Preparation and properties of absorbable fibres from L-lactide copolymers

J. P. Penning, H. Dijkstra and A. J. Pennings*
Department of Polymer Chemistry, University of Groningen, Nijenborgh 4, NL-9747 AG, The Netherlands
(Received 31 March 1992)

Absorbable fibres have been prepared from various copolymers of L-lactide with either D-lactide or ε-caprolactone. The lower crystallinity of these copolymers, compared with the homopolymer, is desirable in the light of their potential use as an absorbable suture material and has a pronounced effect on both preparation procedure and mechanical properties of these fibres. Due to the low crystallinity of the fibres, their mechanical properties are related to the structure of the amorphous phase, as is reflected by the effect of the glass transition temperature and molecular weight on tensile properties. By means of a dry spinning/hot drawing process, low crystalline fibres having strengths of 1 GPa could be prepared, whereas fibres prepared by melt spinning/hot drawing have strengths ranging from 0.19 for a completely amorphous copolymer to 0.53 GPa for the poly(L-lactide) homopolymer.

(Keywords: L-lactide; copolymers; fibres; preparation; properties; crystallinity)

INTRODUCTION

Biodegradable polymers represent a class of materials of growing importance, especially in the field of biomedical applications[1,2]. Among medical devices made out of biodegradable polymers, fibrous materials are playing an increasingly important role. This is attributed to the development of sophisticated surgical procedures, as well as the advances made in synthetic fibres. Examples of medical applications of fibrous materials are hollow fibres, dressings and reinforcing meshes. The use of fibres as absorbable sutures represents a major biomedical application of this form of polymers[1,3-5].

Polylactones form a group of synthetic polymers that are widely used in biomedical applications[6,7]. They are mainly polyesters, produced by ring-opening polymerization, which degrade in the body into non-toxic products by hydrolysis of the main chain ester-linkage. Commercially available absorbable sutures from these polymers include Dexon®, polyglycolide[8,9], and PDS®, poly(*p*-dioxanon)[10]. Absorbable fibres have also been prepared from poly(L-lactide)[11-14].

If fibres are to be used as absorbable sutures in medicine and surgery it is necessary to meet a number of specific criteria, pertinent to biological properties, tensile properties, handling characteristics and surface properties. Desired biological properties encompass a minimum adverse effect on living tissue and retention of tensile strength during functional use followed by a rapid mass absorption, i.e. a suitable degradation profile. As far as tensile properties are concerned, the initial tensile strength of the fibre should be sufficiently high for the specific application, to minimize the amount of material implanted, whereas the Young's modulus should be low enough to retain flexibility. In high modulus fibres, flexibility can be achieved by using thin monofilaments that are braided into pliable structures.

At this stage, it is important to realize that both biological and tensile properties are directly related to the chemical composition of the polymeric material and to the fibre's physical microstructure. For example, tensile properties are related to the degree of molecular orientation, molecular weight of the polymer and the degree of crystallinity and glass transition temperature, T_g[15]. On the other hand, the rate of absorption depends on the accessibility of the amorphous phase (i.e. the T_g of the material), the hydrophilicity of the macromolecule and also on the degree of crystallinity[16]. Since degradation of the polymer is much faster in the amorphous than in the crystalline phase[2,17], highly crystalline materials will degrade inhomogeneously, that is to say, after complete degradation of the amorphous phase, the strength of the material is lost and lamellar debris which degrades slowly and gives rise to tissue reaction, will remain[18,19]. Therefore, from a medical and biological point of view, materials with a low degree of crystallinity are favoured.

Lowering the crystallinity of polymeric materials is commonly achieved through the introduction of comonomeric units that interrupt the chain regularity and thus inhibit the formation of highly ordered structures. The ring-opening polymerization process makes polylactones particularly suitable for copolymerization with other lactones or cyclic carbonates[20,21]. Commercially available absorbable sutures from such copolyesters are Vicryl®, a glycolide/lactide copolymer[22,23], and Maxon®, a copolymer from glycolide and trimethylenecarbonate[24].

In our laboratories, absorbable fibres having a tensile strength as high as 2.3 GPa have been prepared from poly(L-lactide), PLLA, by a process of dry spinning and

---

* To whom correspondence should be addressed

0032-3861/93/050942-10

subsequent hot drawing[25,26]. Due to this high strength, these fibres may be applied for, for instance, bone fixation[27]. Fibres, prepared from glycolide polymers, generally have much lower strengths because of the intractable nature of these polymers which makes them unsuitable for solution spinning processes. The *in vivo* degradation of PLLA fibres is, however, rather slow compared with polyglycolide fibres, due the hydrophobic character of PLLA[16]. Obviously, degradation rates may be improved by copolymerization of L-lactide with other lactones. A suture material based on L-lactide and ε-caprolactone has been shown to degrade at a higher rate than the L-lactide homopolymer, and a minimum tissue reaction was reported[28,29].

The aim of this study is to examine the effects of the introduction of comonomeric units into the L-lactide homopolymer on the various stages of the fibre preparation process, and on the ultimate mechanical properties of the resulting fibres. In other words, to what extent do requirements of medical and biological origin interfere with the several aspects of the development of strong fibre structures. These effects will be discussed in terms of basic concepts of fibre formation, together with the more or less uncommon aspects of PLLA fibre preparation. The various materials investigated comprise copolymers of L-lactide and ε-caprolactone P(LLA-CL) and of L-lactide and D-lactide P(LLA-DLA). Fibres are produced from these polymers by melt and dry spinning and subsequent hot drawing.

EXPERIMENTAL

Materials

Poly(L-lactide), copolymers of L-lactide and ε-caprolactone P(LLA-CL) and copolymers of L- and D-lactide P(LLA-DLA) were obtained by ring-opening polymerization at 110°C, as described elsewhere[33]. Monomer ratios quoted throughout the paper refer to molar ratios, which are determined from the monomer feed and, in the case of ε-caprolactone copolymers, from n.m.r. Thermal characterization was performed using a Perkin-Elmer DSC-7, operating at a heating rate of $10^\circ\mathrm{C\,min^{-1}}$, using 1–5 mg samples. Intrinsic viscosities were determined using an Ubbelohde capillary viscosimeter, thermostatically controlled at 25°C, unless stated otherwise. Viscosity average molecular weights were determined from intrinsic viscosity using $K=5.45\times10^{-4}\ \mathrm{dl\,g^{-1}}$ and $a=0.73$[46].

Melt spinning was performed on as-polymerized material, using a piston-cylinder apparatus equipped with a tapered die with an exit diameter of 0.25 mm. During spinning, the polymer was filtrated using a set of metal filters installed in front of the die entrance. The polymer was conditioned at the spinning temperature for 30 min. Spinning was performed at a speed of $1\ \mathrm{m\,min^{-1}}$ and the fibres were collected 10 cm below the die exit on sandblasted glass bobbins, without applying stress to the filament. Melt-spun fibres were drawn at the appropriate temperature in an electric oven, using a feed- and take-up roll, located outside the oven, rotating at different speeds. The feed velocity is $12.5\ \mathrm{mm\,min^{-1}}$. Draw ratios are defined as the ratio of take up and feed velocity. Drawing is performed in a nitrogen atmosphere.

Solution spinning

Polymer solutions were prepared by dissolving the copolymer in p.a. chloroform (2 days) and subsequent addition of toluene freshly distilled from sodium. The mixtures were allowed to homogenize for 14 days without mechanical stirring. When other poor solvents are used, the solutions are prepared in a similar way. A polymer concentration of 5–6% (wt/vol) was used for all solution-spinning experiments. The solutions were introduced into a piston-cylinder apparatus, equipped with tapered die (exit diameter 0.25 mm) and a set of metal filters, and subsequently homogenized for 3 h at 60°C. In all cases, spinning was conducted at this temperature. Fibres were spun at a speed of $3\ \mathrm{m\,min^{-1}}$ onto sandblasted glass bobbins, without applying stress to the fibre. The surrounding temperature was thermostated at 25°C by an electric oven placed around the spinline and take-up device. The as-spun fibres were drawn after a drying period of 1 day, using the drawing apparatus described above. Feed velocities of $30\ \mathrm{mm\,min^{-1}}$ were employed.

Fibre characterization

Fibres were characterized by d.s.c. as described above. Tensile tests were performed using an Instron 4301 tensile testing machine equipped with Instron Series IX Automated Materials Testing software. A crosshead speed of $25\ \mathrm{mm\,min^{-1}}$ was applied to samples of 50 mm gauge length. Cross-sectional areas were calculated from the weight of a fibre of known length, assuming a density of $1290\ \mathrm{kg\,m^{-3}}$ ($1248\ \mathrm{kg\,m^{-3}}$ for amorphous samples). Scanning electron micrographs were made using an ISI-DS-130 microscope, operating at 40 kV, using gold-covered samples.

RESULTS AND DISCUSSION

Materials

To study the effects of copolymerization on the fibre formation process and the mechanical properties of the resulting fibres, various polymers have been synthesized from L-lactide with either D-lactide or ε-caprolactone as comonomer. The thermal properties of these polymers are summarized in *Table 1*. The percentage of crystallinity can be estimated from the ratio of the heat of fusion of the fibre to the heat of fusion of perfectly crystalline material, which has been reported to be $81\ \mathrm{J\,g^{-1}}$ (ref. 30). This value, however, seems to be too low, since values of $100\ \mathrm{J\,g^{-1}}$ have been found experimentally for PLLA[31].

As can be seen, the way the physical properties respond to the introduction of comonomeric units depends strongly on the nature of the foreign species. The introduction of comonomer is seen to depress melting temperature and heat of fusion, the effect of which is much stronger in the case of D-lactide than it is in the case of ε-caprolactone. The acute sensitivity of thermal properties towards copolymerization with D-lactide arises from the resemblance, with respect to

Table 1 Thermal properties of various copolymers from L-lactide used in this study

Comonomer	Mole fraction	T_g (°C)	T_m (°C)	ΔH ($\mathrm{J\,g^{-1}}$)
None	–	57	191	88
ε-caprolactone	0.10	41	178	51
ε-caprolactone	0.20	38	174	38
D-lactide	0.05	57	151	31
D-lactide	0.15	57	–	0

reactivity, between both monomers, resulting in random copolymers[32].

Copolymers of L-lactide and ε-caprolactone are not completely random, as revealed by analysis of their microstructure with n.m.r. The average length of caprolactoyl sequences is about 2.5 for the 80/20 copolymer, and becomes even higher when polymerization is conducted at a lower temperature, i.e. as differences in reactivity become more pronounced[33]. The extent to which crystallization is inhibited by the presence of foreign monomer units is, however, not only controlled by the randomness of the copolymer, but also by the amount of incorporation of the foreign species into the crystal lattice. In the case of the copolymers studied here, the lack of crystallinity in the central range of compositions indicates that mixing of comonomers in the crystalline phase is very limited. From wide angle X-ray scattering (WAXS), the crystalline material in the 80/20 (LLA-CL) copolymer is found to correspond to the undistorted PLLA α-structure, indicating that there is no substantial incorporation of caprolactoyl units into the crystalline lattice. Degradation studies have shown that some incorporation of foreign monomers units in the crystalline phase occurs, for both D-lactide[30] and ε-caprolactone[34]. The differences between the D-lactide and ε-caprolactone comonomers, with respect to their effect on the physical properties, are, however, mainly attributed to differences in reactivity and, as a result, to the microstructure of the resulting copolymers.

As is seen in *Table 1*, the T_g of PLLA is substantially lowered when ε-caprolactone units are introduced into the polymer, which is explained in terms of the lower T_g of the ε-caprolactone homopolymer ($T_g = -60°C$). The observation of a single T_g, shifting down proportional to the comonomer content, indicates that the amorphous phase is continuous, which appears to be true over a wide range of compositions[33]. As expected, the introduction of D-lactide does not affect the T_g of the material, since the respective homopolymers of L- and D-lactide have the same T_g. As already mentioned, the T_g of the material is of importance in connection with the rate of degradation.

Melt spinning and hot drawing

To examine the effects of copolymer composition on fibre preparation and properties, fibres were manufactured from various copolymers by melt spinning and subsequent hot drawing. In this way, fibres were prepared from PLLA, 90/10 P(LLA-CL), 80/20 P(LLA-CL) and 85/15 P(LLA-DLA), to cover a wide range of physical properties. Spinning and drawing conditions are summarized in *Table 2*. Spinning is performed just above the melting temperature of the polymer, in order to limit thermal degradation, to which these polymers are susceptible[35]. Due to thermal degradation, the molecular weight of the starting materials was found to decrease to approximately 100 000 kg kmol^{-1} during spinning and hot drawing. For the amorphous 85/15 P(LLA-DLA) copolymer, the spinning temperature is, formally speaking, only restricted by its T_g, but the relatively high molecular weight of this sample made the use of a substantially higher spinning temperature necessary, to prevent melt fracture.

In *Figure 1*, the development of strength resulting from drawing at the optimum drawing temperature (see *Table 2*) is given for PLLA, 80/20 P(LLA-CL) and 85/15 P(LLA-DLA) fibres. As can be seen, the maximum attainable fibre strength strongly depends on the composition of the polymer used, and appears to decrease in the same direction as the crystallinity of the material, from 530 for PLLA to 185 MPa for the completely amorphous 85/15 P(LLA-DLA). The higher drawability that is observed for P(LLA-CL) copolymers may be interpreted in terms of a reduction of molecular interactions, associated with the introduction of ε-caprolactone units. Smook *et al.*[36] demonstrated that the maximum draw ratio of flexible polymers is governed by molecular attraction forces, expressed as the cohesive energy density, for a wide range of polymers. Based on this relation, one expects a higher drawability for copolymers.

Drawing of the copolymer fibres shown in *Figure 1* was performed at the optimum temperature for drawing, i.e. the temperature at which fibres with the highest

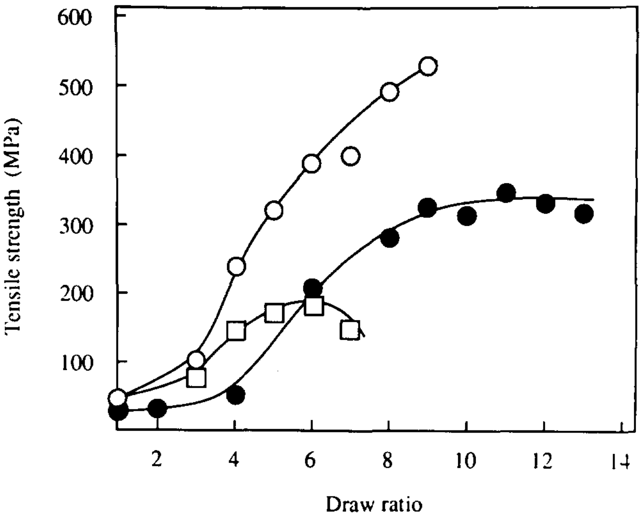

Figure 1 Tensile strength as a function of draw ratio of fibres obtained by melt spinning of (○) PLLA, (●) 80/20 P(LLA-CL) and (□) 85/15 P(LLA-DLA). Drawing temperatures are listed in *Table 2*

Table 2 Properties of various copolymers used for melt spinning experiments and process conditions during melt spinning and hot drawing of the melt spun fibres

Polymer	Molecular weight (kg Kmol^{-1})	Spinning temperature (°C)	Optimum drawing temperature (°C)	T_m (°C)	T_g (°C)
PLLA	280 000	210	110	191	57
90/10 P(LLA-CL)	375 000	190	90	178	41
80/20 P(LLA-CL)	360 000	180	70	174	38
85/15 P(LLA-DLA)	600 000	150	60	–[a]	57

[a] Not applicable

strengths are obtained. As can be seen in *Table 2*, optimum drawing temperatures appear to be some 40–50°C above the T_g of the respective fibres, except for the amorphous polymer. The connection between optimal drawing temperature and T_g may be explained by the fact that all melt-spun fibres lack crystallinity, since they are quenched to room temperature, i.e. below T_g, in the spinning process. In the case of PLLA, however, the drawing temperature is in the range of temperatures at which crystallization is very fast[37], which suggests that crystallization during drawing may be of importance with respect to effective drawing. This point of view is corroborated by the fact that non-crystallizable 85/15 P(LLA-DLA) deviates from the other samples with respect to the optimal drawing temperature. This can be seen in *Figure 2*, where the maximum tensile strength is shown for 80/20 P(LLA-CL) and 85/15 P(LLA-DLA) fibres. Quite pronounced differences between crystallizable and non-crystallizable copolymers with respect to drawing behaviour can be noticed from this plot. For the amorphous 85/15 P(LLA-DLA), the maximum strength is achieved by drawing at the T_g of this material, and the strength of the drawn fibre is very sensitive towards drawing temperature, i.e. the drawing window is narrow. For the crystallizable 80/20 P(LLA-CL), the range of optimum drawing temperatures, which is well above the T_g of this material, is much broader. As the molecules become extended and disentangled in the drawing process, crystallites may provide a solid matrix that prevents the molecules from recoiling[38].

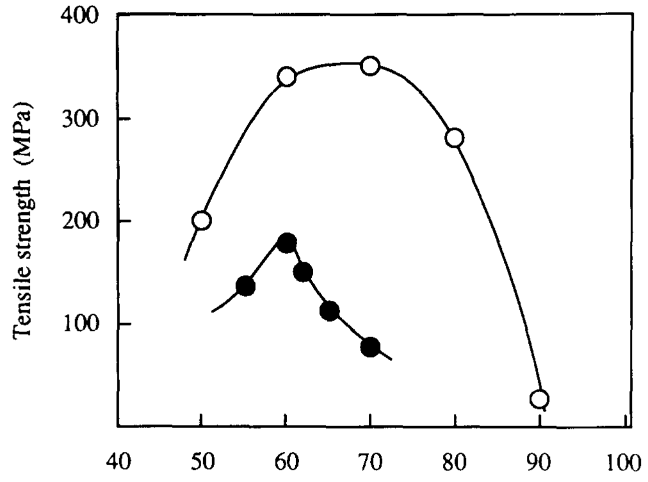

Figure 2 Effect of drawing temperature on the maximum strength of hot drawn fibres, obtained by melt spinning of (○) 80/20 P(LLA-CL), $T_g = 38°C$ and (●) 85/15 P(LLA-DLA), $T_g = 57°C$

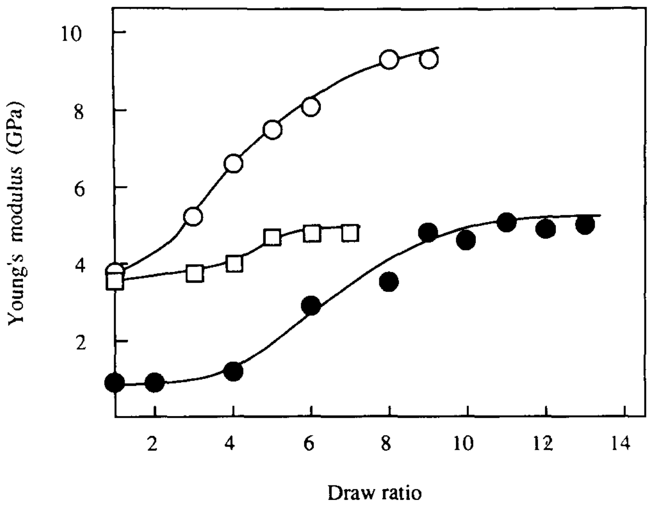

Figure 3 Young's modulus as a function of draw ratio of fibres obtained by melt spinning of (○) PLLA, (●) 80/20 P(LLA-CL) and (□) 85/15 P(LLA-DLA). Drawing temperatures are listed in *Table 2*

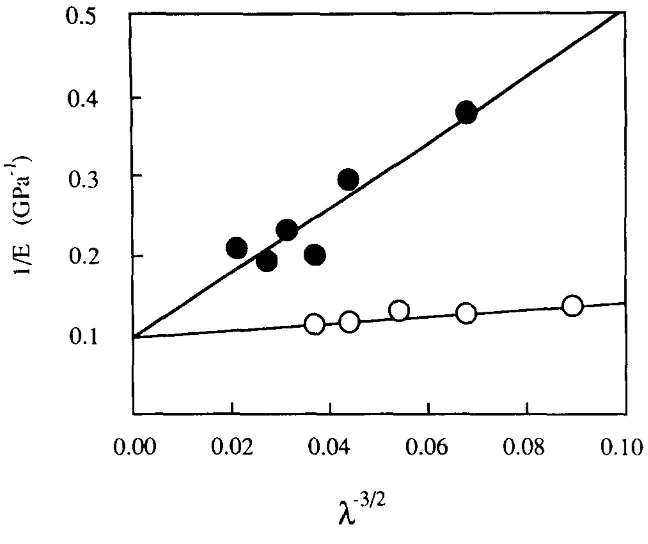

Figure 4 Reciprocal Young's modulus *versus* $\lambda^{-3/2}$ for fibres obtained by melt spinning of (○) PLLA and (●) 80/20 P(LLA-CL)

In *Figure 3*, the Young's modulus of fibres from PLLA, 80/20 P(LLA-CL) and 85/15 P(LLA-DLA) is plotted as function of draw ratio. These data can be interpreted in terms of a simplified model, proposed by Irvine and Smith[38], that accounts for the increase of Young's modulus observed on drawing. According to this model, the partially oriented fibre consists of two types of elastic elements, namely perfectly oriented and completely unoriented elements. Drawing of the fibre results in an increase of the fraction of perfectly oriented material at the expense of unoriented material, this fraction being a function of draw ratio only. The overall modulus of this composite fibre structure, E, is expressed in terms of the moduli of the oriented and unoriented phases, E_h and E_u respectively, by the following relation:

$$E=\left[E_h^{-1}+\frac{3\pi}{4}(E_u^{-1}-E_h^{-1})\lambda^{-3/2}\right]^{-1}$$

in which λ represents draw ratio. The expression is valid for $\lambda \geqslant 5$. From modulus *versus* λ data, E_h and E_u can be obtained by plotting $1/E$ against $\lambda^{-3/2}$, giving a straight line with slope $(3\pi/4)(E_u^{-1}-E_h^{-1})$ and intercept E_h^{-1}. *Figure 4* represents such a plot for PLLA and 80/20 P(LLA-CL) fibres.

As can be seen in this plot, the intercepts coincide for both sets of fibres, showing that these polymers have a similar modulus in the perfectly oriented state (only to be achieved at $\lambda = \infty$), for which a value of 10 GPa is calculated. As a consequence, differences in moduli between PLLA and P(LLA-CL) fibres at a given draw ratio arise from differences in the value of E_u, which is calculated to be 3.5 GPa for PLLA and 0.6 GPa for the copolymer. These values are in good agreement with those measured for isotropic, amorphous samples of the respective polymers. The difference between the two is explained by the difference in T_g of these materials. In

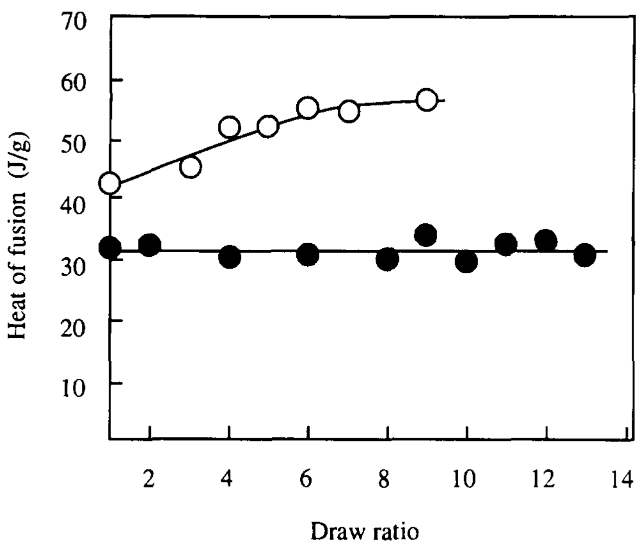

Figure 5 Heat of fusion as a function of draw ratio for fibres obtained by melt spinning of (○) PLLA and (●) 80/20 P(LLA-CL). Drawing temperatures are listed in *Table 2*

other words, careful examination of the development of modulus as a function of draw ratio reveals that the perceived differences arise only from the contribution of amorphous, unoriented phase, which more effectively reduces the modulus in case of the low T_g material.

The model by Irvine and Smith adequately describes our observations, but there are several points which deserve attention. The modulus of the perfectly oriented state is calculated to be 10 GPa for our fibres, which does not agree with the value of 16 GPa that was observed for maximally drawn PLLA fibres prepared by dry spinning[25]. Furthermore, the degree of orientation induced by drawing is assumed to depend on draw ratio only, which excludes effects of, for instance, drawing temperature. Finally, crystallinity is not accounted for in the model. As stated above, crystallization during drawing may be of importance with respect to effective orientation of the long-chain molecules, which is also recognized by Irvine and Smith. In this regard, the small increase in modulus upon drawing, that is observed for 85/15 P(LLA-DLA) fibres (*Figure 3*), suggests that drawing produces little orientation in this case, which may be attributed to the fact that no crystallization can take place in this particular copolymer.

In *Figure 5*, the crystallinity of PLLA and 80/20 P(LLA-CL) is plotted as a function of draw ratio. Data points at $\lambda = 1$ correspond to as-spun fibres, that are subjected to the same thermal treatment as drawn fibres, but without stretching. Remarkably, the level of crystallinity is independent of draw ratio for 80/20 P(LLA-CL) fibres, suggesting that annealing of the (amorphous) as-spun fibre at the drawing temperature, rather than the alignment of the macromolecules induced by drawing, determines the crystallinity of the fibre. In the case of the copolymer, this is to be expected since comonomeric units will inhibit crystallization to the same extent in both oriented and unoriented material. For the homopolymer, an improved molecular alignment is seen to result in a higher level of crystallinity.

Dry spinning and hot drawing

Fibres prepared by solution spinning are generally superior to melt spun fibres with respect to mechanical properties. In solution, the amount of chain entanglement is considerably lower than in the melt[39], and if the structure of this dilute entanglement network is effectively transferred to the solid state in the spinning process[40], the as-spun fibre will exhibit a high drawability, since entanglements are considered to limit the maximum drawability[41,42]. Furthermore, spinning from solution is usually performed at a relatively low temperature, in comparison with melt spinning, so thermal degradation is prevented. By a process of dry spinning and hot drawing, PLLA fibres having a strength 2.3 GPa have been prepared[26], which is considerably higher than strengths obtained by means of melt spinning (530 MPa, see *Figure 1*).

In the light of this pronounced difference in mechanical properties, arising from a combination of the effects discussed above, the dry spinning process is applied to a selected number of L-lactide copolymers. To obtain high-strength PLLA fibres by means of the dry spinning/hot drawing process, ambient temperature during spinning[43], deformation rate and temperature of drawing[26] and, most of all, the composition of the spinning solvent[25] have to be carefully chosen. Spinning from a solvent mixture of chloroform (good solvent) and toluene (poor solvent) was shown to give fibres with a remarkably higher drawability, and, as a result, higher strength after drawing, than fibres spun from, for instance, pure chloroform. It is interesting to note that fibres having a high strength of 2.2 GPa can be prepared from mixtures of PLLA and PDLA by dry spinning from pure chloroform and subsequent hot drawing[44]. The effect of solvent composition appears to be connected to the conformation of the polymer chain in the spinning solution, as is reflected by the peculiar behaviour of the intrinsic viscosity of the polymer as a function of solvent composition.

In *Figure 6*, intrinsic viscosities of PLLA and 80/20 P(LLA-CL), determined at 60°C (the spinning

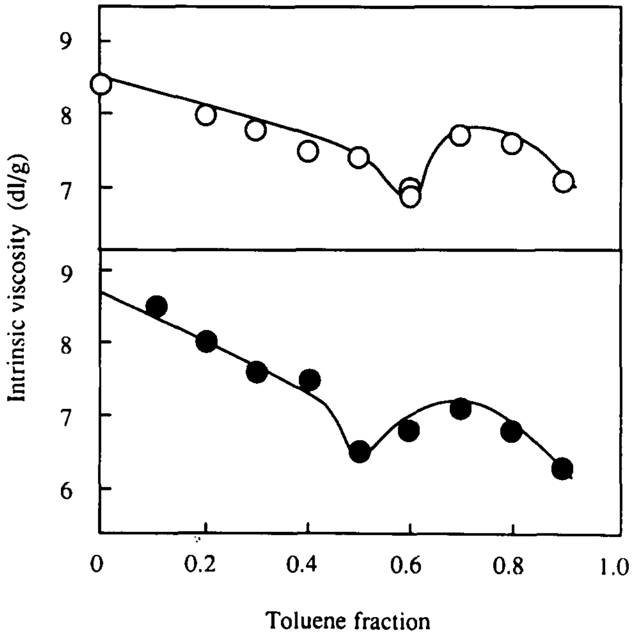

Figure 6 Intrinsic viscosity of (○) PLLA, $M_v = 8.0 \times 10^5$ kg kmol^{-1} and (●) 80/20 P(LLA-CL), $M_v = 7.4 \times 10^5$ kg kmol^{-1}, as a function of the fraction of toluene in chloroform/toluene solvent mixtures. Viscosities determined at 60°C. Data for PLLA are taken from reference 25

temperature), are presented as a function of the fraction of toluene, ϕ, in the solvent mixture. By addition of toluene, the solvent power decreases as is reflected by a decrease in intrinsic viscosity. However, remarkable changes in intrinsic viscosity are observed for both homopolymer (at $\phi = 0.6$) and copolymer (at $\phi = 0.5$). Such behaviour has been observed for other polymer/binary solvent systems and is associated with transition phenomena that occur near θ-conditions[45]. In the case of PLLA, this transition is thought to be a partial coil–helix transition, based on the observation of sudden changes in the optical rotation of PLLA solution coinciding with the discontinuity in viscosity behaviour[25]. Based on viscosity measurements on PLLA, Schindler and Harper[46] also suggest a helical conformation of PLLA in solution. The molecular weight dependence of the transition point that was found for PLLA/chloroform/toluene indicates that in the binary solvent system, the polymer chain preferentially adsorbs the good solvent.

The effect of solvent composition on the strength of the dry spun/hot drawn 80/20 P(LLA-CL) fibres is shown in *Figure 7*. In contrast to the effects observed for PLLA there was no effect of solvent composition on the drawability of the as-spun fibres, the maximum draw ratio being $\lambda_{max} = 5.5$ for all fibres. In spite of the similarity of λ_{max}, fibres with slightly higher strengths were obtained from solutions with $\phi = 0.4$–0.6. Please note that this range of solvent compositions corresponds with the changes in viscosity behaviour of the copolymer (see *Figure 6*). By spinning from a 50/50 chloroform/toluene solvent mixture, fibres having a strength of 1.05 GPa and a modulus of 7.5 GPa are obtained. The ultimate strength of melt spun/hot drawn 80/20 P(LLA-CL) fibres (350 MPa, see *Figure 1*) is improved by a factor of 3 by the dry spinning procedure.

To explain that there is no effect of solvent composition on the drawability of the P(LLA-CL) fibres in contrast to the homopolymer, it is first noticed that the maximum attainable draw ratios of the dry spun fibres are very low ($\lambda_{max} = 5.5$), knowing that they are spun from dilute solution. As stated above, if the entanglement network is effectively transferred to the solid state in the spinning process, the maximum draw ratio of the as-spun fibre is inversely proportional to the concentration of the spinning solution. The low drawability of the dry spun P(LLA-CL) fibres indicates a high concentration of entanglements, that may have been formed in the spinning thread upon evaporation of the solvent. This process of re-entangling may be prevented by a rapid solidification of the extrudate, which was not observed during spinning of the copolymer; during spinning of PLLA from 40/60 chloroform/toluene, instantaneous solidification of the extrudate was noticed. We found that the concentration of polymer in the spinning solution (ranging from 5 to 15 wt%) did not affect the maximum draw ratio, which shows that the entanglement topology, as present in the spinning solution, is not preserved in the as-spun fibre.

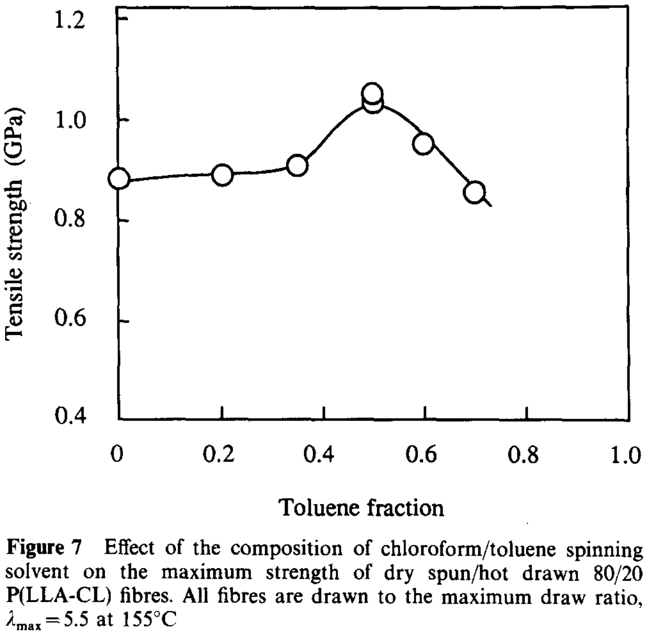

Figure 7 Effect of the composition of chloroform/toluene spinning solvent on the maximum strength of dry spun/hot drawn 80/20 P(LLA-CL) fibres. All fibres are drawn to the maximum draw ratio, $\lambda_{max} = 5.5$ at 155°C

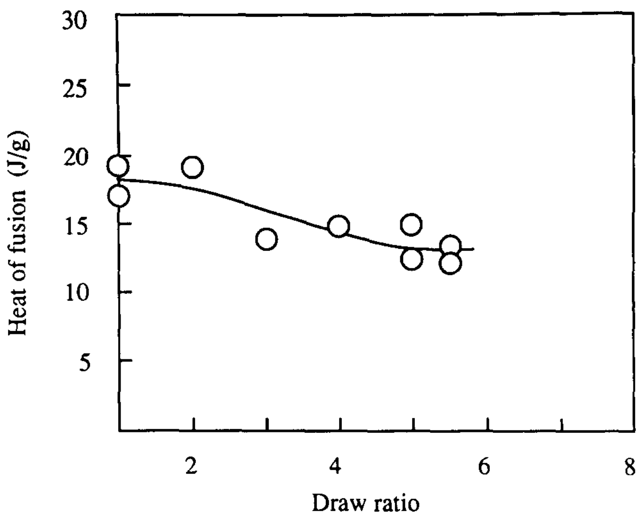

Figure 8 Heat of fusion of 80/20 P(LLA-CL) fibres, obtained by spinning from a 50/50 chloroform/toluene solvent mixture, as a function of draw ratio. Drawing temperature 155°C

In *Figure 8*, the heat of fusion of 80/20 P(LLA-CL) fibres, spun from 50/50 chloroform/toluene is presented as a function of draw ratio. Analogous to melt spun fibres of this polymer, there is no increase in the level of crystallinity with increasing draw ratio. Furthermore, it is noticed that the heat of fusion of the dry spun/hot drawn fibres is considerably lower than that of the melt spun fibres, namely 15–20 J g^{-1} *versus* 32 J g^{-1} (cf. *Figure 5*). It has been reported that the heat of fusion may be regarded as a relative measure for entanglement concentration[47] and the low heat of fusion found for fibres obtained by solution spinning therefore indicates a high concentration of entanglements. Since any polymeric material cannot have an entanglement density exceeding that of the equilibrium melt, it is clear from these data that the entanglement topology of melt spun fibres does not correspond to a equilibrium state. This can be explained by the fact that these fibres are spun using as-polymerized material with a low entanglement density[31], that is not likely to reach equilibrium within the time-scale of the spinning experiment.

To induce a more rapid solidification, P(LLA-CL) fibres were spun using a different poor solvent, di-n-butylether, which depresses the solvent quality of chloroform to higher extent than toluene. The effect of solvent composition on the drawing behaviour of dry spun P(LLA-CL) fibres is shown in *Figure 9*, where the tensile strength is plotted as a function of draw ratio for 80/20 P(LLA-CL) fibres spun from 50/50 chloroform/toluene, 80/20 chloroform/di-n-butylether and 60/40 chloroform/di-n-butylether. During spinning from

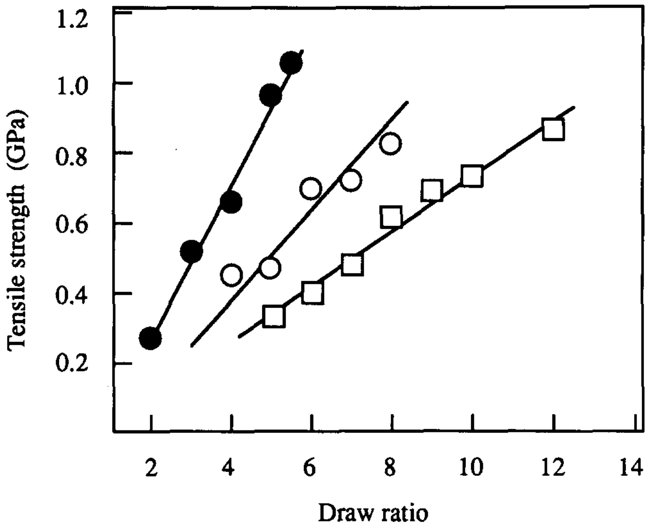

Figure 9 Tensile strength *versus* draw ratio of 80/20 P(LLA-CL) fibres spun from (●) 50/50 chloroform/toluene, (○) chloroform/di-n-butylether and (□) 60/40 chloroform/di-n-butylether solvent mixtures. Drawing temperature 155°C

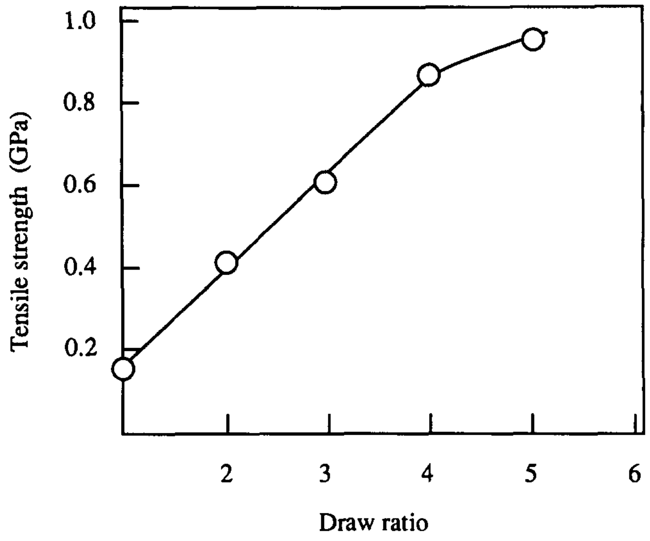

Figure 10 Tensile strength as a function of draw ratio for 95/5 P(LLA-DLA) fibres, spun from a 40/60 chloroform/toluene solvent mixture. Drawing temperature 145°C

60/40 chloroform/di-n-butylether, a rapid solidification (i.e. within a few seconds) was indeed observed. As is seen in *Figure 9*, these fibres showed the highest drawability ($\lambda_{max} = 12$), which supports the idea that the drawability is limited by entanglements, formed in the spinning thread, when rapid solidification fails to appear. A higher drawability does, however, not lead to improved mechanical properties, which suggests that other factors limit the maximum strength of these copolymeric fibres.

Fibres have also been prepared by solution spinning of a copolymer of L-lactide and D-lactide, 95/5 P(LLA-DLA). This copolymer resembles 80/20 P(LLA-CL) with respect to crystallinity and melting point. Spinning was applied to solutions of the copolymer in a 40/60 chloroform/toluene solvent mixture. As in the case of 80/20 P(LLA-CL), no rapid solidification in the spinline occurred. In *Figure 10*, the tensile strength of fibres, spun from these solutions and subsequently hot drawn at the optimum drawing temperature of 145°C, is plotted *versus* draw ratio. The maximum draw ratio of the as-spun fibres is $\lambda_{max} = 5$ and maximally hot drawn fibres have a strength of 0.95 GPa and a modulus of 9.2 GPa. The difference in modulus between 95/5 P(LLA-DLA) and 80/20 P(LLA-CL), 9.2 *versus* 7.5 GPa, are explained in terms of the T_g of the respective materials. Spinning of solutions of the L-/D-lactide copolymer from solvent mixtures of chloroform and di-n-butylether gave very brittle fibres that could not be drawn to strong fibres. Possibly, liquid–liquid phase separation has taken place in the spinning thread, due to the poor quality of these particular solvent combinations, leading to fibres with little coherence. A similar behaviour has been observed for nylon-6 fibres, spun from binary solvent mixtures with a high content of non-solvent[48].

From the experiments involving the solution spinning of 80/20 P(LLA-CL) and 95/5 P(LLA-DLA) the following picture emerges. In the dry spinning process of the copolymers, no effect of the composition of chloroform/toluene solvent mixtures is found, contrary to the behaviour of the PLLA homopolymer. In the case of PLLA, the effect of solvent composition on drawability of the as-spun fibres seems to be primarily determined by the rate of solidification of the fibre during spinning. The low concentration of entanglements in the spinning solution can only be preserved in the as-spun fibre if the entanglements become trapped by crystallization of the polymer. It was suggested that the partial helical structure of PLLA in solution may serve as a precursor for crystallization[25]. During spinning of copolymer solutions, a rapid solidification does not occur, irrespective of solvent composition. Therefore, a low maximum draw ratio is found for all solvent compositions due to extensive re-entangling during spinning. The slow solidification observed for copolymers may result from differences in solution behaviour, with respect to the homopolymer, or from the intrinsically low crystallizability of copolymers resulting from the presence of foreign monomer units in the polymers chain. It cannot be decided which of these effects is responsible for the observed behaviour, but the low crystallizability of the copolymers, being a general phenomenon, is the most probable explanation. Increasing the maximum draw ratio, however, did not lead to an improvement of fibre strength, from which one may conclude that other factors put a limit on the maximum strength of these materials.

Fibre properties

Table 3 summarizes the mechanical properties of the various copolymer fibres obtained in this study. Fibre properties strongly depend on method of preparation and crystallinity. In fibres of low crystallinity, small crystalline domains are embedded in a highly oriented amorphous phase, in which stresses are transferred by tie molecules. Consequently, the tensile behaviour will depend strongly on the structure of the amorphous phase. In *Figure 11*, the stress–strain curves of dry spun/hot drawn copolymer fibres are shown. Fibres from 80/20 P(LLA-CL) (curve B) are seen to have a higher elongation, at a given stress, than 95/5 P(LLA-DLA) fibres (curve A). This effect may be attributed to the higher T_g of the latter material, analogous to the dependence of initial modulus on T_g (see *Figure 4*).

The strength of the fibre will depend on the extent of orientation of the chains in the amorphous phase, achieved through hot drawing, since the efficiency of

Table 3 Ultimate mechanical properties and heats of fusion of hot drawn fibres from various copolymers used in this study

Sample	Preparation method	Tensile strength (MPa)	Young's modulus (GPa)	Strain at break (%)	Heat of fusion ($J g^{-1}$)
PLLA[a]	Dry spinning	2300	16	22	–
80/20 P(LLA-CL)	Dry spinning	1050	7.3	25	15
95/5 P(LLA-DLA)	Dry spinning	950	9.2	21	19
PLLA	Melt spinning	530	9.3	26	57
90/10 P(LLA-CL)	Melt spinning	400	8.2	23	45
80/20 P(LLA-CL)	Melt spinning	350	5.6	29	32
85/15 P(LLA-DLA)	Melt spinning	185	5.0	50	0

[a] Data from reference 26

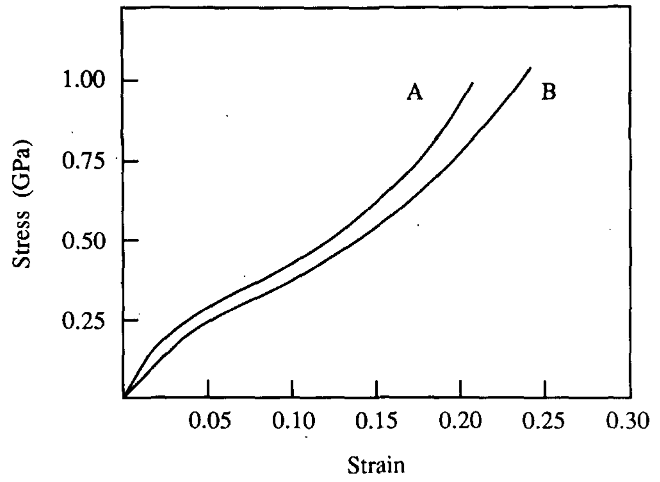

Figure 11 Stress–strain curves of dry spun/hot drawn fibres from 95/5 P(LLA-DLA) (curve A) and 80/20 P(LLA-CL) (curve B). The fibres are drawn to the maximum draw ratio at the optimum drawing temperature

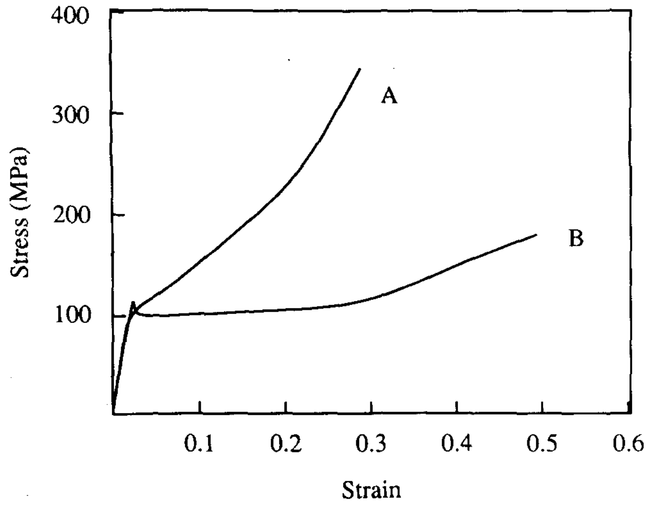

Figure 12 Stress–strain curves of melt spun/hot drawn fibres from 80/20 P(LLA-CL) (curve A) and 85/15 P(LLA-DLA) (curve B). The fibres are drawn to the maximum draw ratio under optimum drawing conditions

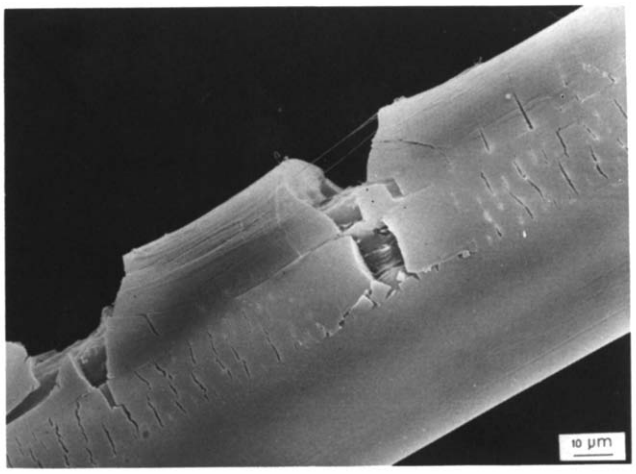

Figure 13 Scanning electron micrograph of a melt spun/hot drawn PLLA fibre, after cold deformation during the tensile test

chain packing, i.e. the number of load bearing chains per unit of cross-sectional area, will increase with increasing orientation[49]. The non-crystallizable 85/15 P(LLA-DLA) fibres deviate from other fibres studied here, with respect to drawing behaviour, as is seen in *Figure 2*, which indicates that crystallization during drawing may play an important role in achieving orientation. This point of view is corroborated by the stress–strain behaviour of 85/15 P(LLA-DLA) fibres, that is shown in *Figure 12* (curve B). In spite of the fact that these fibres are drawn to the maximum draw ratio, the strain at break is as high as 50%, and the fibres show a distinctive yield point, indicating that the orientation achieved by hot drawing is far from complete. All other fibres studied here have a strain at break of about 25% and do not yield when drawn to the maximum ratio (see *Figure 11* and curve A in *Figure 12*). Furthermore, it is of interest that the maximally drawn 85/15 P(LLA-DLA) fibre has a glass transition temperature of $T_g = 58°C$, which is identical to the T_g of undrawn PLLA and P(LLA-DLA) samples. Apparently, the T_g is not affected by the chain orientation that is introduced upon hot drawing.

In *Figure 13*, a scanning electron micrograph of a melt spun/hot drawn PLLA fibre, after cold deformation during tensile testing, is shown. The fibre surface reveals numerous cracks, at various stages of development, indicating a brittle behaviour of this material. This may seem at odds with the relatively high macroscopic strain at break of 26% of this fibre, but this brittle behaviour seems to be restricted to the fibre skin. Furthermore, numerous cracks develop simultaneously, and such multiple mechanisms are known to lead to a tough, or even a ductile, material response[50].

If strength is primarily determined by the amorphous parts of the fibre, one also expects an effect of molecular weight on strength, since the length of the chain determines the probability that it spans the amorphous region between two successive crystalline domains, and thus the amount of load bearing in the amorphous region. According to Flory[51], the dependence of tensile strength

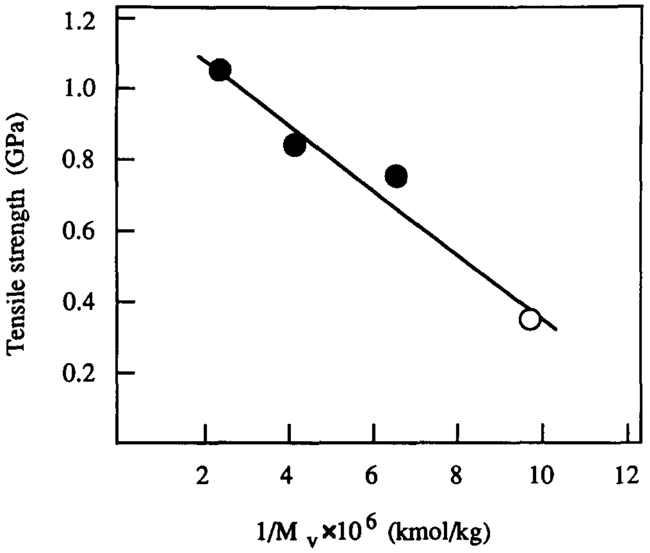

Figure 14 Tensile strength of 80/20 P(LLA-CL) fibres, obtained by (●) dry spinning from 50/50 chloroform/toluene and (○) melt spinning, as a function of reciprocal viscosity average molecular weight

(σ) on molecular weight (M_n) is given by

$$\sigma = A - B/\overline{M}_n$$

where A and B are numerical constants. In *Figure 14*, the strength of 80/20 P(LLA-CL) fibres is plotted against reciprocal molecular weight. The use of the viscosity average molecular weight (M_v), instead of M_n, seems to be justified by the relatively narrow molecular weight distribution of these polymers[12]. As can be seen, a good correlation is found between strength and molecular weight. Remarkably, this relation holds for both melt and solution spun fibres, which indicates that, in the case of P(LLA-CL), the superior properties of solution spun fibres, as compared with melt spun fibres, merely arise from the preservation of molecular weight during the low temperature solution spinning process. Properties of melt spun fibres can therefore be improved by taking special precautions to prevent thermal degradation, such as removal of catalyst and monomer from the as-polymerized material or end-capping of the chains[35]. This is of importance from an economical point of view, because of the advantages of melt spinning over solution spinning in this regard.

CONCLUSIONS

The introduction of comonomeric units in PLLA, in order to reduce the level of crystallinity and to promote the rate of degradation, which is desirable with respect to its use as biodegradable implant material, has been shown to exert a strong effect on the preparation and properties of fibres from these materials. During dry spinning, the low crystallizability of copolymers hinders a rapid solidification of the fibre, allowing re-entangling of the macromolecules to take place, resulting in fibres with low drawability. During hot drawing of copolymeric fibres, the level of crystallinity is not improved, in contrast to the behaviour of homopolymer fibres. Furthermore, if crystallization cannot take place during drawing, as is the case for the non-crystallizable 85/15 copolymer of L- and D-lactide, a poor level of orientation is reached.

The mechanical properties are also strongly determined by the level of crystallinity of the fibre. The maximum attainable strength for a 80/20 copolymer of L-lactide and ε-caprolactone appears to be 1.05 GPa, which is about half of the maximum strength of fibres prepared from the PLLA homopolymer. Because of the low level of crystallinity of copolymer fibres, their properties are mainly determined by the structure of the amorphous phase. The modulus of the fibres was shown to be determined by the T_g of the material, which in itself can be affected by copolymerization. The maximum strength of the copolymer fibres appears to be related to the molecular weight of the polymer, which is explained by the fact that a higher molecular weight will increase the number of chains that can transfer stresses in the amorphous domains. This molecular weight dependence also explains the differences between mechanical properties of melt spun and solution spun fibres. Strengths of melt spun fibres generally are about three times lower than those of solution spun fibres, since thermal degradation during melt spinning substantially reduces the molecular weight of the polymer. Properties of melt spun fibres may be improved by limiting thermal degradation during spinning, which is interesting in the light of the economic advantages of the melt spinning process.

ACKNOWLEDGEMENTS

Thanks are due to D. W. Grijpma and A. J. Nijenhuis for many helpful discussions. The authors express their gratitude to Dr J. Smook for his valuable contributions to this work. This study was financially supported by Akzo, The Netherlands.

REFERENCES

1 Vainionpää, S., Rokkanen, P. and Törmälä, P. *Progr. Polymer Sci.* 1989, **14**, 679
2 Williams, D. F. *J. Mater. Sci.* 1982, **17**, 1233
3 Shalaby, S. W. in 'Handbook of Fiber Science and Technology' (Eds M. Lewin and J. Preston), Vol. 3, Marcel Dekker Inc., New York, 1985, Part A, Ch. 3
4 Ikada, Y. in 'Handbook of Fiber Science and Technology' (Eds M. Lewin and J. Preston), Vol. 3, Marcel Dekker Inc., New York, 1989, Part B, Ch. 8
5 Forrester, J. C. *Br. J. Hosp. Med.* 1972, **11**, 578
6 Gilding, D. K. in 'Biocompatibility of Clinic Implant Materials' (Ed. D. F. Williams), Vol. 2, CRC Press, Boca Raton, 1982, Ch. 9
7 Daniels, A. U., Chang, M. K. O. and Andriano, K. P. *J. Appl. Biomater.* 1990, **1**, 57
8 Schmitt, E. E. and Polistina, R. A. *US Pat. 3 297 033*, 1967
9 Frazza, E. J. and Schmitt, E. E. *J. Mater. Res. Symp.* 1971, **1**, 43
10 Bartholomew, R. S. *Ophthamology* 1981, **183**, 81
11 Schneider, A. K. *US Pat. 3 636 956*, 1972
12 Eling, B., Gogolewski, S. and Pennings, A. J. *Polymer* 1982, **23**, 1587
13 Gogolewski, S. and Pennings, A. J. *J. Appl. Polym. Sci.* 1983, **28**, 1045
14 Hyon, S.-H., Jamshidi, K. and Ikada, Y. *Am. Chem. Soc., Polym. Prepr.* 1983, **24**, 6
15 Hearle, J. W. S. in 'Fibre Structure' (Eds J. W. S. Hearle and R. H. Peters), The Textile Institute and Butterworth, London, 1963, Ch. 19
16 Reed, A. M. and Gilding, D. K. *Polymer* 1981, **22**, 494
17 Chu, C. C. *J. Appl. Polym. Sci.* 1981, **26**, 1727
18 Rozema, F. R. *PhD Thesis* University of Groningen, 1991
19 Rozema, F. R., de Bruijn, W. C., Bos, R. R. M., Boering, G., Nijenhuis, A. J. and Pennings, A. J. *J. Biomed. Mater. Res.* submitted
20 Kricheldorf, H. R., Jonte, J. M. and Berl, M. *Makromol. Chem., Suppl.* 1985, **12**, 25
21 Keul, H. and Hocker, H. *Makromol. Chem.* 1988, **189**, 2303
22 Conn, J., Oyasu, R., Welsh, M. and Beal, J. M. *Am. J. Surg.* 1974, **128**, 19

23 Graig, P. H., Williams, J. A., Davis, K. W., Magoun, A. D., Levy, A. J., Bogdansky, S. and Jones, J. P. *Surg. Gynecol. Obstet.* 1975, **141**, 1

24 Katz, A. R., Muckerjee, D. P., Kaganov, A. L. and Gordon, S. *Surg. Gynecol. Obstet.* 1981, **161**, 213

25 Leenslag, J. W. and Pennings, A. J. *Polymer* 1987, **28**, 1695

26 Postema, A. R. and Pennings, A. J. *J. Appl. Polym. Sci.* 1989, **37**, 2351

27 Cutright, D. E., Hunsuck, E. E. and Beasly, J. D. *J. Oral. Surg.* 1971, **29**, 393

28 Nakamura, T., Shimizu, Y., Matsui, T., Okamura, N., Hyon, S.-H. and Nishiya, K. 'Degradation Phenomena of Polymeric Biomaterials', 4th ITV Int. Conference on Biomaterials, Denkendorf, 3–5 Sept. 1991

29 Jamshidi, K., Hyon, S.-H. and Ikada, Y. 'Proc. Int. Symp. on Fibre Science and Technology', Hakone, Japan, 1985, p. 251

30 Fischer, E. W., Sterzel, H. J. and Wegner, G. *Koll. Z. Z. Polym.* 1973, **251**, 980

31 Nijenhuis, A. J., Grijpma, D. W. and Pennings, A. J. *Polym. Bull.* 1991, **26**, 71

32 Lillie, E. and Schulz, R. C. *Makromol. Chem.* 1975, **176**, 1901

33 Grijpma, D. W. and Pennings, A. J. *Polym. Bull.* 1991, **25**, 335

34 Grijpma, D. W. and Pennings, A. J. to be published

35 Jamshidi, K., Hyon, S.-H. and Ikada, Y. *Polymer* 1988, **29**, 2229

36 Smook, J., Vos, G. J. H. and Doppert, H. L. *J. Appl. Polym. Sci.* 1990, **41**, 105

37 Vasanthakumari, R. and Pennings, A. J. *Polymer* 1983, **24**, 175

38 Irvine, P. A. and Smith, P. *Macromolecules* 1986, **19**, 240

39 De Gennes, P.-G. 'Scaling Concepts in Polymer Physics', Cornell University Press, Ithaca, 1979, Ch. 3

40 Bayer, R. K. *Coll. Polym. Sci.* 1991, **269**, 421

41 Kalb, B. and Pennings, A. J. *J. Mater. Sci.* 1980, **15**, 2584

42 Smith, P., Lemstra, P. J. and Booij, H. C. *J. Polym. Sci., Polym. Phys. Edn.* 1981, **19**, 877

43 Postema, A. R., Luiten, A. H. and Pennings, A. J. *J. Appl. Polym. Sci.* 1990, **39**, 1265

44 Ikada, Y. and Gen, S. *Eur. Pat. 0 288 041 A2*, 1988

45 Tsitsilianis, C. and Dondos, A. *Polymer* 1985, **26**, 1838

46 Schindler, A. and Harper, D. *J. Polym. Sci., Polym. Phys. Edn.* 1979, **17**, 2593

47 Pennings, A. J. *Makromol. Chem., Suppl.* 1979, **2**, 99

48 Gogolewski, S. and Pennings, A. J. *Polymer* 1985, **26**, 1394

49 Penning, J. P., Dijkstra, D. J. and Pennings, A. J. *J. Mater. Sci.* 1991, **26**, 4721

50 Kinloch, A. J. and Young, R. J. 'Fracture Behaviour of Polymers', Applied Science Publishers, London, 1983, Ch. 5

51 Flory, P. J. *J. Am. Chem. Soc.* 1945, **67**, 2048