Biodegradable materials of poly(L-lactic acid): 1. Melt-spun and solution-spun fibres

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Poly(L-lactic) PLLA fibres with a high degree of molecular orientation and crystallinity were produced by hot-drawing of the melt-spun and solution-spun fibres. Solution-spun fibres show better tensile properties as compared with those of the melt-spun fibres. This may be caused by a lower number of entanglements trapped in the solution-spun fibres. The highest values of the tensile strength found for PLLA fibres in the present study were 0.5 and 1.0 GPa for the melt-spun and solution-spun fibres, respectively. Tensile strength of PLLA fibres increases with the draw ratio, and above a certain molecular weight, also with molecular weight of the polymer. Tensile strength was found to be strongly dependent on the drawing temperature which may be associated with the occurrence of two crystal modifications.

Keywords Biodegradable materials; polylactic acid; fibres; hot-drawing; mechanical properties; crystalline modification

INTRODUCTION

Poly(L-lactic acid) (PLLA) belongs to the group of polymers that include poly(glycolic acid) or poly(hydroxybutyric acid) which, because of their biodegradibility to nontoxic products, may have wider practical applications in medicine[1]. Poly(L-lactic acid) is biocompatible and in the body, in the course of time, it will undergo hydrolitic scission to the lactic acid, which is a natural intermediate in carbohydrate metabolism[2-4].

This feature of PLLA makes it suitable for use in producing the resorbable sutures, implants for orthopedic surgery or blood vessels, which finally can be replaced by the body's tissues. It is important however that the products from PLLA should be sufficiently strong to maintain their stability during the healing process.

Fibres of PLLA have already been obtained[2-5], however a maximum tensile strength at break of these fibres, made from polymer of relatively low molecular weight, was in the range of 0.02–0.5 GPa, which may not be sufficient for certain medical applications, e.g. in microsurgery very thin and strong suture material may be required. Therefore, it was considered to be of interest to explore whether in analogy to the ultra-high strength fibres of polyethylene[6,7], PLLA fibres with comparable mechanical properties could be produced.

Poly(L-lactic acid) can be obtained from the dilactide by a cationic ring-opening polymerization[2-4,8,9]. The monomer of PLLA, L-lactic acid is easily prepared in a high yield by fermentation of molasses[10] or potato starch[11], thus in addition to its medical application, the polymer might become a potential substitute for nondegradable synthetic polymers causing environmental problems.

PLLA crystallizes in the pseudo-orthorombic[12] or hexagonal[13] crystalline modification with 10_3 helix conformation[12]. The glass transition temperature of the polymer is around 55°C [4] and the equilibrium melting temperature is 215°C[4]. Density of the crystalline phase of PLLA $d_c = 1290$ kg m^{-3}, density of the amorphous phase $d_a = 1248$ kg m^{-3} and the heat of melting of the crystalline regions of PLLA, $\Delta H_m = 8.1$–93.1 Jg^{-1}.[14]

Crystallization of PLLA or PDLA from the melt gives negatively birefringent spherulites[14] while crystallization from dilute solution yields lamellar single crystals 10 nm thick[12,13].

In this paper the results on mechanical properties of PLLA fibres, obtained by hot-drawing of the melt-spun as well as solution-spun fibres, are presented. It will be shown that for a certain molecular weight range, the tensile strength of the fibres is strongly dependent on the molecular weight of PLLA as well as on the drawing conditions.

EXPERIMENTAL

Materials

Poly(L-lactic acid) was obtained by a ring opening polymerization of L-lactide[2-4,8,9] in presence of stannous octoate (stannous 2-ethyl hexanoate) as a catalyst[4]. Concentration of the catalyst was in the range of 2×10^{-5} to 1×10^{-4} moles per mole of L-lactide. In order to obtain PLLA with a high molecular weight, it was necessary to use the reagents of the highest purity since water, lactic acid or lactoyllactic acid may act as chain transfer agents during polymerization[4].

L-lactide (supplied by C. V. Chemie Combinatie Amsterdam C.C.A., Arkelsedijk 46, Postbox 21, Gorinchem, Holland) was recrystallized 4 times from ethyl acetate. Ethyl acetate, dichloromethane, chloroform, methanol, ethanol and acetone were distilled twice over drying agents such as phosphorous pentoxide, calcium chloride or molecular sieves.

Freshly recrystallized L-lactide was polymerized at 130°C for 48 hours in silanized glass ampoules, heat-sealed under high vacuum. The polymer was purified from

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residual lactide by dissolution in dichloromethane and subsequent precipitation with methanol.

The polymer was dried at 50°C in a vacuum oven and stored over phosphorous pentoxide.

The intrinsic viscosity of the samples in chloroform was measured at 25°C. This viscosity average molecular weight of PLLA was calculated according to the relation[9]:

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

The optical rotation of the samples, being a measure of stereoregularity, was measured with a Perkin-Elmer 241 polarimeter at a wavelength of 589 nm, using a polymer solution of concentration 0.1 g/100 ml. The characterization of the samples are given in *Table 1.*

Spinning of PLLA fibres

Fibres of PLLA with molecular weight in the range 3–5×10^5 were produced by extrusion of the polymer solutions in toluene at 110°C through a conical capillary with diameter 1 mm. Concentrations of these solutions were 12% by weight for the polymer with $\bar{M}_v = 3.5 \times 10^5$ and 6% by weight for the polymer with $\bar{M}_v = 5.3 \times 10^5$. After spinning, the fibre was dried at room temperature.

The wind-up speed for the solution-spun fibres was in the range 25–35 cm min^{-1}. These fibres did not exhibit any orientation as checked by WAXS. PLLA fibres with molecular weight below 3×10^5 could not be spun under these conditions, due to the low viscosity of the polymer solution at 110°C. These samples were transformed into fibres by melt-extrusion at 185°C through a capillary with diameter 1 mm and length 10 mm. Before melt-extrusion the polymer was evacuated in glass ampoules at a vacuum of 2×10^{-5} Torr for 3 h, and subsequently melted to form cylindrical bars. The outer diameter of these bars was only slightly smaller than the inner diameter of the extruder cylinder. This procedure protected the polymer against void formation during extrusion. This was checked by electron microscopy of the fracture-surface of the as-spun fibres.

As in the case of the solution-spun fibres, the take-up speed for the melt-spun fibres was in the range of 25–35 cm min^{-1}.

It was not possible to extrude the fibres from the melt above 185°C, because of the low viscosity of the melt.

Hot-drawing

Hot-drawing experiments were carried out in an electric tube furnace, 500 mm in length. The temperature gradient was maintained in the furnace in order to avoid neck formation during the hot-drawing, which may result in a decrease in the tensile strength of the drawn fibre[7]. The spinning velocity at the entrance of the tube was about 20 mm min^{-1}.

Analysis of fibres

The mechanical properties of the fibres were measured at room temperature using an Instron tensile tester at a cross-head speed of 12 mm min^{-1}. Length of the specimens was 25 mm. The cross-sectional areas of the fibres were calculated from the fibre weight and length, assuming a value of 1290 kg m^{-3} [14] as a density of the fibre.

All the tensile properties given in this paper represent average values of six tests.

Table 1 PLLA samples used in the experiments

Intrinsic viscosity (dl/g)	Molecular weight $\bar{M}_v$ (Kg kmol^{-1})	Optical rotation $[\alpha]^{25}_{D}$
3.8	1.8×10^5	−166
4.9	2.6×10^5	−163
6.2	3.5×10^5	−159
8.2	5.3×10^5	−156

Melting thermograms of constrained and unconstrained fibres were recorded on a Perkin-Elmer DSC-2 instrument at a scan speed of 5°C/min, using fibre sections with a length of 70 mm. Fibres were constrained by winding them around a copper wire and knotting at the ends.

Wide-angle X-ray diffraction patterns were obtained at room temperature using a Philips diffractometer with Ni filtered CuKα radiation.

A Jeol JSM 35C scanning electron microscope was used for observation of the fibre surfaces.

RESULTS AND DISCUSSION

Mechanical properties of melt-spun fibres

PLLA fibres with molecular weights of 1.8×10^5 and 2.6×10^5, which were spun from the melt, reached maximum tensile properties at a drawing temperature of about 110°C and draw ratio of 8. This temperature was found to be the optimum drawing temperature.

The fibre sample with $\bar{M}_v = 1.8 \times 10^5$ had a tensile strength-at-break of 0.5 GPa, an initial modulus of 6 GPa and an elongation-at-break of 25%. The sample with $\bar{M}_v = 2.6 \times 10^5$ had a tensile strength-at-break of 0.48 GPa, an initial modulus of 7 GPa and an elongation-at-break of 20%. Both the samples showed yielding at about 4% strain. The yield stress was about 35–40% of the tensile strength-at-break. The fibres split into fibrils when fractured, due to the stress applied at room temperature. The maximum tensile strengths-at-break found for both the molecular weight samples are lower than those found by Schneider[5]: for PLLA with $\bar{M}_v = 2.0 \times 10^4$–0.5 GPa, and $\bar{M}_v = 1.8 \times 10^5$–0.7 GPa.

The difference in the tensile strengths may be due to the different experimental procedure as for instance the melt-spinning and drawing, as well as to the tensile testing conditions. For instance, it is well known that the specimen length and the strain rate have a marked influence on the measured tensile strength-at-break.

It was found that for PLLA fibres with molecular weights 1.8×10^5 and 5.3×10^5 the tensile strength-at-break increases with the applied strain by about 10% per decade.

These observations show that it is difficult to compare tensile strength data given in the literature[2,3,5], as the strain rate is generally omitted.

Mechanical properties of solution-spun fibres

Effect of draw ratio. Figure 1 shows the stress–strain dependence for the fibre samples with molecular weight 5.3×10^5 drawn at a temperature of 200.5°C and a draw ratio of 18(A), 17(B), 14(C) and 8(D).

It can be seen that the initial modulus, as assessed from the slope, is the same for all draw ratios and that the tensile strength increases and the initiation of yielding becomes less with increasing draw ratio. Under applied drawing conditions the drawing stress had a minute effect on the tensile properties of the PLLA fibres. *Figure 2* illustrates the dependence of the tensile strength-at-break, *TS*, on the draw ratio λ for PLLA fibres obtained from the polymer with molecular weights of 3.5×10^5 and 5.3×10^5, respectively.

Table 2 presents the typical mechanical properties of these fibres, which were drawn at temperatures at which the highest *TS* values were achieved. It is clear that, for the samples with lower molecular weight, the ultimate mechanical properties are obtained at draw ratios between 18 and 25. This is reflected by a plateau on the TS/λ curve shown in *Figure 2* and indicates that under these conditions the maximum number of molecular entanglements and crystalline defects have been removed[15]. No plateau was observed on the TS/λ dependence for the higher molecular weight samples, while even at highest achievable draw ratios there was still some yield on the stress–strain curves. This shows that the drawing limits and optimal drawing conditions, which

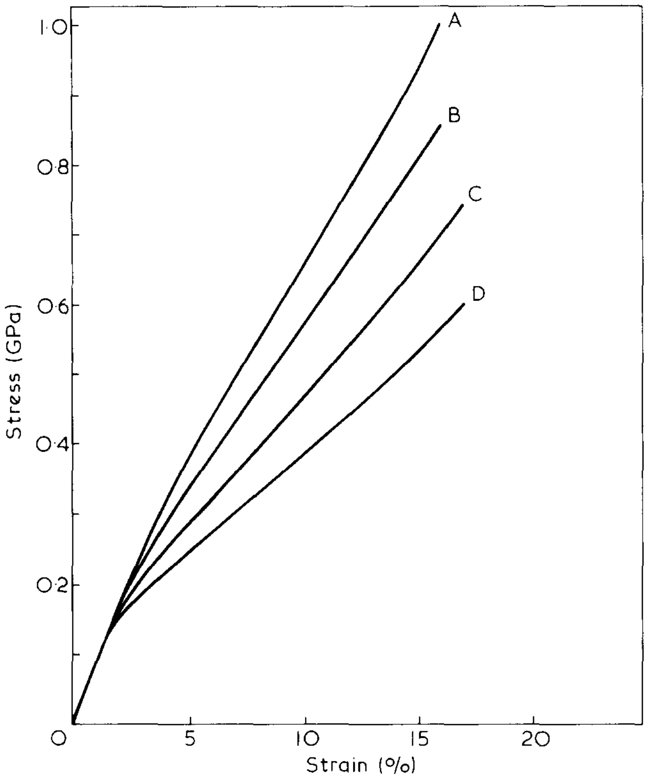

Figure 1 Stress–strain dependence for fibre with $\bar{M}_v = 5.3 \times 10^5$ drawn at 200.5°C to various draw ratios. (A) 18; (B) 17; (C) 14; and (D) 8

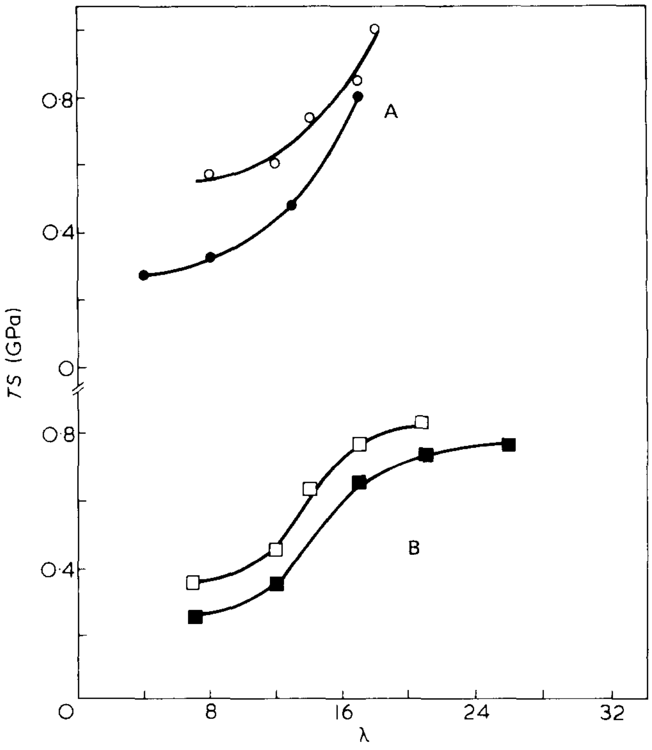

Figure 2 Dependence of the tensile strength *TS* on the draw ratio λ, for two samples of PLLA with different molecular weights drawn at indicated temperatures. (A) $M_v = 5.3 \times 10^5$, ○, 200.5°C; ●, 196.5°C. (B) $M_v = 3.5 \times 10^5$, □, 180°C; ■, 190°C

Table 2 Mechanical properties of PLLA fibres with different molecular weight

Molecular weight (Kg kmol^{-1})	Drawing temperature (°C)	Draw ratio λ	Tensile strength (GPa)	Elongation-at-break (%)	Initial modulus (GPa)
5.3×10^5	196.5	4	0.28	18	7
		8	0.32	18	7
		13	0.46	18	8
		17	0.80	16	9
	200.5	8	0.57	17	9
		12	0.60	17	9
		14	0.74	17	9
		17	0.85	16	9
		18	1.00	16	9
3.5×10^5	180.0	7	0.35	26	7
		12	0.46	22	8
		14	0.63	18	9
		18	0.77	15	9
		21	0.80	15	9
	190.0	7	0.26	23	6
		12	0.35	19	8
		18	0.65	13	10
		21	0.69	13	10
		26	0.75	12	10

would lead to the maximum tensile strength, have not been attained for these samples. A similar effect of molecular weight on the draw ratio was also observed for hot-drawn polyethylene[16].

It was recently suggested[7,17] that larger draw ratios are required for a full molecular extension of higher molecular weights. As for the fibre with a molecular weight of 5.3×10^5, the highest achievable draw ratio was about 18 (25 for a lower molecular weight PLLA), it is not surprising that this sample did not achieve the ultimate mechanical properties. The limit in the draw ratio may result from the fact that the rate of drawing applied to the fibre was still too low[18]. Nevertheless, the draw ratios reached in the present study are much higher than those obtained earlier for PLLA with a comparable molecular weight[5]. Relatively good drawability of the PLLA fibres obtained by us, may be due to the spinning of the fibre from solution, which results in a morphology containing only a few entanglements[7].

It can be seen from *Table 2* that contrary to polyethylene[19] and polypropylene[20] the initial modulus of PLLA fibres is almost independent of the draw ratio. This may be associated with the elastic deformation of the α-crystalline modification consisting of flexible helices.

Effect of drawing temperature. Figure 3 illustrates the effect of drawing temperature on the maximum draw ratio λ_{max} and the tensile strength TS at λ_{max} for the solution-spun fibres obtained from PLLA with molecular weights of 3.5×10^5 and 5.3×10^5.

For the fibres of both molecular weights, there exist two maxima on the TS/T curves. At these temperatures the ultimate mechanical properties can be reached. These maxima fall at 180°C and 190°C for the lower molecular weight samples, and at 180°C and 200°C for the higher molecular weight samples. The maxima are separated by a clear minimum in the tensile strength at temperatures of about 184° and 190°C for the lower and higher molecular weight PLLA, respectively. Thus four temperature regions can be distinguished in the TS/T and λ_{max}/T dependence presented in *Figure 3*. They are called arbitrarly regions I, II, III and IV. These regions fall at temperatures 50°–180°C (region I), 180°–190°C (region II), 190°–200°C (region III) and above 200°C (region IV) for PLLA fibres with $M_v = 5.3 \times 10^5$, and respectively at 50°–180°C (I), 180°–184°C (II), 184°–190°C (III) and above 190°C (IV) for PLLA fibres with $M_v = 3.5 \times 10^5$.

The mechanical properties of PLLA fibres drawn at temperatures in region I of TS/T dependence result from the cold-drawing of the crystals formed in the fibre upon solution-extrusion. The chain mobility in the range of T_g (55°C) is high enough to ensure a reasonable tensile strength, as the cold-drawing at room temperature already leads to a tensile strength in the range 0.5–0.7 GPa[5].

In region II the maximum draw ratio, i.e., tensile strength, drops gradually with an increase in the drawing temperature. This could be due to the fact that at temperatures close to the melting point of the polymer (180°C), the poor crystals undergo melting. The stress applied to the fibre shifts its melting point to higher temperatures and therefore increases the supercooling, i.e. the rate of crystallization[21]. The molten material reorganizes quickly into the larger crystals which decreases the chain mobility and reduces drawability of the fibre. Further increase of drawing temperature (region III) increases the molecular mobility as a result of thermal motions, which leads to higher draw ratios and tensile strength with the optimum at 200°C.

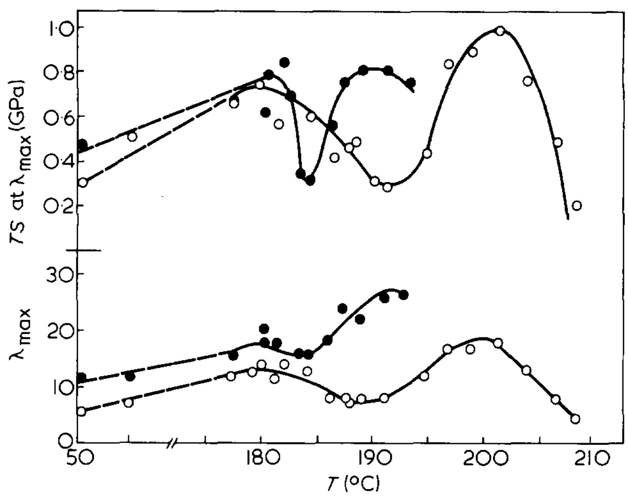

Figure 3 Effect of the drawing temperature on the λ_{max} and the tensile strength at λ_{max} for PLLA fibres with different molecular weight. ●, $M_v = 3.5 \times 10^5$; ○, $M_v = 5.3 \times 10^5$

At temperatures above the optimum in TS (region IV) the molecular relaxation process becomes dominant which decreases the tensile strength. It should be noted that the temperature at which the spinning and drawing processes were carried out has an influence on the molecular weight of the samples. The molecular weight of PLLA fibres decreased by about 15% during the spinning and by about 3–5% on hot-drawing.

Effect of molecular weight. According to the literature[22,23], the dependence of the tensile strength on the molecular weight for linear polymers and network is given by the equation:

$$TS = A - B/\bar{M}_n$$

where: A, B and $\bar{M}_n$, are two constants and the number-average molecular weight respectively.

For PLLA with relatively narrow molecular weight distribution[4] one can use $\bar{M}_v$ instead of $\bar{M}_n$.

In *Figure 4* the dependence of the maximum tensile strength TS_{max} on the reciprocal of the viscosity-average molecular weight $1/\bar{M}_v$ of PLLA fibres is presented. For molecular weights in the range 1.0×10^5 and 3.0×10^5 there is almost no influence of the molecular weight on the tensile strength of PLLA fibres. Similar results were obtained by Schneider[5] for the melt-spun PLLA with molecular weights in the range 2.0×10^4 to 1.8×10^5.

For molecular weights above 3.0×10^5 the tensile strength of the PLLA fibres increases strongly with the molecular weight, reaching the highest value of 1.0 GPa. This behaviour of PLLA subjected to hot-drawing may result from the fact that for the polymer with a lower molecular weight which was melt-spun, the highly flexible molecules are involved in numerous entanglements which remain as defects after drawing, and together with a high number of chain ends incorporated in the drawn fibre, effectively decrease its tensile strength. Significant increase in the tensile strength for the fibres with the higher molecular weight above 3.0×10^5, which were spun from the solution, may be due not only to a lower number of the chain ends, i.e. less defects involved in the crystal

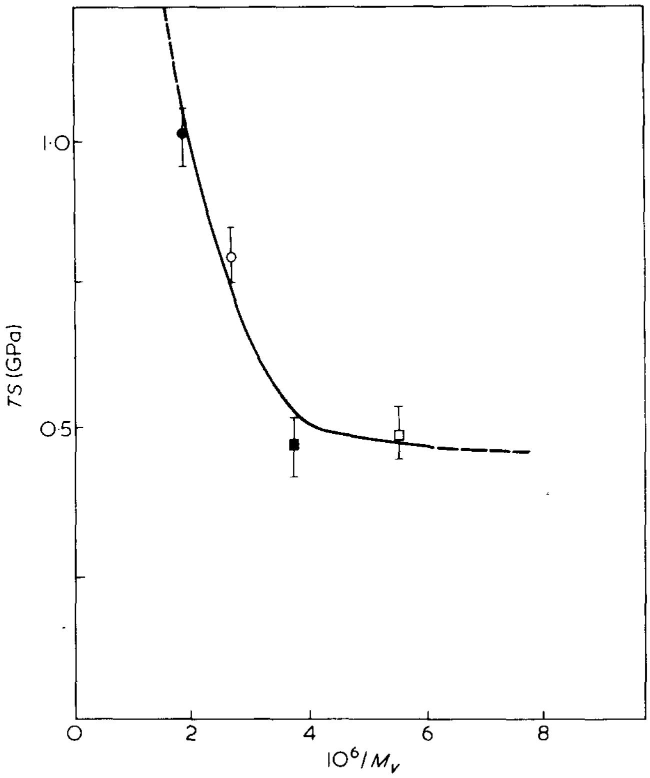

Figure 4 Effect of the viscosity-average molecular weight on the tensile strength of PLLA fibres. Fibres were drawn at optimum temperatures to λ_{max}. Fibre diameters: ●, 0.45 x 10^{-4} m; ○, 0.69 x 10^{-4} m; ■, 1.6 x 10^{-4} m; □, 1.7 x 10^{-4} m

lattice, but additionally to less trapped entanglements.

The tensile strength will also be affected by the crystal distorsions arising from stereo-irregularities along the chains and by the fact that the strongest fibres have a smaller diameter. Furthermore the fibrillation, as demonstrated by the scanning electron micrograph in *Figure 5*, will influence the mechanical properties.

Very similar data for the tensile strength vs. molecular weight dependence were obtained for PLLA fibres with identical 'spinning history', spun at room temperature from a good solvent[24].

Melting characteristics

Figure 6 shows the the melting thermograms of PLLA fibres with $\bar{M}_v = 5.3 \times 10^5$ drawn at 200.5°C to λ_{max}, and illustrates the effect of sample preparation on the shape of the melting endotherms.

Thermogram A was recorded for a fibre of 70 mm in length which was constrained by knotting two ends. Thermograms B and C were obtained for unconstrained fibres 70 mm in length and for the fibres cut into pieces 2–3 mm in length, respectively.

The small peak at the lower temperature region of thermogram A is probably due to the free ends of the fibre at the knotting points, and the second broad melting peak at a temperature of 20°–30°C higher than that of the first peak is due to the stress applied to the fibre. On release of this stress, the intensity of the small peak present in thermogram A, strongly increases for B and C, while the high temperature melting peak disappears.

X-ray diffraction

Figures 7 and *8* show the wide-angle X-ray diffraction patterns of the melt-spun fibre with molecular weight of 1.8×10^5 and a tensile strength-at-break of 0.5 GPa, and the solution-spun fibre with molecular weight of 5.3×10^5 and a tensile strength of 1 GPa, respectively.

As can be concluded from the patterns, both the fibres have a high molecular orientation and crystallinity. The X-ray diffraction pattern of the melt-spun fibre is quite similar to that of found by de Santis and Kovacs[12] and shows that these fibres consist mainly of the α-crystalline modification, although new reflections present in the fibre would suggest the presence of another type of crystalline form. This problem has to be investigated further. The reflections in the patterns are extended in the lateral direction and the layer lines are smeared, pointing to a high disorder in the planes orthogonol to the fibre axis.

The X-ray diffraction pattern for the solution-spun fibres is different to that for the melt-extruded fibres and

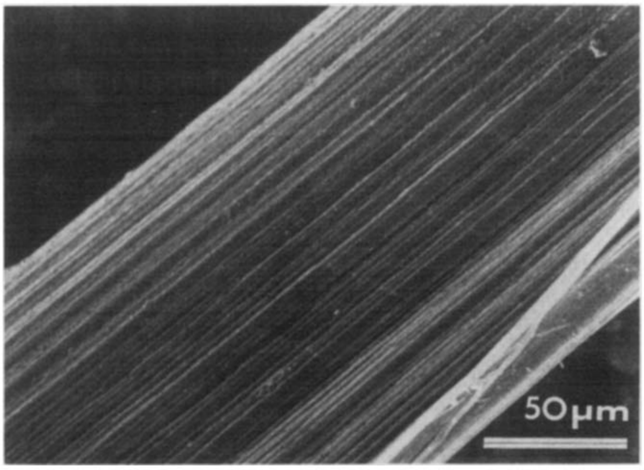

Figure 5 Scanning electron micrograph of the surface of PLLA fibre with a tensile strength of 1.0 GPa drawn at 200.5°C

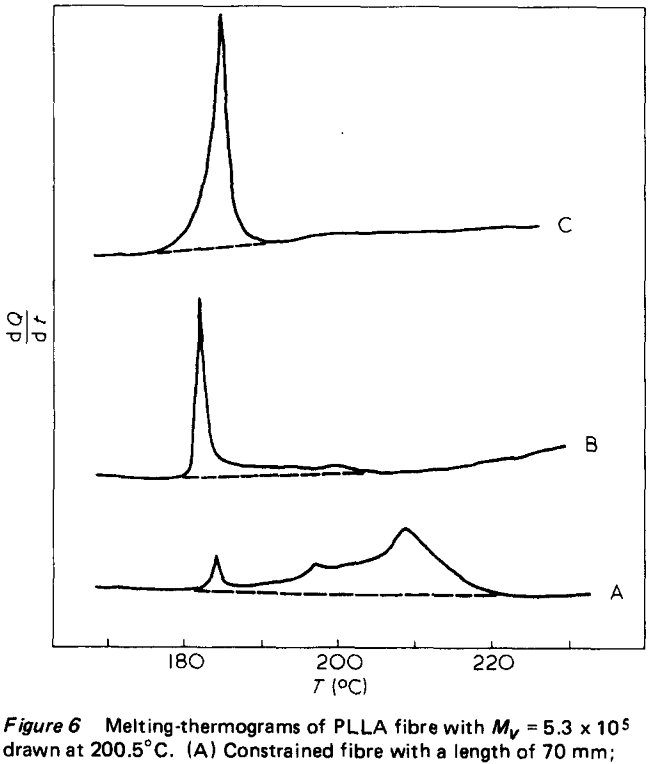

Figure 6 Melting-thermograms of PLLA fibre with $M_v = 5.3 \times 10^5$ drawn at 200.5°C. (A) Constrained fibre with a length of 70 mm; (B) unconstrained fibre with a length of 70 mm; (C) fibre cut into pieces of 2–3 mm in length

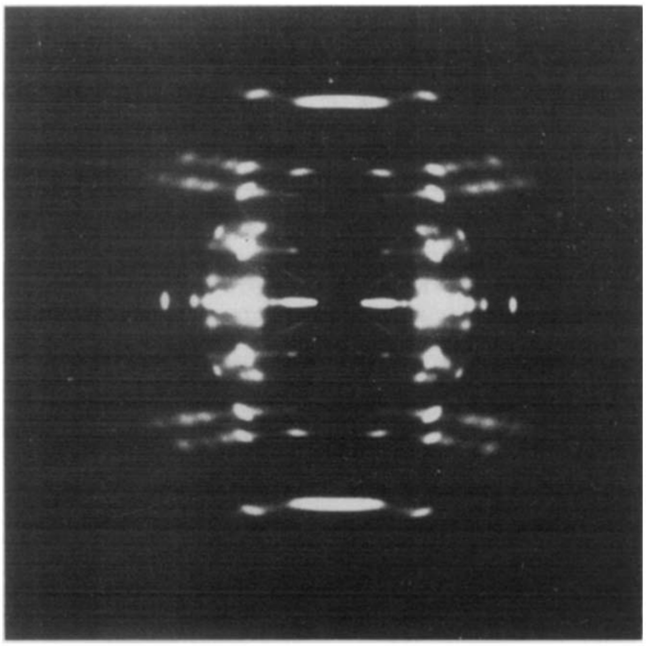

Figure 7 Wide-angle X-ray diffraction pattern of the melt-spun fibre with a tensile strength of 0.5 GPa (M_v = 1.8 x 10^5)

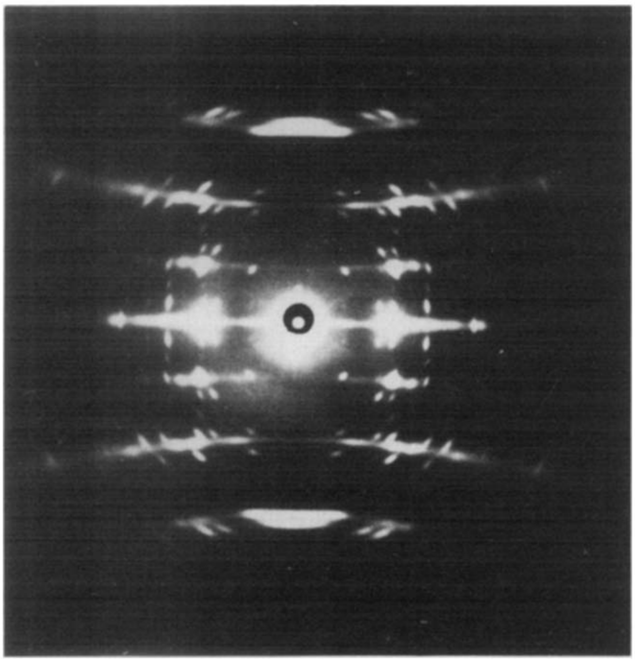

Figure 8 Wide-angle X-ray diffraction pattern of the solution-spun fibre with a tensile strength of 1 GPa (M_v = 5.3 x 10^5)

shows the presence of two crystalline modifications: alpha (α) and beta (β) in the fibre.

In the α-modification the chains assume a helix conformation while the β-modification is characterized by an extended-helix conformation. In PLLA the α-phase gives sharp reflections, whereas the β-phase gives only diffuse reflections seen as smeared layer lines in the diffraction patterns. The positions of the layer lines of the β-phase fall on the positions 3,2; 6,2 and 9.6 in the layer line sequence of the α-phase. Although the presence of the α-form in PLLA was already discussed by Kovacs[12], the existence of a β-form is reported here for the first time.

The smeared layer lines of the β-form indicate that in the plane orthogonal to the fibre axis, there exists a high degree of disorder. Similarly as for polypivolactone PPL[25] the β-form content in the PLLA fibres increases with increase in the draw ratio, and at a low draw ratio the fibre consists almost exclusively of the α-modification. This phenomenon gives the PLLA fibres a certain kind of 'memory' which is formed on the drawing process. It is remarkable that the lower molecular weight fibres as for instance the fibre with $\bar{M}_v = 3.5 \times 10^5$ and a tensile strength of 0.8 GPa drawn to the same draw ratio as the fibre with $\bar{M}_v = 5.3 \times 10^5$ and a tensile strength of 1.0 GPa, however, contained less of the β-phase. This may be due to the fact that the low molecular weight PLLA chains slip more easily past each other, and the helix structure cannot be extended[26].

CONCLUSIONS

Hot-drawing of PLLA fibres obtained by the melt-spinning of the polymer with molecular weight in the range 1.8–2.6 x 10^5 at temperatures close to its melting point, produces fibres with a tensile strength of 0.5 GPa.

PLLA fibres with a tensile strength up to 1 GPa are obtained by hot-drawing of the solution-spun fibres with molecular weight in the range 3.5–5.3 x 10^5.

Tensile strength *TS* of PLLA fibres increases strongly with the draw ratio applied to the fibre and for $\bar{M}_v$ above 3.0 x 10^5, *TS* increases with the molecular weight of the polymer.

Increasing the drawing temperature results in two maxima in the tensile strength *versus T* curve. Optimum drawing temperatures are 180°C and 190°C for PLLA with $\bar{M}_v = 3.5 \times 10^5$, and 180° and 200°C for PLLA with $\bar{M}_v = 5.3 \times 10^5$.

In PLLA fibres with molecular weight above 3.0 x 10^5 drawn to a high draw ratio, a partial transformation of the α-crystalline modification into the β-crystalline modification takes place.

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