gives the effect of chloroform/toluene composition in the spinning solution on the ultimate σ_b of the fibres prepared, revealing a very pronounced maximum of 2.1 GPa at a toluene volume fraction (ϕ) of 0.6. *Table 1* shows the typical mechanical properties of these optimal hot drawn PLLA fibres.

Polymer concentration

Figure 3 demonstrates the influence of PLLA concentration (c) in the spinning solutions ($\phi = 0.6$) on their spinnability and ultimate fibre tenacity for different $\bar{M}_v$ (*Figure 3*, curve A, $\bar{M}_v = 9 \times 10^5$, curve B, $\bar{M}_v = 6.5 \times 10^5$). For both $\bar{M}_v$ values investigated there seems to be quite a pronounced maximum in the σ_b vs. c curves (*Figure 3*, curve A, 4% (w/v) and curve B, 5–6% (w/v)) in accord with previous observations that the polymer concentration (c) is able to affect the spinning process, fibre drawability and subsequent tensile properties[5]. Within the framework of the entanglement concept for drawing of weakly bonded macromolecules

Table 1 Typical mechanical properties of PLLA fibres ($\bar{M}_v = 9 \times 10^5$) spun at 60°C from various solvent(s) (mixtures) and hot drawn at 204°C to λ_{max}

Solvent composition						
Chloroform (ϕ)	Toluene (ϕ)	σ_b (GPa)	E (GPa)	ε (%)	λ_{max}	Cross sectional area $\times 10^{10}$ (m^2)
1	0	0.75	9	20	5	11
0.5	0.5	1.45	10	23	10.5	3.45
0.4	0.6	2.10	16	23	20	1.36
0.3	0.7	1.40	11	23	14.5	2.67
0	1	1.05	10.5	23	13.5	4.21

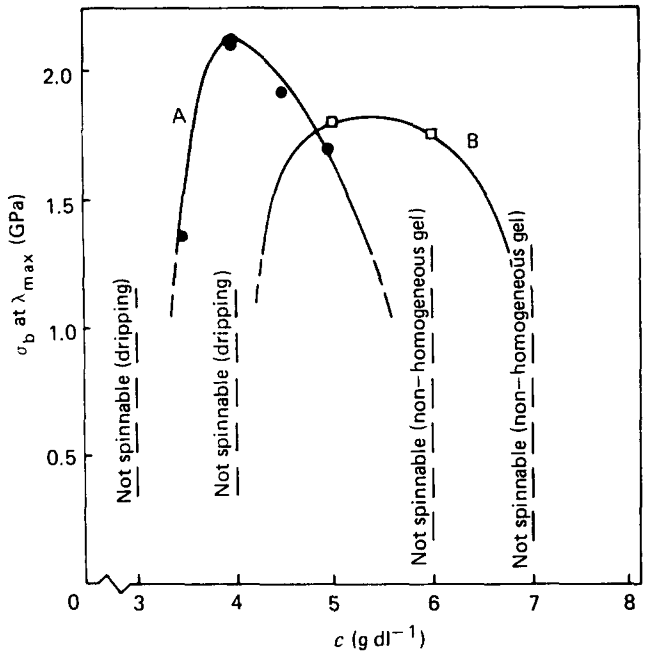

Figure 3 Dependence of the tensile strength of maximal hot-drawn PLLA filaments on the polymer concentration (c) in the spinning solution: curve A (●) $\bar{M}_v = 9 \times 10^5$; curve B (□) $\bar{M}_v = 6.5 \times 10^5$

one can expect this PLLA concentration to be inversely proportional to the MW of the polymer[5,13,16,17]. The effects of polymer concentration on the ultimate tensile properties of the fibre became more pronounced with increasing $\bar{M}_v$.[5,13] This phenomenon can likely be attributed to the increase in complexity of the entanglement network with the use of a higher MW, which can easily hamper appropriate disentangling of the chains at dissolution or at hot drawing[5,13,16]. Only a low number of entanglements should be present in the transient polymeric network during orientation strengthening in order to achieve proper alignment and extension of the high MW chains[5,16,17]. Therefore at solution spinning of high MW flexible polymers, solidification (gelation) of the polymer should preferably take place near the onset of coil overlap ($[\eta]c \sim 1$) in order to minimize the entanglement density in the filaments prepared[5,18,19]. As such, polymer MW, MWD, polymer concentration and solvent quality will therefore have a strong impact on fibre drawability.

Fibre spinning

The spinning of PLLA solutions (*Table 1*) at room temperature gave rise to extrudate distortion ('solution fracture') as described in detail in two previous papers[5,7]. It has been suggested that elastically recoverable strains generated in the polymer flow are mainly responsible for the appearance of elastic turbulences and can lead to spiralling flow[20]. In this study a higher spinning temperature (60°C) was applied in order to be able to suppress these turbulences. The spinning at 60°C resulted in a smooth shaped extrudate and enhanced solvent evaporation. Viscosity measurements showed that during the spinning process no decrease in $\bar{M}_v$ of the polymer had taken place. Because of the ternary polymer/good solvent/poor solvent systems investigated, premature phase separation at a high ϕ before or at the spinning process could become a point of concern. In the case of nylon-6 fibres a possible stress-induced liquid–liquid phase separation at the spinning process leads to less drawable filaments with a typical ball-like structure[13]. For the fibres presented in *Figure 1* no macroscopic evidence for premature phase separation (either liquid–liquid or liquid–solid) was found. However, at 60°C after prolonged periods of time in the case of higher PLLA concentrations (*Figure 3*) or toluene fractions ($\phi > 0.8$) gel inhomogenities were observed indicating that phase separation actually had taken place.

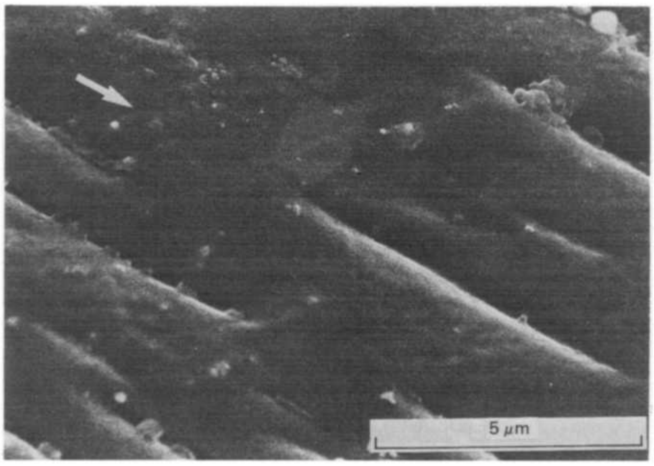

Figure 4 Scanning electron micrograph (SEM) of an as-spun PLLA fibre ($\bar{M}_v = 9 \times 10^5$) prepared from a 4% (w/v) PLLA solution in chloroform at 60°C

As-spun fibres and drawability

Figures 4 and *5* present scanning electron micrographs of as-spun PLLA fibres (*Figure 1*) prepared from chloroform and chloroform/toluene 40/60 (v/v) respectively. It was observed that, except for the chloroform-spun fibres, the as-spun filaments exhibited a porous texture probably to be attributed to a more rapid phase separation in the presence of the poor solvent.

Figure 6 shows stress–strain curves of both as-spun filaments as recorded at room temperature. It was noticed that the chloroform-spun fibres were cold drawn (*Figure 6*, curve A) and hot drawn by formation of a typical neck leading to undesired fibre irregularities[21,22]. Drawing of the porous filaments of PLLA proceeded by a more

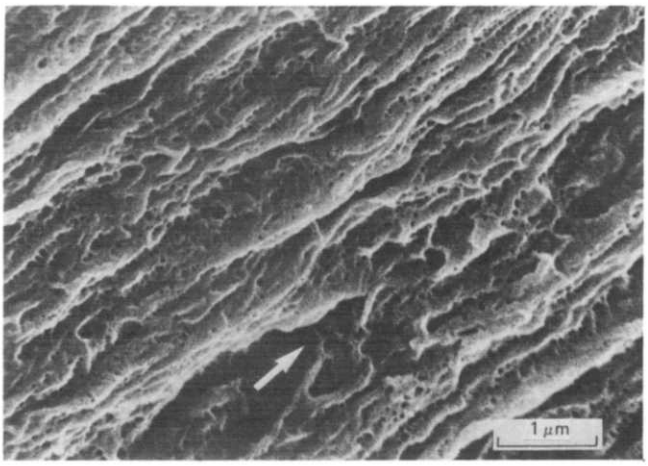

Figure 5 SEM of an as-spun PLLA fibre ($\bar{M}_v = 9 \times 10^5$) produced from a 4% (w/v) PLLA solution in chloroform/toluene 40/60 (v/v) at 60°C

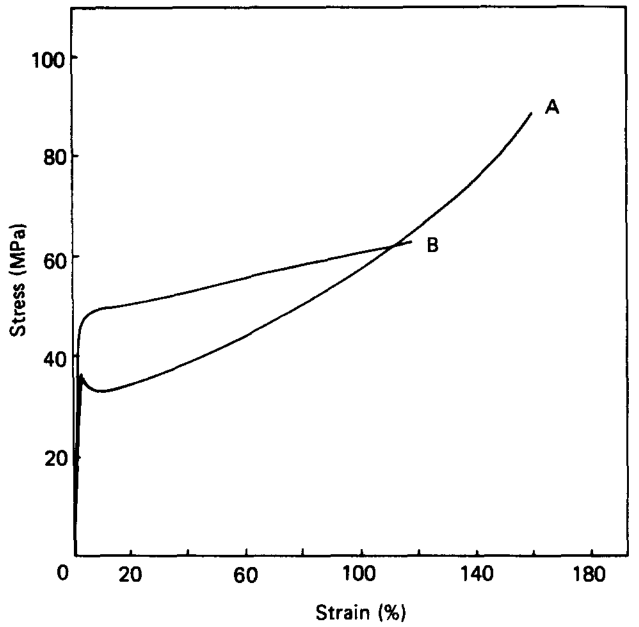

Figure 6 Stress–strain curves of as-spun PLLA filaments ($\bar{M}_v = 9 \times 10^5$) produced at 60°C from 4% (w/v) PLLA solutions in chloroform (curve A) and chloroform/toluene 40/60 (v/v) (curve B) respectively

homogeneous deformation of the polymer (*Figure 6*, curve B) resulting in regular shaped fibres[16]. When subjected to load the filaments with a porous texture likely will contain numerous spots of stress concentrations at which the polymer will be simultaneously deformed. In addition to the aforementioned effects of polymer concentration and fibre texture, there seemed to be a clear relationship between solvent composition applied, heat of fusion (ΔH_m) of the as-spun filaments and their drawability.

Figures 7 and *8* present the ΔH_m of the various as-spun filaments with applied solvent composition (*Figure 7*) and maximum obtained draw ratio (*Figure 8*) respectively. It was noticed that the ΔH_m vs. ϕ curve exhibited a quite pronounced maximum. PLLA fibres spun from chloroform/toluene 40/60 (v/v) were found to have the highest initial crystallinity (53.4%) and λ_{max} (20) when hot drawn. In general, fibre drawability appeared to improve with increasing ΔH_m of the as-spun filaments. It has been reported before that the ΔH_m can be regarded as a relative measure for the concentration of chain entanglements, which seems to be confirmed by the findings of this study[23–25].

It was noticed that at a lower ϕ (high content of good solvent) the solidification of PLLA from the as-spun solution took more time, which may have led to the formation of new entanglements upon solvent evaporation. On the one hand this phenomenon may have affected the observed increase in ΔH_m and fibre drawability when using higher toluene contents in the solvent mixture. However, with increasing ϕ, lowering of the solvent power of the good solvent/poor solvent mixture can be expected. Reduction of solvent quality will hamper appropriate dissolution of PLLA and in the extreme may lead to formation of intramolecular chain entanglements and phase separation, which will lower the

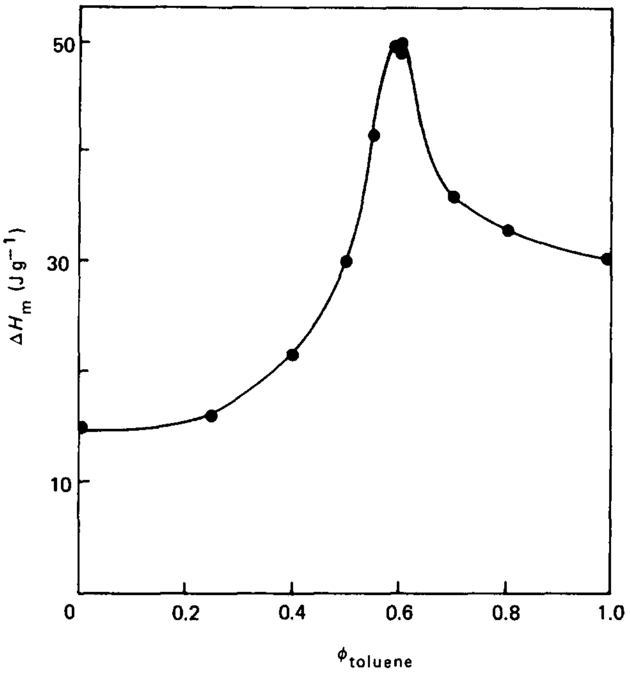

Figure 7 Effect of the chloroform/toluene ratio in the PLLA ($\bar{M}_v = 9 \times 10^5$) spinning solution (4% w/v; 60°C) on the heat of fusion of the as-spun filaments

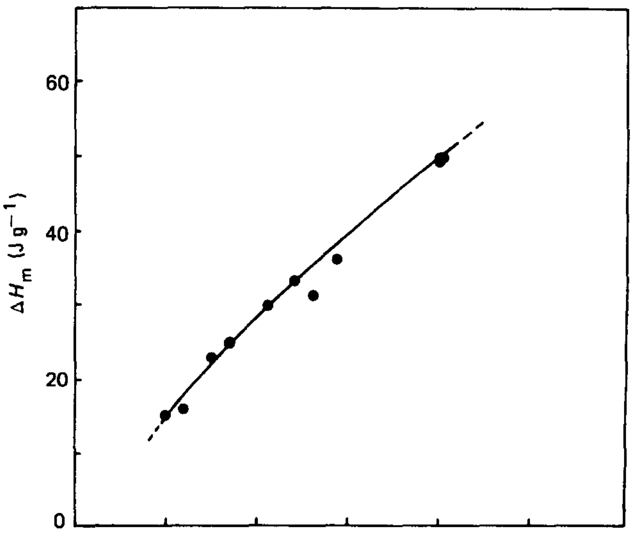

Figure 8 Effect of the heat of fusion of the as-spun filaments (*Figure 7*) on their λ_{max} at 204°C

ΔH_m and λ_{max} of the fibres prepared. In addition at a high ϕ, the starting, more concentrated, PLLA solution in chloroform may exceed the onset for coil overlap, which can result in the formation of more entanglements[19].

These two opposing effects may account for the observed optimal fibre drawability at $\phi = 0.6$ (*Figures 7* and *8*).

However, in exceptional cases binary solvent mixtures can exhibit a higher degree of solvent power as compared to the separate components[26]. A detailed study on the solvent quality of the solvent mixtures applied therefore seemed to be of importance.

Figure 9 shows the intrinsic viscosity $[\eta]$ of PLLA ($\bar{M}_v = 8 \times 10^5$ and $\bar{M}_v = 1 \times 10^6$) as measured at different ϕ and various temperatures. The viscosity data revealed that such a synergetic cosolvent effect had not taken place. However, at certain toluene fractions, dependent on the temperature and $\bar{M}_v$ studied, remarkable changes in $[\eta]$ were observed. It has been reported that the $[\eta]$ in binary solvent systems can show sudden changes near the θ conditions of the polymer[27,28]. When preferential adsorption of the good solvent takes place an inter and intra θ condition, dependent on polymer *MW*, can be distinguished[28]. If not, both conditions coincide. For PLLA ($\bar{M}_v = 1 \times 10^6$) at 60°C, the inter and intra θ conditions show up in the vicinity of $\phi = 0.4$ and $\phi = 0.6$ respectively. For PLLA with $\bar{M}_v = 8 \times 10^5$ these conditions were observed at $\phi = 0.5$ and $\phi = 0.7$.

According to a scaling expression connecting the polymer *MW* between entanglements ($\bar{M}_e$) and the overall polymer concentration (c) of a semidilute polymer solution, the $\bar{M}_e$ in the case of a θ solvent ($\bar{M}_e \propto c^{-2}$) should be much larger than using a good solvent ($\bar{M}_e \propto c^{-1.5}$)[29]. In comparable situations, a polymer dissolved in a θ solvent may therefore contain a lower number of entanglements than in the case of using a good solvent. In addition to the afore-mentioned effects of the various solvent mixtures on the rate of phase separation of PLLA, this phenomenon may have contributed to the excellent drawability of the PLLA fibres spun from polymer solutions near the θ conditions. PLLA is known to be an optically active polymer and is claimed to crystallize in a (10/3) helical conformation[4,15]. In solution, eventual changes in the polymer conformation like a coil–helix transition (or the reverse) should be detectable by measuring the specific optical rotation $[\alpha]$ (Ref. 30). It seemed to be of interest to investigate whether the viscosity changes observed eventually were related to such a transition. *Figure 10* presents the specific rotation $[\alpha]$ of PLLA ($\bar{M}_v = 1 \times 10^6$) at 60°C and at different ϕ. It was noticed that a pronounced increase in $[\alpha]$ took place between $\phi = 0.4$ and $\phi = 0.55$ (near the θ conditions) although the extent of this effect (−153 to −161°C) did not point to a complete coil–helix transition. However, like that observed for amylose, an intermediate transition into an interrupted helical structure may have occurred[31,32]. The formation of an interrupted rod-like structure will lead to a slight increase in $[\alpha]$ and decrease in $[\eta]$ and seems to be a suitable precursor for the crystallization (chain-folding) process. Both the θ conditions and interrupted helical structure may have induced the rapid formation of a gel after extrusion of the PLLA solutions. In these swollen networks, helical aggregates most probably have acted as crystalline junctions impeding formation of new entanglements and leaving a rather crystalline, good drawable fibre[17].

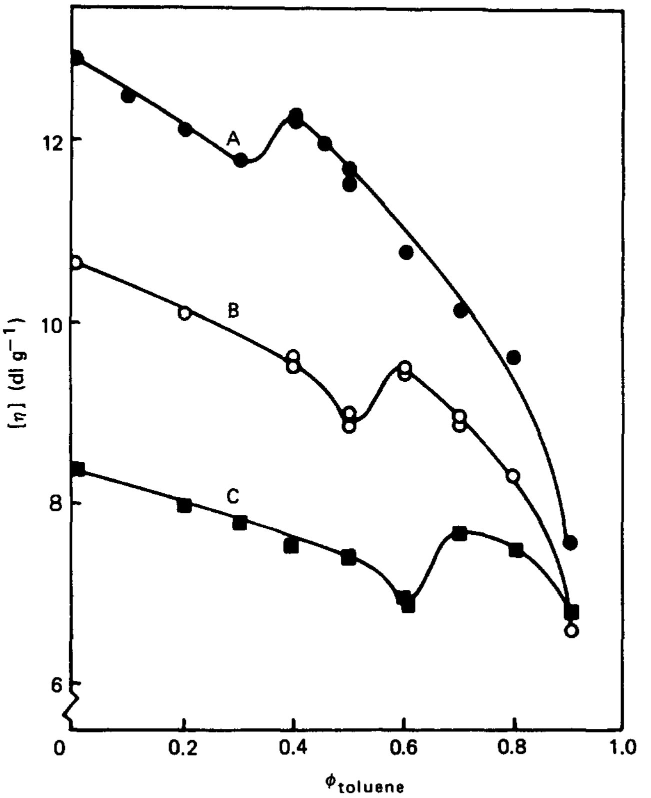

Figure 9 Effect of chloroform/toluene composition and temperature on the intrinsic viscosity of PLLA: curve A (●) $\bar{M}_v = 1 \times 10^6$, 25°C; curve B (○) $\bar{M}_v = 1 \times 10^6$, 60°C; curve C (■) $\bar{M}_v = 8 \times 10^5$, 60°C

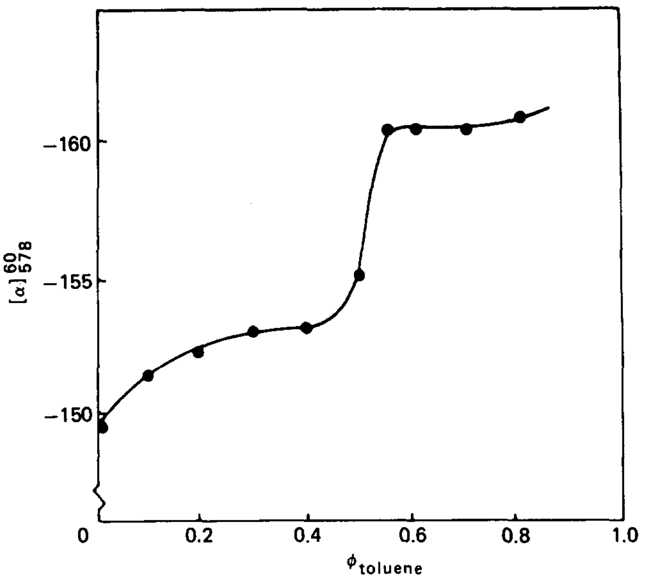

Figure 10 Specific rotation of PLLA ($\bar{M}_v = 1 \times 10^6$) in different chloroform/toluene compositions at 60°C (wavelength 578 nm)

Despite the identical spinning conditions, the dry weight of the as-spun fibres appeared to be notably different. *Figure 11* shows the dry weight of as-spun PLLA fibres (*Figure 1*) with the applied solvent composition. PLLA fibres ($\bar{M}_v = 9 \times 10^5$) spun from chloroform/toluene 40/60 (v/v) exhibited a minimum in weight which is to be attributed to a minimal degree or absence of extrudate swell at the spinning process[14,16]. Apparently in this range of toluene fractions the spinning solutions showed a low degree of elasticity, corroborated by the appearance of both the θ conditions and

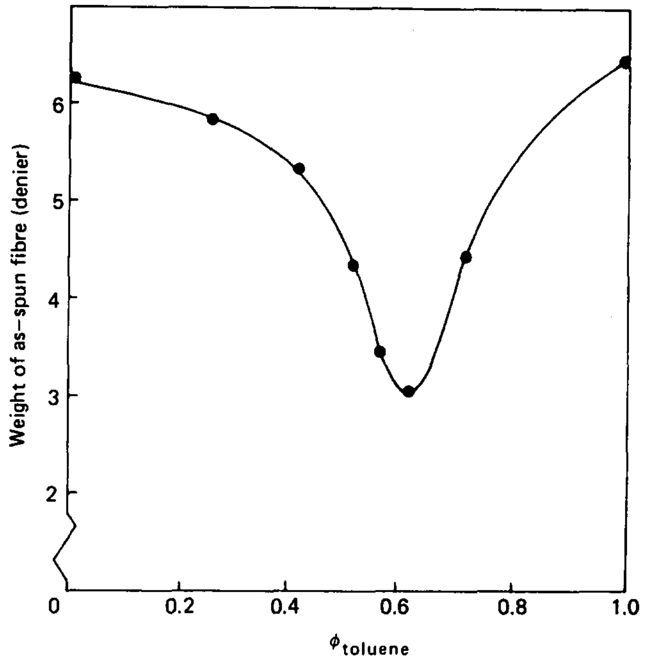

Figure 11 Dry weight of as-spun PLLA fibres ($\bar{M}_v = 9 \times 10^5$) prepared under identical spinning conditions at 60°C using 4% (w/v) PLLA solutions in various chloroform/toluene compositions. (Note that denier is used to indicate mass in grams of 9000 m of fibre)

interrupted (semi rod-like) helical structure. The absence of extrudate swell at fibre spinning can be of technological interest.

The most favourable spinning solutions (*Figure 1*) were prepared at room temperature by dissolving the polymer in chloroform followed by a slow diffusion of toluene into the PLLA solutions which may have introduced some additional effects. For this reason a spinning solution in which PLLA was directly dissolved (4% w/v) in the solvent mixture ($\phi = 0.6$) was processed into fibres. At 70°C and after 8 h a macroscopic homogeneous solution was obtained. However, the as-spun filaments revealed a rather low ΔH_m (26.5 J g^{-1}) and $\lambda_{\max}$ (8) as illustrated in *Figure 12*. Apparently, appropriate dissolution of PLLA in this solvent mixture (close to a θ solvent for the polymer at this temperature) had not taken place yet. However, prolonged heating of the spinning solution probably would result in degradation of the polymer. Obviously this should be avoided. In this respect our method of preparation of the spinning solution seems to be an attractive route. In a first step the highly crystalline PLLA can be readily dissolved in the good solvent at room temperature leading to highly expanded coils at moderate polymer concentrations[5,18]. In a second step the addition of poor solvent will result in shrinkage of these coils eventually followed by polymer crystallization (gelation at $\phi \geqslant 0.5$). In this manner a suitable gel of PLLA can be obtained ($\phi = 0.5$–0.7) without degradation of the polymer.

Hot drawing

Figure 13 presents the σ_b of PLLA fibres ($\bar{M}_v = 9 \times 10^5$ and $\bar{M}_v = 1 \times 10^6$ (fractionated sample)) hot drawn to $\lambda_{\max}$ at different temperatures. The fibres were spun at 60°C from a 4% (w/v) PLLA solution in chloroform/toluene 40/60 (v/v).

Wide-angle X-ray experiments showed that the discontinuity in tensile properties between 190 and 200°C (*Figure 13*, curve A) most probably can be attributed to a crystal transition of PLLA[33]. Fibres hot drawn up to 190°C revealed a usual α modification. At higher temperatures (up to 204°C) the α form was found to be gradually replaced by a β form (assumed 3/1 helix)[33]. PLLA fibres hot drawn at the optimun drawing temperature (204°C) consisted of the β form only. Synchrotron radiation studies by Hoogsteen and ten Brinke indicate that this β form, if present, probably is the load-bearing structure in the PLLA fibres[33]. The sudden lowering of tensile properties due to drawing in the

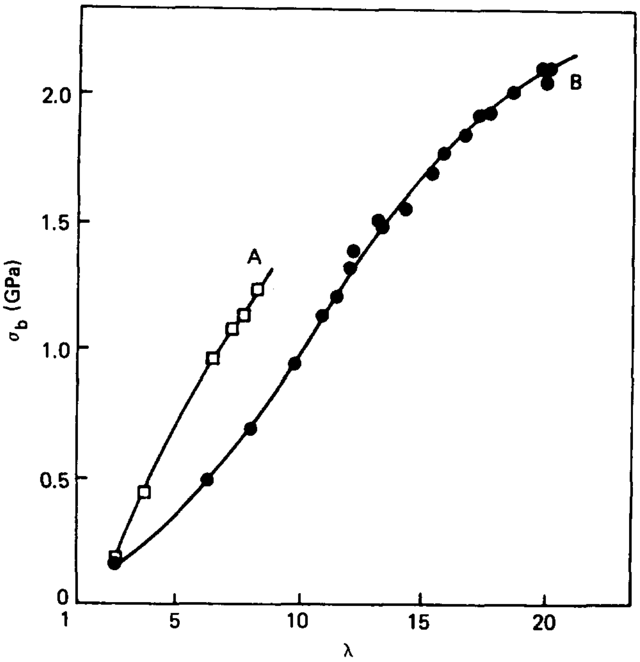

Figure 12 Effect of preparation procedure of the PLLA ($\bar{M}_v = 9 \times 10^5$) spinning solution (4% w/v; $\phi = 0.6$; spinning temperature 60°C) on fibre drawability at 204°C and subsequent tensile strength of the filaments: curve A (□) PLLA dissolved directly in the solvent mixture; curve B (●) PLLA first dissolved in chloroform followed by addition of toluene

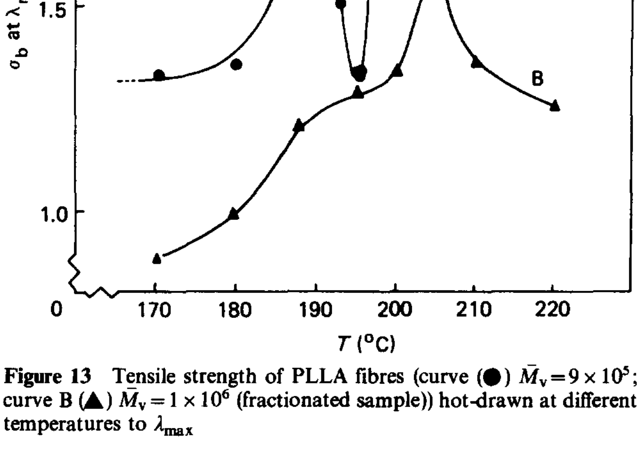

Figure 13 Tensile strength of PLLA fibres (curve (●) $\bar{M}_v = 9 \times 10^5$; curve B (▲) $\bar{M}_v = 1 \times 10^6$ (fractionated sample)) hot-drawn at different temperatures to $\lambda_{\max}$

temperature range of 190–204°C may be ascribed to the presence of both crystal modifications in these fibres.

PLLA filaments prepared from the fractionated sample ($\bar{M}_v = 1 \times 10^6$) were found to have a ΔH_m of 42.7 J g^{-1}, a value which is slightly lower than that observed for the fibres prepared from the as-polymerized sample ($\Delta H_m = 50$ J g^{-1}). Topological defects like knots may have been introduced into the polymer during the process of fractionation (stirred dissolution/precipitation)[34]. Obviously these had not all disappeared upon preparation of the fibres, which may explain the observed lowering of the ΔH_m. Hot drawing of these filaments probably resulted in areas with severe topological imperfections (e.g. tight knots) impeding proper alignment and extension of the chains, as demonstrated by the moderate draw ratios ($\lambda_{max} = 13$) and fibre properties obtained (σ_b up to 1.65 GPa)[34]. The optimum hot-drawn fibres ($\lambda = 13$) consisted of both the α and β crystalline modifications.

Tensile strength and fibre diameter

According to the concept of Griffith, fracture of materials under load is initiated at surface flaws where cracks are supposed to be formed[35]. Usually sudden failure of the solid takes place after these cracks have reached a critical dimension. In view of this concept the tensile properties of a polymeric fibre should possibly be affected by the concentration of surface flaws (e.g. surface area of the fibre). Indeed, in comparable situations thinner polymeric filaments usually yield higher values for the breaking strength[36,37]. For ultra-high-strength polyethylene fibres a linear relationship between the reciprocal σ_b of fully oriented filaments and the square root of their diameter has been observed[37]. Extrapolation to fibre diameter zero yielded a strength of 26 GPa for a flawless fibre. This value is very close to the theoretical strength of polyethylene (25 GPa)[37]. *Figure 14* presents the reciprocal tensile strength of hot-drawn PLLA filaments ($\bar{M}_v = 6.5$–9×10^5) with the square root of their diameter. The strongest PLLA filament ($\sigma_b = 2.1$ GPa) was found to have the smallest cross section (1.36×10^{-10} m^2) Only highly oriented fibres of PLLA fitted the predicted linear relationship. Extrapolation to fibre diameter zero (*Figure 14*) yields a value of 8 GPa for a flawless fibre. This value may be close to the theoretical strength of PLLA. For the range of $\bar{M}_v$ investigated (6.5–9×10^5) the ultimate tensile strength of the fibres was not dependent on molecular weight but seems to be determined by the final cross section of the filaments.

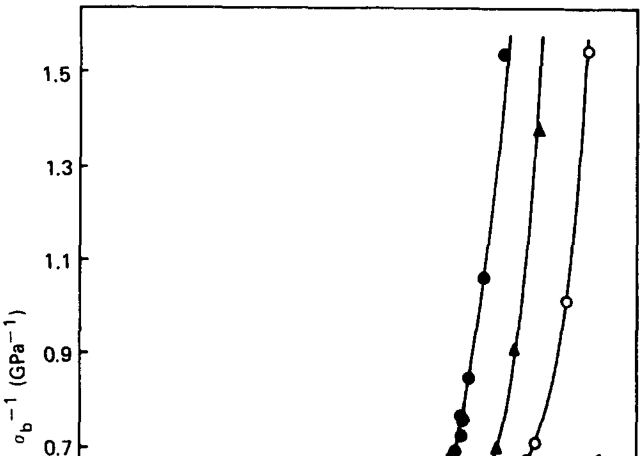

Figure 14 Reciprocal tensile strength of hot-drawn PLLA filaments (○, ● and □, $\bar{M}_v = 9 \times 10^5$; ▲ and △, $\bar{M}_v = 6.5 \times 10^5$) with the square root of their diameter. The fibres were spun from various PLLA solutions (*Figures 3*) at 60°C and subsequently hot drawn at 204°C

CONCLUSIONS

High-strength PLLA fibres ($\sigma_b = 2.1$ GPa, $E = 16$ GPa) can be produced by dry spinning of a PLLA ($\bar{M}_v = 9 \times 10^5$) solution (4% w/v) in chloroform/toluene 40/60 (v/v) at 60°C, followed by hot drawing at 204°C. Viscosity measurements and optical rotation data indicated that fibre spinning should have taken place near the θ conditions and where PLLA adopts an interrupted helical conformation. Solidification of PLLA from the solutions is initiated by the formation of a gel in which helical aggregates form crystalline junctions that hamper re-entangling, leading to a rather crystalline (53.4%) polymer and good drawable fibre ($\lambda_{max} = 20$). Fibre drawability appears to improve with increasing heat of fusion of the as-spun filaments. PLLA can exhibit an α to β crystal transition upon hot drawing. The optimal hot-drawn PLLA fibres ($\sigma_b = 2.1$ GPa) consisted of the β modification only (probably 3/1 helix). The ultimate tenacity of hot-drawn PLLA fibres was found to be inversely proportional to the square root of their diameter but independent of the $\bar{M}_v$ studied (6.5–9×10^5). Extrapolation to fibre diameter zero yielded a hypothetical flawless PLLA fibre of 8 GPa, which may approach the theoretical strength of PLLA.

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