

# Biodegradable fibres of poly(L-lactic acid) produced by melt spinning

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(Received 19 December 1995; revised 13 March 1996)

Starting with poly(L-lactic acid) (PLLA) of molecular weight 330 000, fibres were obtained through a two stage process: (i) melt-extrusion at various collecting rates (ranging from 1.8 to 10 m min<sup>-1</sup>, and (ii) hot-drawing at various drawing rates. The molecular weight of PLLA fell to about 100 000, as a consequence of the production process. Ninety per cent of the molecular weight loss occurred during extrusion and ten per cent during hot-drawing. At fixed extrusion rate, properties of as-spun fibres strongly depended on their collection rate. The higher the collection rate, the higher the modulus and strength, and the lower the strain at break. While almost amorphous fibres were obtained at lower collection rates (1.8 and 3.1 m min<sup>-1</sup>), about 30 and 38% crystalline as-spun fibres were produced at rates of 5 and 10 m min<sup>-1</sup>, respectively. Moreover, the capability of fibres to sustain a further hot-drawing process, was found to be dependent on the collection speed during extrusion. Tensile modulus of 9.2 GPa and tensile strength of 0.87 GPa were obtained for fibres collected at 5 m min<sup>-1</sup> and drawn 10 times. Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(lactic acid); melt spinning; biodegradable fibres)

## INTRODUCTION

Among biodegradable materials<sup>1–4</sup>, poly(L-lactic acid) (PLLA) plays a role in biomedical applications. In recent years, due to increasing demand for biodegradable polymers and the favourable mechanical properties/degradation characteristics of this synthetic polyester, much attention has been devoted to the study of its synthesis<sup>5–11</sup>, morphology<sup>12–18</sup>, thermal and mechanical properties<sup>18–25</sup>, and degradation kinetics both in *in vitro* and *in vivo* conditions<sup>26–31</sup>. Poly(lactic acid) represents one of the most important biodegradable polymers, being the preferred alternative to its homologous poly(glycolic acid) whenever a slower degradation rate is required. Drug delivering implants<sup>32</sup>, vascular prosthesis<sup>20,33</sup>, and orthopaedic surgery<sup>21,31,34,35</sup> are main fields of clinical applications.

Poly(lactic acid) derives from the polymerization of the lactide or lactic acid, a monomer produced in mammalian muscles during glycogenolysis and correlated with the Krebs cycle through piruvic acid and acetyl CoA<sup>36</sup>. Two different enantiomeric forms, D- and L-lactic acids exist (but only the L configuration is present in living systems), thus producing different corresponding enantiomeric polymers, as a consequence on the maintenance of the chiral centre. While the D,L polymers (both *mesomeric* and *racemic* D,L-lactide derivatives) are fully amorphous, as a result of the syndiotacticity and/or atacticity of methyl groups, PLLA can crystallize having an isotactic chain. The degree of crystallinity depends on many factors, such as molecular weight, thermal and processing history, temperature and time of annealing treatments<sup>22,25</sup>.

The mechanical properties and degradation kinetics of the semicrystalline PLLA are quite different from those of homologous and completely amorphous poly(D,L-lactic acid). In particular PLLA is always preferred whenever higher mechanical strength and longer degradation time are required. In the literature, for PLLA, tensile modulus and strength of 3 GPa and 50 MPa<sup>24</sup>, and flexural modulus and strength of about 4 GPa and 100 MPa<sup>26</sup>, respectively, are reported.

PLLA fibres have been extensively studied, especially in the last decade. Investigations in the 1970s led to the production of PLLA and PDLA fibres<sup>6</sup>, both having tensile strength of 2.5 g denier<sup>-1</sup> (0.28 GPa). However, in this case the spinning process seemed not to be very accurate, afterwards Schneider<sup>37</sup> obtained fibres having stress at break in the range of 0.5–0.7 GPa. Furthermore, in 1982, Eling *et al.*<sup>38</sup> through melt spinning and drawing, realized fibres with tensile strength of 0.5 GPa and modulus of 7 GPa.

A few years later, PLLA fibres having tensile strength up to 0.7 GPa and tensile modulus close to 9 GPa, were produced by Hyon *et al.*<sup>39,40</sup>. Other researchers who focused their attention on PLLA melt spun fibres, reached strengths of about 0.4 GPa<sup>29,33</sup> but in some cases too large diameters (0.25 mm<sup>33</sup>, and 0.35 mm<sup>41</sup>). Recently, in 1993, Pennings *et al.*<sup>42</sup>, spinning from the melt using slightly different conditions (a spinning rate of 1 m min<sup>-1</sup> at 210°C instead of 0.3 m min<sup>-1</sup> at 185°C, and drawing at 100°C) prepared fibres with a modulus of 9 GPa and almost the same strength previously reported, 0.53 GPa.

Mechanical properties of melt-spun fibres taken from the present literature, as well as the adopted processing conditions are summarized in *Table 1*.

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**Table 1** Extrusion conditions and final properties of fibres produced by different authors

Author (year)	Initial $M_v$ ( $\times 10^{-3}$ )	Extrusion temperature ( $^{\circ}\text{C}$ )	Collection speed ( $\text{m min}^{-1}$ )	Nozzle diameter (mm)	As-spun fibre crystallinity (%)	Final $M_v$ ( $\times 10^{-3}$ )	Drawn fibre diameter ( $\mu\text{m}$ )	Fibre strength/ modulus (GPa)
Schneider <sup>37</sup> (1972)	19 182	160–190	?	0.13–3.8	?	< 114	25–500	0.48 / 0.69 / 7
Eling <sup>38</sup> (1982)	< 300	185	0.25–0.35	1	?	180–260	?	0.5 / 7
Hyon <sup>39</sup> (1984)	360	200	?	1	$\approx 5$	110	150	0.7 / 8.5
Dauner <sup>39</sup> (1992)	98	190	?	0.5	?	38	76	0.4 / ?
Pennings <sup>42</sup> (1993)	280	210	1	0.25	42	100	83	0.53 / 9
This paper (1995)	330	240	2 (5–20)	1	5 (20–40)	110	80	0.87 / 9

A method capable of producing higher strength PLLA fibres, is dry-spinning, where the fibre is produced by spinning in air or other gases a solution of the polymer and drawing it under certain conditions. Pennings and co-workers, after preliminary studies where they obtained fibres with a strength of 1.2 GPa<sup>43</sup>, later produced fibres having stress at break up to 2.3 GPa<sup>44,45</sup>, starting from solutions of PLLA in a chloroform/toluene mixture. Other authors investigated the production of such fibres through a dry spinning process, such as Horacek and Kalisek (study of the effect of radiation on fibre resistance, strength of 0.5 GPa<sup>46</sup>; dry spinning for porous fibre production, strength of 0.4 GPa<sup>47–49</sup>) and Tsuji *et al.*<sup>50</sup> (stereo-complex PDLA and PLLA fibres, strength of 0.9 GPa). Recently we produced fibres having a strength of 1.1 GPa, starting from PLLA/chloroform solutions<sup>51</sup>. In our opinion, possible extensions of this process to industrial application are limited by its quite low spinning and drawing rates.

In this paper the manufacture and physical characterization of PLLA fibres produced by melt-spinning are reported, paying particular attention to the effect of the fibre collection rate after extrusion on their drawability and final properties.

## EXPERIMENTAL

### Material

Polymer of L-lactic acid, PLLA, with molecular weight 330 000 was supplied by Boehringer (Ingelheim, Germany) and was stored under vacuum in a desiccator until use. D.s.c. analysis showed that the melting point of the as received polymer was 186 $^{\circ}\text{C}$  and the crystallinity content was about 75%.

### Fibres production

PLLA fibres were produced by a two-stage process: first *melt-extrusion* with fibres collection at various rates, and then *hot-drawing*. Before extrusion the polymer was dried at 50 $^{\circ}\text{C}$  in a vacuum oven for 48 h.

*Melt extrusion.* The polymer was melt-spun in nitrogen by using a single screw extruder (Estru 13 made by Friulfiliere, Buia (UD), Italy) equipped with a cooling jacket, to prevent polymer flakes from melting inside the feed hopper, and three heating bands located along the screw and kept at different temperatures. Fibres were initially spun through a single-nozzle circular spinnerette (1 mm diameter), and then collected on a glass drum located at 50 cm with different speeds ranging from 1.8 to 20  $\text{m min}^{-1}$ .

*Hot drawing.* In a second step as-spun fibres were drawn at 160 $^{\circ}\text{C}$  with a hot-plate drawing apparatus (Giudici DGF, Sala al Barro, Lecco, Italy) modified in order to flush in nitrogen during drawing.

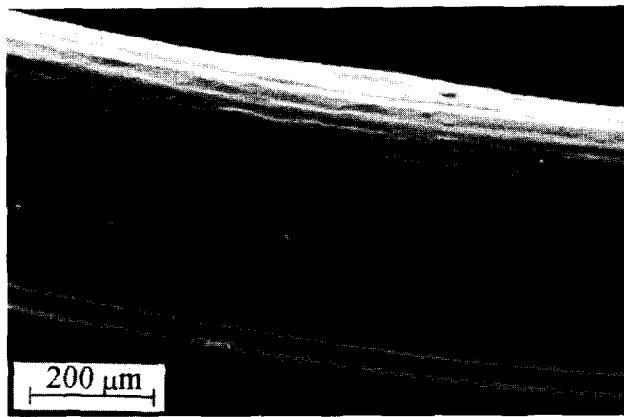
*Draw ratio.* Draw ratio was defined as  $\lambda = (D_{\text{in}}/D_{\text{fin}})^2$ , where  $D_{\text{in}}$  and  $D_{\text{fin}}$  are the initial and final diameters of fibre before and after the process, respectively. Fibre diameter was measured using a Palmer-type micrometer. Considering the fact that fibres underwent two drawings, i.e. during extrusion ( $\lambda_{\text{ext}}$ ) and in the drawing apparatus ( $\lambda_{\text{draw}}$ ), an overall draw ratio ( $\lambda_{\text{over}}$ ) has been defined as  $\lambda_{\text{over}} = \lambda_{\text{ext}} \times \lambda_{\text{draw}}$ . An initial diameter of 1 mm was assumed for the calculation of  $\lambda_{\text{ext}}$ . In the following the term 'maximum attainable draw ratio' is the maximum value of  $\lambda_{\text{draw}}$  at which fibres can be drawn without breaking.

### Methods

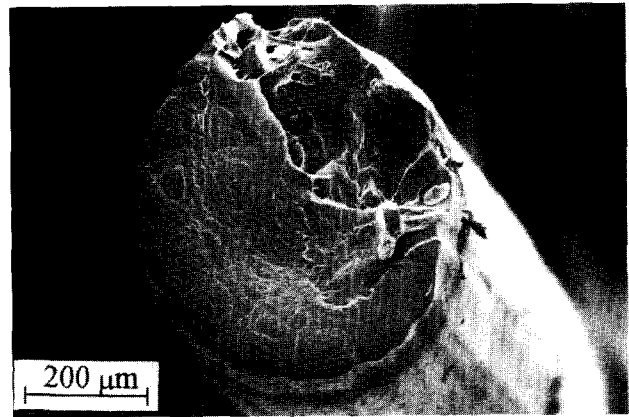
*Molecular weight analysis.* Molecular weight determinations were made by means of viscometric measurements on diluted chloroform/polymer solutions in a Ubbelohde viscometer (type I) at 25.0 $^{\circ}\text{C}$ . The viscometric molecular weight,  $M_v$ , was calculated from the intrinsic viscosity,  $\eta$ , using the following equation<sup>13</sup>.

$$[\eta] = 5.45 \times 10^{-4} \times M_v^{0.73}$$

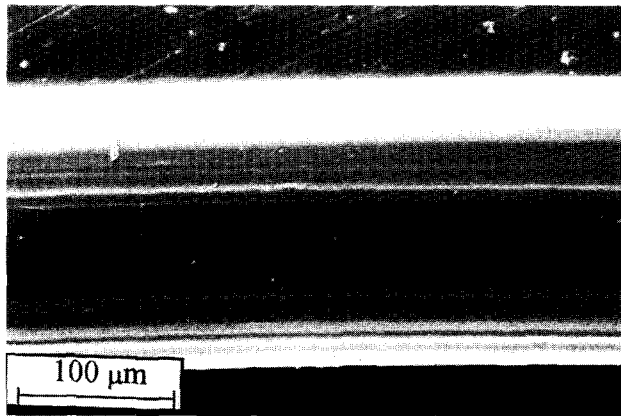
*Thermal analysis.* Differential scanning calorimetry (d.s.c.) was performed using a Mettler DSC 30 calorimeter, from 0 to 230 $^{\circ}\text{C}$  with a heating rate of 10 $^{\circ}\text{C min}^{-1}$  in nitrogen flushing at 100  $\text{ml min}^{-1}$ . A second scan was also performed under the same conditions on samples quenched at the end of the first run, with a cooling rate of about -100 $^{\circ}\text{C min}^{-1}$ . Samples consisted of approximately 15 mg of fibres carefully wound around cylindrical wire in order to avoid any stress and weighed with an analytical balance having a sensitivity of 0.1 mg. The glass transition temperature,  $T_g$ , was measured as the inflection point of the thermogram. The crystallinity content of the specimens was determined by rating the difference between enthalpies of melting and crystallization peaks to the reference melting enthalpy of the 100% crystalline polymer (93.6  $\text{J g}^{-1}$ )<sup>12</sup>. In the following  $T_{C1}$  and  $T_{C2}$  will denote the temperatures of the detected lower and higher temperature crystallization exothermic peaks,  $T_m$  the melting temperature,  $C1$ ,  $C2$  and  $C_m$ , the corresponding energies involved in these processes, expressed as a percentage of 93.6  $\text{J g}^{-1}$ . All the reported



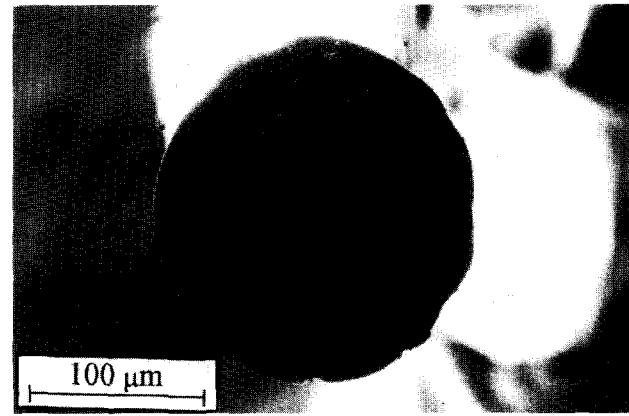
(a)



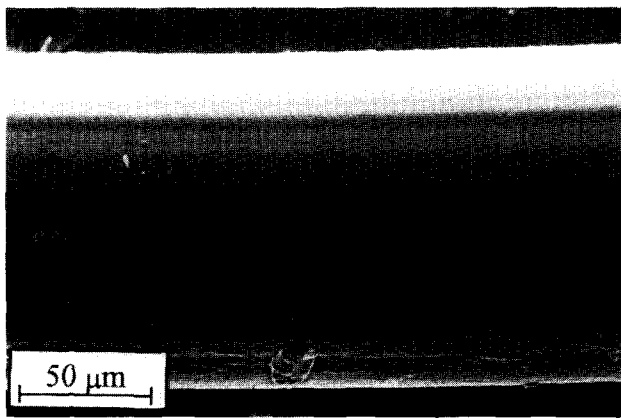
(d)



(b)



(e)



(c)

**Figure 1** SEM micrographs of lateral surface of as-spun fibres produced at a collection speed of (a)  $1.82 \text{ m min}^{-1}$ , (b)  $10 \text{ m min}^{-1}$  and (c)  $20 \text{ m min}^{-1}$ . Fracture surface of fibres collected at a collection speed of (d)  $1.82 \text{ m min}^{-1}$  and (e)  $10 \text{ m min}^{-1}$ , and broken in liquid nitrogen

temperatures have an accuracy of  $0.1^\circ\text{C}$ , whereas an error of 0.5% can be estimated in the determination of enthalpy percentage.

**Mechanical properties.** Tensile mechanical properties of PLLA fibres were measured at room temperature using an Instron tensile tester, at a cross-head speed of  $12 \text{ mm min}^{-1}$ . Specimens with a gauge length of 25 mm were prepared using a thin paper test specimen mounting tab as recommended in standard ASTM D 3379. Yield strength was evaluated as the stress at 0.003 strain offset. Fracture always occurred approximately in the centre of the fibre. All the reported tensile properties represent average values of at least five tests.

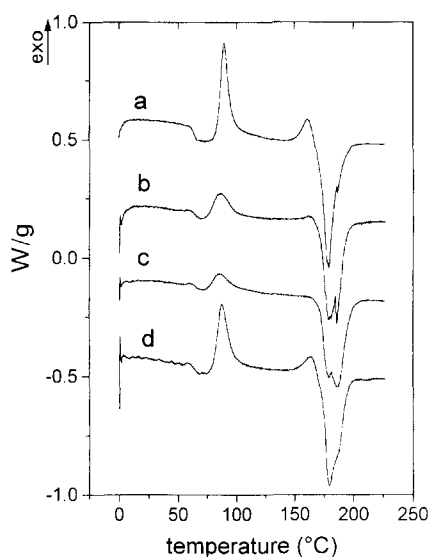
**Dynamic mechanical thermal analysis.** Tensile dynamic mechanical tests were conducted on 20 mm long single fibres with a dynamic mechanical thermal analyser

(DMTA Mk II by Polymer Laboratories) at a frequency of 5 Hz with  $16 \mu\text{m}$  of deformation, from  $-20$  to  $150^\circ\text{C}$  at a heating rate of  $2^\circ\text{C min}^{-1}$ .

**Scanning electron and optical microscopy.** A Cambridge scanning electron microscope (SEM) model Stereoscan 200 was used to observe the surface topography and fracture surface of fibres (Figure 1). Fibres were examined using an accelerating voltage of 10 kV. The diameter of as-spun fibres measured both from SEM and optical micrographs (Ortholux II POL-BK, Leitz), was in good agreement with the micrometer Palmer-type measurements.

## RESULTS AND DISCUSSION

All PLLA fibres produced by melt spinning showed a considerable reduction of viscometric molecular weight,



**Figure 2** D.s.c. thermograms of as-spun fibres produced at a collection speed of (a) 1.82 m min<sup>-1</sup>, (b) 5 m min<sup>-1</sup>, (c) 10 m min<sup>-1</sup> and (d) 20 m min<sup>-1</sup>

from 330 000 to about 120 000 and 105 000 for as-spun and drawn fibres, respectively. This molecular weight degradation should be compared with the slight  $M_w$  drop (about 6%) found in fibres produced by a dry spinning process<sup>51</sup>.

In previous works the authors reported extensively on thermal degradation of PLLA after different thermal treatments<sup>22,25,26</sup>. This degradation could be attributed to the ester group cleavage, as a consequence of the hydrolytic process whenever small amounts of water are present, and of a 'ring closing depolymerization' starting from the last two units of the chain<sup>19</sup>. End capping obtained by acetylation of terminal groups showed an increased stability compared to unencapped PLLA during thermal treatment performed in d.s.c.<sup>19</sup>. However, the same polymer used for fibre melt-spinning at 200°C gave no significant improvement in comparison with untreated polymer, showing degradation of about 70%<sup>39</sup>. Eling *et al.*<sup>38</sup> produced fibres in which degradation was no higher than 40%, but this result can be attributed to the low extrusion temperature used (185°C). In fact a higher extrusion temperature, i.e. 210°C, determined a molar mass reduction higher than 60%, as reported by Pennings *et al.*<sup>42</sup>. A recent study by von Oepen and Michaeli<sup>52</sup> on injection moulded PLLA showed the synergistic degradation role played by shear stresses applied for times longer than about 4 min. In our case, the residence time was about 10 min. The shear

stress effect could account for the higher degradation, from 480 000 to about 90 000 in as-spun fibre, that we have observed in a higher molecular weight PLLA.

#### Spinning of the fibres

The influence of the fibre collection rate after extrusion, on the physical-mechanical properties of the as-spun fibres was extensively studied, in order to determine the dependence, if any, of drawability and final characteristic on the fibres on the spinning conditions. By using a constant screw rotation rate, corresponding to an extrusion rate of 0.4 m min<sup>-1</sup>, the fibre collection rate was changed in the range 1.8–20 m min<sup>-1</sup>. Depending on the rate at which fibres were collected on the glass drum at the exit of the extruder, they exhibited different thermal transitions, as reported in the d.s.c. thermograms of Figure 2, and summarized in Table 2.

During the first scan (see Figure 2a) two crystallization peaks, named primary (C1) and secondary (C2) can be detected at about 90° and 160°C, respectively, whose area decreased with the fibre collection rate. The difference between the normalized melting ( $C_m$ ) and crystallization ( $C1 + C2$ ) peaks, gave the resulting initial crystallinity of as-spun fibres,  $C_r = C_m - (C1 + C2)$ . Fibres collected at rates of 1.8–3 m min<sup>-1</sup> were almost amorphous (4.7–6.0% crystallinity content), whereas  $C_r$  of 29.9 and 37.5% were exhibited from fibres collected at 5 and 10 m min<sup>-1</sup>. The difference can be mainly related to the better efficiency of the cooling due to the nitrogen flux at the die exit for lower fibre speeds. The apparent exception (11.9% crystallinity) for fibres drawn collected at 20 m min<sup>-1</sup>, could result from a re-established cooling efficiency due to the higher surface/volume ratio (SVR) of the fibre. Reduction of 30% of diameter (from 190 to 133  $\mu\text{m}$ ) determined an increase of 50% of SVR (from 21 to 30 mm<sup>-1</sup>) and consequently a decrease of crystallizability during winding (from 37.5 to 11.9%). Moreover, the higher the  $C_r$ , the lower the crystallization temperature  $T_{c1}$ , evaluated at the maximum of the primary crystallization peak and reported in Table 2. Another consequence of the different crystallinity of as-spun fibre was the change of specific heat at the glass transition temperature, which slightly decreased with  $C_r$ , changing from 0.36, to 0.30, 0.19, and 0.14 Jg<sup>-1</sup> K<sup>-1</sup> for fibres drawn at 1.8, 20, 5 and 10 m min<sup>-1</sup>, respectively.

After careful examination of the d.s.c. thermograms in Figure 2, two different melting peaks can be distinguished, at about 179 and 186°C, respectively. Although a partial overlapping does not allow their exact determination, one could assume the first peak to be related to the crystallization developed during the d.s.c.

**Table 2** D.s.c. analysis of as-spun fibres

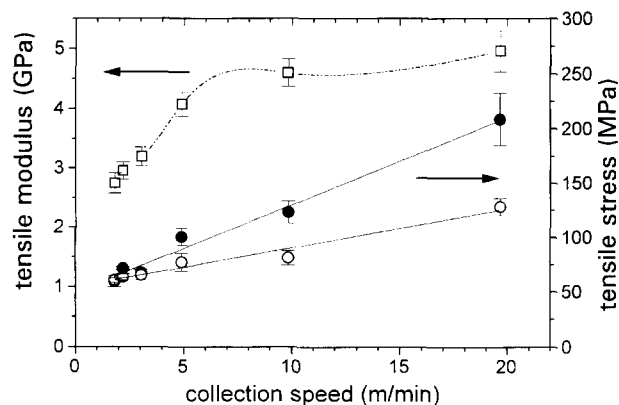
Collection speed (m min <sup>-1</sup> )	1st scan							2nd scan						
	$T_g$ (°C)	$T_{C1}$ (°C)	$C_1$ (%)	$T_{C2}$ (°C)	$C_2$ (%)	$T_{m1}^a$ (°C)	$C_{m1}$ (%)	$T_g$ (°C)	$T_{C1}$ (°C)	$C_1$ (%)	$T_{C2}$ (°C)	$C_2$ (%)	$T_{mII}$ (°C)	$C_{mII}$ (%)
1.8	63.1	89.6	29.2	161.1	5.7	179.1	39.6	65.1	109.8	38.3	167.2	1.2	185.2	38.7
5	64.3	87.4	12.9	161.2	0.7	186.7	43.5	63.3	109.8	38.7	166.2	1.6	182.6	39.8
10	64.2	85.3	8.0	—	—	186.4	45.5	64.1	109.9	38.2	166.1	1.1	183.2	39.0
20	64.3	87.6	25.8	164.3	4.8	179.6	42.5	63.3	108.9	39.9	166.3	2.6	181.5	42.2

<sup>a</sup> Melting temperature of the most intense peak

**Table 3** Molar mass, crystallinity and geometrical draw ratio of as-spun and drawn fibres

Collection speed (m min <sup>-1</sup> )	Extrusion				Drawing				
	$M_v$ of as-spun fibre	Crystallinity of as-spun fibres (%)	Diameter of as-spun fibres ( $\mu\text{m}$ )	$\lambda_{\text{ext}}$	$M_v$ of drawn fibre	Crystallinity of drawn fibres (%)	Diameter of drawn fibres ( $\mu\text{m}$ )	$\lambda_{\text{draw}}$	$\lambda_{\text{over}}$
1.8	118 800	4.7	480	4.3	104 900	53.1	106	20.5	89
5	121 600	29.9	235	18.1	105 000	59.2	80	10.6	156
10	122 400	37.5	190	27.7	102 000	65.0	74	6.6	183
20	101 900	11.9	133	57.6	n.m. <sup>a</sup>	n.m. <sup>a</sup>	48	7.3	420

<sup>a</sup> Not measured due to the low amount of available fibre

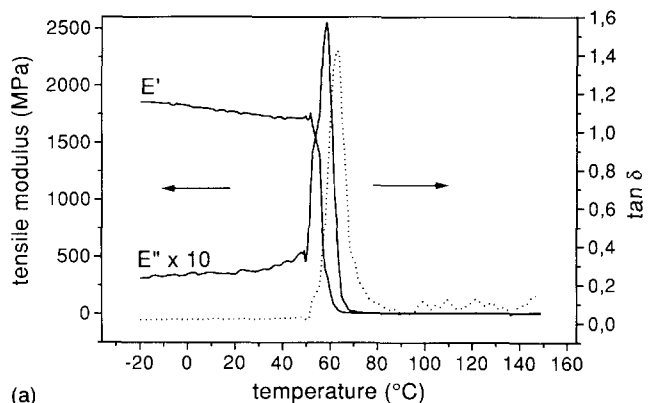


**Figure 3** Tensile modulus (□), yield strength (○) and stress at break (●) of as-spun fibres as a function of the collection speed

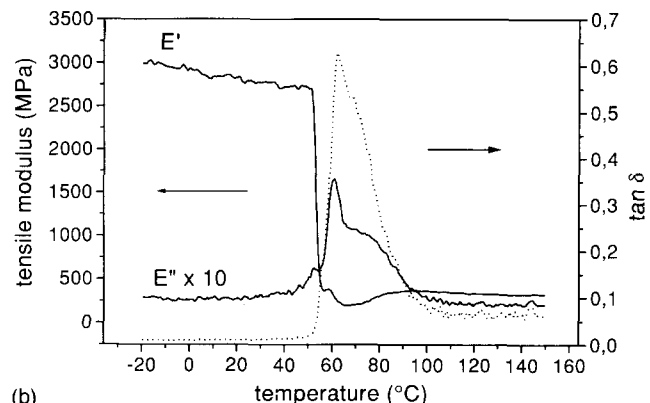
scan, the second one being the consequence of the spinning process. In fact, the higher the crystallinity, the higher the intensity of the peak at 186°C. Whereas the second d.s.c. scan (after melting and quenching), the first three samples showed almost the same value, fibre collected at 20 m min<sup>-1</sup> displayed a slightly higher crystallizability (42.2 vs *ca* 39%) and lower crystallization and melting temperatures, suggesting a lower molar mass of the polymer, as confirmed by viscometric molecular weight measurements (Table 3).

Of course, the higher the collection rate, the lower the fibre diameter. In Figure 1a–c the effect of fibre orientation in the spinning direction is evident and also the 'nerivation/veining-pattern' on the lateral surface especially for the lower winding speed. Notwithstanding, the fibre break was performed in liquid nitrogen, the fracture surface showed a residual plastic deformation for the fibre collected at 1.8 m min<sup>-1</sup> due to almost negligible crystallinity content (Figure 1d). On the other hand, a degree of crystallinity of about 30% gave a brittle fracture, as shown in Figure 1e.

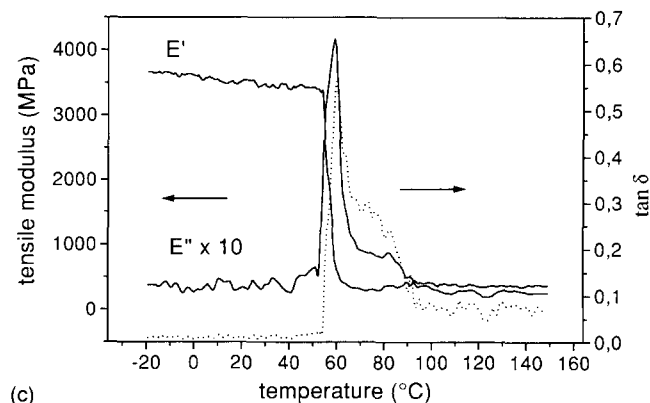
A direct consequence of both crystallinity development and cross-section reduction during extrusion, was the modification of mechanical properties (Figure 3) as a combined effect of partial alignment of polymer chains, crystallization and predrawing phenomena. The tensile modulus increased steeply at first from 2.8 to 4.1 GPa, reaching almost constant values for higher collection rates. Whereas yield stress and strength increased linearly with the collection speed up to 128 and 209 MPa, respectively, strain at break decreased rapidly at first from 580% (at 1.8 m min<sup>-1</sup>) to 94% (at



(a)



(b)



(c)

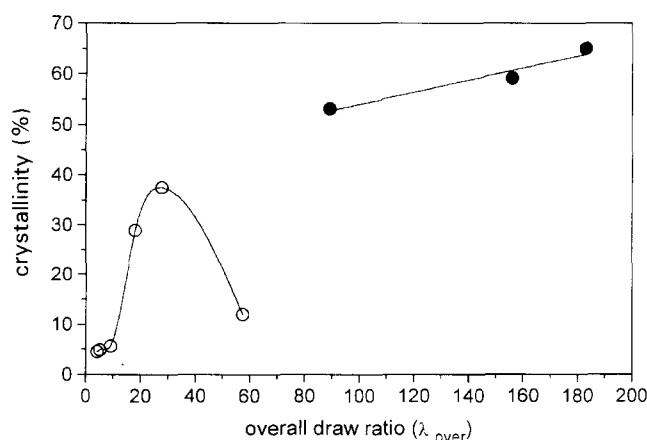
**Figure 4** D.m.t.a. thermograms of as-spun fibres produced at a collection speed of (a) 1.82 m min<sup>-1</sup>, (b) 10 m min<sup>-1</sup> and (c) 20 m min<sup>-1</sup>

5 m min<sup>-1</sup>), and then slowly to 60% (at 10 m min<sup>-1</sup>) and 23% (at 20 m min<sup>-1</sup>).

As previously shown, the crystallinity of fibres increased with the collection rate up to 5 m min<sup>-1</sup>. This

**Table 4** Mechanical properties of fibres obtained from different collection conditions and drawn at 160°C

Collection speed (m min <sup>-1</sup> )	Tensile modulus (GPa)	Yield strength (GPa)	Tensile strength (GPa)	Strain at break (%)
1.8	7.0 ± 0.9	0.21 ± 0.04	0.66 ± 0.04	24.5 ± 2.1
5	9.2 ± 1.7	0.29 ± 0.18	0.87 ± 0.11	18.7 ± 1.9
10	9.0 ± 0.4	0.22 ± 0.01	0.63 ± 0.06	17.7 ± 1.6
20	8.1 ± 1.3	0.15 ± 0.02	0.41 ± 0.08	18.0 ± 2.4

**Figure 5** Crystallinity as a function of total draw ratio ( $\lambda_{over}$ ) for as-spun (○) and hot-drawn fibres (●)

increase in crystallinity could be to some extent responsible for the modulus growth that was also confirmed by the dynamic mechanical analysis (Figure 4). However, as it will be pointed out in the following, one should consider the combined effects of orientation, orientation induced crystallization and plastic deformation. The storage modulus,  $E'$ , at room temperature was 1.8, 2.8 and 3.5 GPa for fibres collected at 1.8, 10 and 20 m min<sup>-1</sup>, respectively (Figure 4a–c). As the collection speed increases, the modulus increases, even when the fibre crystallinity begins to decrease. A parameter very sensitive to the degree of molecular motion is  $\tan \delta$ , whose value decreases as a consequence of an increase either of  $C_r$  or molecular orientation<sup>53</sup>.  $\tan \delta$  values range from 1.4 for fibres collected at 1.8 m min<sup>-1</sup> to about 0.6 for fibres collected at 10 or 20 m min<sup>-1</sup>. Even if crystallinity does not monotonically increase with the collection rate, the increase in orientation of the amorphous phase affects and to some extent improves the fibre mechanical properties.

#### Drawing

Drawing of fibres spun at different collection speeds, was performed at 160°C as for a previous study by Hyon *et al.*<sup>39</sup>. By using a constant entrance rate (i.e. 2.5 m min<sup>-1</sup>), fibres were progressively drawn up to different levels in order to determine the maximum attainable draw ratio. As expected, the higher the collection speed of as-spun fibres, the lower the maximum attainable draw ratio (see values reported in Table 3). Whereas crystallinity of as-spun fibres reached a maximum (37.5%) for a collection speed of 10 m min<sup>-1</sup> (i.e.  $\lambda_{extr} = 27.7$ ), hot-drawing increased the fibre crystallinity up to 65.0% (Figure 5), with values depending on the overall applied draw ratio.

Similarly, the mechanical properties of fibres (Table 4)

appeared to be dependent on  $\lambda_{over}$ , a tensile modulus higher than 8 GPa being reached for overall draw ratios or crystallinity higher than 90 or 53%, respectively. On the other hand, the quite low modulus value of 7 GPa for the fibre collected at 1.8 m min<sup>-1</sup>, could be a consequence of premature fracture induced by a dishomogeneous temperature distribution in the fibre during the process<sup>54</sup>.

Moreover, fibres collected at 5 m min<sup>-1</sup> and drawn 10 times reached a tensile strength of 0.87 GPa. This result appears quite satisfactory, but could perhaps be improved further, as evidenced by some preliminary results, not reported here.

Other authors produced PLLA fibres having almost the same modulus, but significantly lower tensile strength. For instance, Pennings *et al.*<sup>42</sup> drawing fibres at a temperature of 110°C reached stresses at a break of 0.5 GPa, limited perhaps by the too high crystallinity of as-spun fibres. A too high initial crystallinity reduced the maximum attainable draw ratio and consequently lower the final fibre mechanical properties. In our case, the nitrogen flow partially quenches fibres (crystallinity in the range 4–38%), so permitting higher drawings and, thus, strength. In agreement, Hyon and co-workers<sup>39,40</sup>, starting from as-spun fibres with crystallinity not higher than 5%, drawing them six times at 160°C, reached strength and crystallinity of 0.7 GPa and 60%, respectively.

Therefore, from our findings and from results reported in the literature, it appears evident that high strength PLLA fibres can be produced with balanced crystallizability and drawability during the extrusion and hot-drawing processes.

#### CONCLUSIONS

High strength PLLA fibres were produced by a combined melt-extrusion and hot-drawing process. Depending on the rate at which fibres were collected at the exit of the extruder, crystallization and/or molecular orientation prevailed, but without significant effects of the materials mechanical properties, i.e. up to 5.1 and 0.21 GPa for tensile modulus and strength, respectively. However, a second drawing performed at 160°C greatly increased the material mechanical properties.

The final mechanical properties of the fibres depended on their drawability, in turn correlated to the as-spun fibres initial crystallinity and diameter. The lower the as-spun fibre collection speed, the higher the maximum attainable draw ratio.

Moreover, the higher the overall draw ratio, defined as  $\lambda_{over} = \lambda_{extr} \times \lambda_{draw}$ , the higher the final crystallinity. PLLA fibres showing the best mechanical properties (modulus and strength of 9.2 and 0.87 GPa, respectively) were obtained drawing 10 times fibres collected at 5 m min<sup>-1</sup> and having a relative low initial crystallinity.

In conclusion, the production of high strength PLLA fibre resulted from a compromise of extrusion, collection and drawing rates, in order to optimize both crystallinity and molecular orientation.

## ACKNOWLEDGEMENTS

This work was partially supported by CNR (Comitato Nazionale Ricerche Tecnologiche e Innovazione, Progetto Strategico Materiali Innovativi) and Cremascoli S.r.l. (Milano, Italy).

## REFERENCES

- Gilding, D. K. in 'Biocompatibility of Clinical Implant Materials' (Ed. D. F. Williams), CRC Press, Boca Raton, FL, Vol. II, 1981, p.209
- Feijen, J. in 'Polymeric Biomaterials' (Eds. E. Piskin and A. S. Hoffmann), Martinus Nijhoff, Dordrecht, The Netherlands, 1986, p.62
- Barrows, T. J. *Clin. Mater.* 1986, **1**, 233
- Vainionpaa, S., Rokkanen, P. and Tormala, P. *Prog. Polym. Sci.*, 1989, **14**, 679
- Dittrich, V. W. and Schulz, R. C. *Angew. Makromol. Chem.*, 1971, **109**, 15
- Kulkarni, R. K., Moore, E. G., Hegyeli, A. F. and Leonard, F. *J. Biomed. Mater. Res.* 1971, **5**, 169
- Gilding, D. K. and Reed, A. M. *Polymer* 1979, **20**, 1459
- Kohn, F. E., van den Berg, J. W. A., van Ridden, G. and Fejen, J. *J. Appl. Polym. Sci.* 1984, **29**, 4265
- Kricheldorf, H. R. and Dunsing, R. *Makromol. Chem.* 1986, **187**, 1611
- Leenslag, J. W. and Pennings, A. J. *Makromol. Chem.* 1987, **188**, 1809
- Jedlinski, Z., Watach, W., Kurcok, P. and Adamus, G. *Makromol. Chem.* 1991, **192**, 2051
- Fisher, E. W., Stergel, H. J. and Wegner, G. *Kolloid Z. Z. Polym.* 1973, **251**, 980
- Schindler, A. and Harper, D. *J. Polym. Sci. Polym. Chem. Ed.* 1979, **17**, 2593
- Kalbe, B. and Pennings, A. J. *Polymer* 1980, **21**, 607
- Vasanthakumari, R. and Pennings, A. J. *Polymer* 1983, **24**, 175
- Kishore, K. and Vasanthakumari, R. *J. Polym. Sci., Polym. Phys. Ed.* 1984, **22**, 537
- Hoogsteen, W., Postema, A. R., Pennings, A. J., ten Brinke, G. and Zugenmaier, P. *Macromolecules* 1990, **23**, 634
- Mazzullo, S., Paganetto, G. and Celli, A. *Progr. Polym. Sci.* 1987, **87**, 32
- Jamshidi, K., Hyon, S. H. and Ikada, Y. *Polymer* 1988, **29**, 2229
- Leenslag, J. W., Kroes, M. T., Pennings, A. J. and Van der Lei, B. *New Polym. Mater.* 1988, **1**, 111
- Tunc, D. G. *Clin. Mater.* 1991, **8**, 119
- Migliarese, C., De Lollis, A., Fambri, L. and Cohn, D. *Clin. Mater.* 1991, **8**, 111
- Celli, A. and Scandola, M. *Polymer* 1992, **33**, 2699
- Engelberg, I. and Kohn, J. *Biomaterials* 1991, **12**, 292
- Migliarese, C., Cohn, D., De Lollis, A. and Fambri, L. *J. Appl. Polym. Sci.* 1991, **43**, 83
- Migliarese, C., Fambri, L. and Cohn, D. *J. Biomater. Sci., Polym. Edn.* 1994, **5**, 591
- Leenslag, J. W., Gogolewski, S. and Pennings, A. J. *J. Appl. Polym. Sci.* 1984, **29**, 2829
- Li, S., Garreau, H. and Vert, M. *J. Mater. Sci. Mater. Med.* 1990, **1**, 198
- Dauner, M., Muller, E., Wagner, B. and Planck, H. in 'Degradation Phenomena on Polymeric Biomaterials' (Eds. H. Planck, M. Dauner and M. Renardy), Springer, Berlin, 1992, p. 107
- Chawla, A. S. and Chang, T. M. S. *Biomater. Med. Dev., Art. Org.* 1985-86, **13**, 153
- Eitenmuller, J., Muhr, G., Gerlach, K. L. and Schmickal, T. *J. Bioact. Compat. Polym.* 1989, **4**, 215
- Lewis, D. H. in 'Biodegradable Polymers as Drug Delivery Systems' (Eds. M. Chasin and R. Langer), Marcel Dekker, New York, 1990, p.1
- Agrawal, C. M., Haas, K. F., Leopold, D. A. and Clark, H. G. *Biomaterials* 1992, **13(3)**, 176
- Vert, M. and Chabot, F. *Makromol. Chem. Suppl.* 1981, **5**, 30
- Maiola, A., Vainionpaa, S., Rokkanen, P., Mikkola, H. M. and Tormala, P. *J. Mater. Sci. Mater. Med.* 1992, **3**, 43
- Lehninger, A. L. 'Biochemistry' (Eds. S. Anderson and J. Fox), 2nd Ed., Worth Publisher, New York, 1975
- Schneider, A. K. *US Patent* 3,636,956, 1972
- Eling, B., Gogolewski, S. and Pennings, A. J. *Polymer* 1982, **23**, 1587
- Hyon, S. H., Jamshidi, K. and Ikada, Y. in 'Polymers as Biomaterials' (Eds. S. Shalaby, A. S. Hoffmann, B. D. Ratner and T. A. Horbett), Plenum Press, New York, 1984, p. 51
- Jamshidi, K., Hyon, S. H., Nakamura, T., Ikada, Y., Shimizu, Y. and Teramatsu, T. in 'Biological and Biomechanical Performance of Biomaterials' (Eds. P. Christel, A. Meunier and A. J. C. Lee), Elsevier, Amsterdam, 1986, p. 227
- Laitinen, O., Tormala, P., Taurio, R., Skutnabb, K., Saarelainen, K., Iivonen, T. and Vainionpaa, S. *Biomaterials* 1992, **13**, 1012
- Penning, J. P., Dijkstra, H. and Pennings, A. J. *Polymer* 1993, **34**, 942
- Gogolewski, S. and Pennings, A. J. *J. Appl. Polym. Sci.* 1983, **28**, 1045
- Leenslag, J. W. and Pennings, A. J. *Polymer* 1987, **28**, 1695
- Postema, A. R., Luiten, A. H., Oostra, H. and Pennings, A. J. *J. Appl. Polym. Sci.* 1990, **39**, 1275
- Horacek, I. and Kudlacek, L. *J. Appl. Polym. Sci.* 1993, **50**, 1
- Horacek, I. and Kalisek, V. *J. Appl. Polym. Sci.* 1994, **54**, 1751
- Horacek, I. and Kalisek, V. *J. Appl. Polym. Sci.* 1994, **54**, 1759
- Horacek, I. and Kalisek, V. *J. Appl. Polym. Sci.* 1994, **54**, 1767
- Tsujj, H., Ikada, Y., Hyon, S. H., Kimura, Y. and Kitao, T. *J. Appl. Polym. Sci.* 1994, **51**, 337
- Fambri, L., Pegoretti, A., Mazzurana, M. and Migliarese, C. *J. Mater. Sci. Mater. Med.* 1994, **5**, 679
- von Oepen, R. and Michaeli, W. *Clin. Mater.* 1992, **10**, 21
- Nielsen, L. E. 'Mechanical Properties of Polymers and Composites' (Ed. M. Dekker), New York, 1974
- Postema, A. R. and Pennings, A. J. *J. Appl. Polym. Sci.* 1989, **37**, 2351