JOURNAL OF MATERIALS SCIENCE LETTERS 12 (1993) 1048–1051

Hot-drawing of poly(lactide) networks

J. P. PENNING, D. W. GRIJPMA, A. J. PENNINGS
Department of Polymer Chemistry, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands

Poly (L-lactide), PLLA, obtained by ring opening polymerization of the L-lactide, degrades hydrolytically into non-toxic products, which is useful property in biomedical applications [1]. Thus, poly(lactide)s can be used as biodegradable implants such as bone fixation devices [2] and can be converted into strong fibres for suture applications [3, 4]. However, PLLA is a highly crystalline polymer and therefore the rate of degradation in a biological environment is rather slow [5]. Furthermore, crystalline domains remaining after partial degradation of the implant material give rise to a secondary inflammatory response of the surrounding tissue [6]. For this reason, materials having a low crystallinity are preferred in surgical applications. The crystallinity of the L-lactide homopolymer can conveniently be modified by copolymerization of L-lactide with other lactones and cyclic carbonates. For example, copolymers of L-lactide with D-lactide have a much lower crystallinity than PLLA, and are completely amorphous at D-lactide concentrations in excess of 12%. However, amorphous poly(lactide)s show brittle tensile behaviour and have a low impact strength, which is a serious limitation to their use as safe and reliable implant materials. Recently, it was shown that copolymerization of L-lactide with the tetrafunctional spiro-bis-dimethylene-carbonate (spiro-bis-DMC) leads to the formation of very homogeneous PLLA networks, that have a higher tensile and impact strength and a lower crystallinity than the linear PLLA homopolymer [7, 8]. In this study, the possibility of producing fibres semi-crystalline and amorphous poly(lactide) networks is investigated. Fibres produced from these materials may be applied as sutures or as reinforcing fibres in biodegradable implants. Moreover, fixation devices with superior mechanical properties can be manufactured from fibrous materials using, for instance, solvent welding techniques [9].

Since cross-linked materials cannot be processed by conventional spinning techniques, fibres were produced from the as-polymerized poly(lactide) networks. Both semi-crystalline and amorphous networks, prepared by copolymerization of spiro-bis-DMC with L-lactide and with 85/15 mixtures of L- and D-lactide respectively, were used in this study. The structure of these networks is of prime importance with respect to the drawing behaviour of the fibres, and will be discussed first. The chemical cross-links that are present in the network are formed through incorporation of the tetrafunctional spiro-bis-DMC comonomer into the growing poly(lactide) chain. In this type of polymerization, homogenous networks can only be formed if both monomers have similar reactivities leading to a random incorporation of the tetrafunctional units. If, for example, the bifunctional monomer has a higher reactivity than the tetrafunctional monomer, the latter will react mainly at high monomer conversions, leading to inhomogeneities in cross-link density. Swelling experiments on L-lactide/spiro-bis-DMC networks, however, show that the networks formed are very homogeneous: lightly cross-linked L-lactide/spiro-bis-DMC networks exhibit very high degrees of swelling, up to $q = 50$, and maintain mechanical stability in the swollen state; the experimentally determined molecular weight between cross-links, M_c, corresponds very well to values that are calculated from the mole fractions of bi- and tetrafunctional reactants in the monomer feed and gel-percentages above 96% can already be achieved at cross-linker concentrations as low as 0.1 mol %.

The chemical cross-links introduced by the spiro-bis-DMC monomer, however, are not the only junctions present in the network structure, because the molecular chains are entangled and such entanglements can be considered as permanent physical cross-links since they are effectively trapped by the chemical cross-links. Therefore, both chemical cross-links, characterized by M_c, and entanglements, characterized by the average molecular weight between entanglements M_e, must be considered in relation to the drawing behaviour of the network. In the polymer melt, M_e is a material property determined by the chemical constitution of the chain [10]. In as-polymerized materials, however, the average entanglement spacing may be much higher than in the equilibrium melt due to, for instance, simultaneous formation and crystallization of polymer chains, preventing extensive entanglement formation. Experimental results indicate that this is also the case in the bulk polymerization of L-lactide at 110 °C where the growing chains crystallize from the monomer melt which is a poor solvent for the polymer [11]. For this reason, the as-polymerized L-lactide homopolymer has a low entanglement density corresponding to $M_e \approx 22 \times 10^3$ g mol^{-1} [7]. Due to this low entanglement density, linear as-polymerized poly(L-lactide) can be drawn to very high ratios, up to $\lambda_{max} = 18$ [12]. During the bulk polymerization of 85/15 mixtures of L- and D-lactide, crystallization cannot take place and consequently the as-polymerized amorphous copolymers possess an average entanglement spacing comparable to that of the random melt, which is estimated at $M_e \approx 9 \times 10^3$ g mol^{-1} [13]. The differences in entanglement densities between amorphous and crystalline networks have a pronounced effect on the drawing behaviour of these materials, as will be shown.

The poly(lactide) networks were prepared by bulk polymerization of either pure L-lactide or 85/15 mixtures of L- and D-lactide in the presence of small amounts of spiro-bis-DMC at 110 °C using tin(II) bis(2-ethylhexanoate) as a catalyst. The polymerization vessels were charged with teflon tubings from which rod-like specimens of approximately 1 mm diameter were obtained after completion of the polymerization. These specimens were drawn either on a hot-plate with controlled temperature or using an Instron tensile testing machine, equipped with a high-temperature cabinet. After drawing to the desired draw ratio, the fibres were cooled down to room temperature keeping them at constant length, so as to maintain the molecular orientation. Fig. 1 shows the maximum draw ratio of the networks from semi-crystalline PLLA and amorphous 85/15 L/D poly(lactide) as a function of the concentration of spiro-bis-DMC cross-linker. Semi-crystalline specimens were drawn at 200 °C, i.e. above the polymer melting temperature of T_m = 180–190 °C, whereas amorphous materials were drawn at 100 °C, i.e. above the glass-transition temperature of T_g = 57 °C. Fig. 1 reveals remarkable differences in drawing behaviour between semi-crystalline and amorphous networks. Amorphous networks exhibit lower maximum draw ratios which is explained by the higher entanglement densities in these materials, as was discussed above. Since the concentration of chemical cross-links is quite low in the materials studied, the entanglements are the most important restraints to which the network chains are subjected. At a cross-linker concentration of 0.1 mol %, the molecular weight between chemical cross-links is approximately 60×10^3 g mol^{-1}, as determined from swelling data, whereas $M_e \approx 9 \times 10^3$ g mol^{-1}. One can actually calculate the maximum draw ratio of the network from the ratio of the contourlength L_c to the radius of gyration R_g of the average chain segment betwen network points, i.e. $\lambda_{max,calc} = L_c/2R_g$ [14]. In the case of the amorphous network containing 0.1% spiro-bis-DMC, this leads to $\lambda_{max,calc} = 6.7$, which is in good agreement with the experimentally found value of $\lambda_{max,} = 7$. If the contribution of chemical cross-links is neglected in this calculation, one finds $\lambda_{max,calc} = 7.2$. Although this approach is obviously an oversimplification, it demonstrates that, in the range of cross-linker concentrations used (0–0.35 mol %), the maximum draw ratio of the amorphous networks is hardly affected by the presence of chemical cross-links. Semi-crystalline networks, however, are less densely entangled and can therefore be drawn to higher ratios, and the chemical cross-links are more effective in reducing the maximum draw ratio at these low cross-link concentrations. The results suggest that the maximum draw ratio of the amorphous networks could be enhanced by carrying out the cross-linking polymerization in solution. In the polymer solution, the chains are less entangled as a result of which a smaller number of entanglements becomes trapped by the chemical cross-links [15]. Preliminary experiments on amorphous networks prepared in a 50% solution in dry toluene showed that the maximum draw ratio increased slightly, from $\lambda_{max} = 7$ for bulk-polymerized samples to $\lambda_{max} = 8.6$ for solution-polymerized networks.

In Fig. 2, the strength of the drawn networks is shown as a function of draw ratio. The strength of the networks is seen to increase linearly with draw ratio and both amorphous and semi-crystalline networks follow the same strength–draw ratio relation. Since the crystalline networks can be drawn to higher ratios, the possess a higher ultimate stength than amorphous ones. At the maximum draw ratio the crystalline PLLA networks have a strength of 800 MPa, a modulus of elasticity of 11 GPa and a strain at break of 15%. The 85/15 L/D lactide

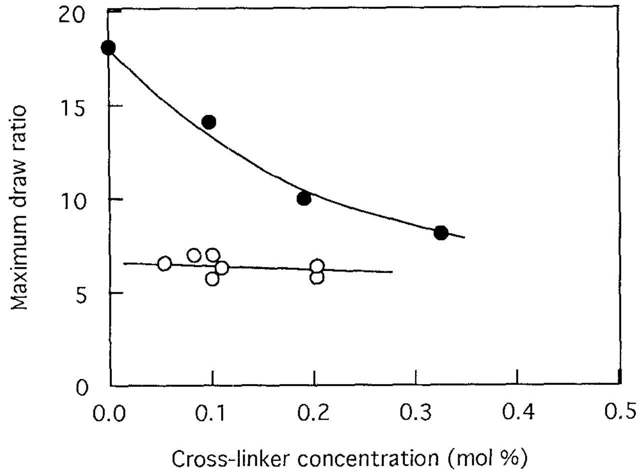

Figure 1 Maximum draw ratios of (●) semi-crystalline poly(L-lactide) networks drawn at 200 °C and (○) amorphous 85/15 L/D poly(lactide) networks drawn at 100 °C as a function of the concentration of the spiro-bis-dimethylene-carbonate cross-linker in the polymerization mixture.

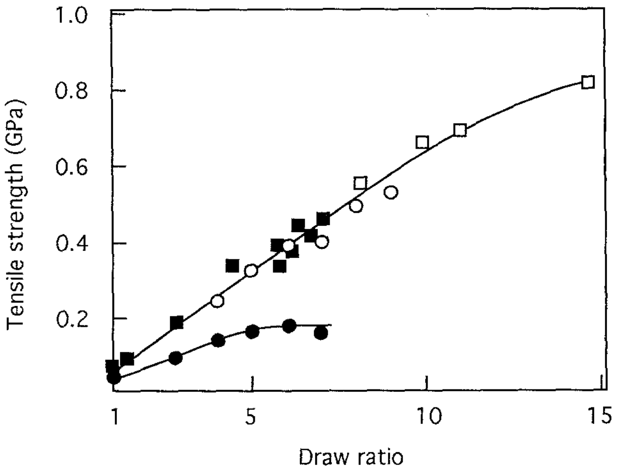

Figure 2 The tensile strength of fibres prepared by drawing of (□) as-polymerized, crystalline poly(L-lactide) networks, (■) as-polymerized, amorphous 85/15 L/D poly(lactide) networks, (○) melt-spun poly(L-lactide) fibres and (●) melt-spun 85/15 L/D poly(lactide) fibres as a function of the draw ratio.

networks have a maximum strength of 460 MPa, which is quite high taking into consideration that these materials are completely amorphous. The amorphous networks that were prepared in solution have a somewhat higher strength of 500 MPa, which is attributed to the better drawability of this material. The maximally drawn amorphous networks have a modulus of elasticity of 7.5 GPa and a strain at break of 22%. In Fig. 2, the strength–draw ratio data of linear PLLA and 85/15 L/D poly(lactide) fibres, produced by melt-spinning [16], are also shown. The development of strength of the crystalline PLLA melt-spun fibres is similar to that observed for the cross-linked materials. In the amorphous melt-spun fibres, however, the strength increases less steeply and the ultimate strength of these fibres is only 185 MPa at a draw ratio of $\lambda = 6$, indicating that orientation is difficult to achieve in these fibres. A necessary requirement for achieving orientation of polymeric chains by drawing is that these chains are bound at either end to the network which they are part of. In cross-linked materials, the polymer chains are connected to each other by chemical bonds and drawing of these networks amounts to a spatial rearrangement of the chemical cross-links that forces the chains to assume a more extended configuration. In linear polymers, the situation is more complicated since the molecules are connected only by physical cross-links that can rearrange irreversibly under the appropriate conditions. In the drawing process of melt-spun fibres prepared from linear PLLA, the polymeric chains become extended between physical cross-links formed by entanglements as well as crystallites, since drawing is performed at 110 °C, i.e. well below the melting temperature of the polymer. From the strength–draw ratio relation for these fibres shown in Fig. 2, it appears that drawing under these conditions produces a similar amount of orientation as in the case of the chemical networks. In the linear, amorphous 85/15 L/D poly(lactide), the only network junctions present are chain entanglements. The low strength levels that can be attained upon drawing of this material suggest that entanglements do not provide the sufficient permanence of structure that is required to achieve orientation. This point becomes especially clear when the effect of drawing temperature on the strength of the drawn fibres is considered. Fig. 3 shows these effects for fibres prepared from both cross-linked and linear 85/15 L/D poly(lactide). In the case of the uncrosslinked material, drawing is only possible in a very narrow range of temperatures and the strength of the resulting fibres goes through a sharp maximum at 60 °C, which coincides with the glass-transition temperature of the polymer. Below this temperature, the mobility of the polymeric chains is limited which prevents substantial elongation of the material, whereas at temperatures above T_g the increased mobility allows relaxation phenomena, which dissipate the orientation induced by drawing, to occur. In the case of the cross-linked material, the increase of chain mobility above T_g results in higher maximum draw ratios leading to fibres with improved strength. Since relaxation of the uncoiled chains cannot take place, unless molecular bonds are broken, drawing at temperatures well above T_g also produces fibres with good mechanical properties, contrary to the behaviour of the uncrosslinked polymer. In connection with the observed the differences in drawing behaviour between the cross-linked and linear 85/15 L/D poly(lactide)s, it is important to note the molecular weight of the linear polymer is appoximately 1×10^5 g mol^{-1}. In ultra-high molecular weight polymers, $M \approx 10^6$ g mol^{-1}, orientation *can* be achieved by drawing above the melting temperature, since relaxation times are substantially longer in these materials [17].

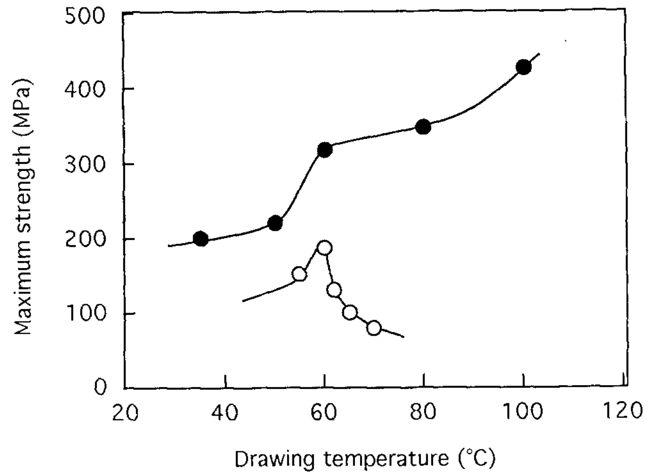

Figure 3 The effect of drawing temperature on the strength of maximally drawn fibres from (●) as-polymerized, amorphous 85/15 L/D poly(lactide) networks and from (○) amorphous melt-spun 85/15 L/D poly(lactide) fibres.

In order to establish whether a permanent structural rearrangement of the network has taken place as a result of hot-drawing, the degree of swelling of the network was determined before and after the drawing experiment, using a method proposed by Voorn and Hermans [18]. Swelling experiments were performed in chloroform at 25 °C using 85/15 L/D poly(lactide) containing 0.1 mol % cross-linking agent. Prior to drawing, the degree of swelling of this network is $q = 29.5$. After the drawing experiment, however, a considerable increase in the degree of swelling was found, $q = 158$ after drawing to the maximum draw ratio of $\lambda_{\max} = 7$ at 100 °C and $q = 146$ after drawing to $\lambda_{\max} = 4.4$ at 50 °C. Concomitantly, the gel-percentage of the network strongly decreases, from 94% for the undrawn material to approximately 60% after drawing. These results indicate that a substantial degradation of network chains has taken place during drawing.

In conclusion it can be said that fibres can conveniently be prepared from crystalline as well as amorphous poly(lactide) networks by drawing of the as-polymerized material. The fibres possess strengths exceeding those of fibres prepared by melt-spinning of the analogous linear polymers, in the case of the amorphous materials the ultimate strengths differ by a factor 2.5. The results demonstrate that fibres having appreciable strengths can be prepared from completely amorphous poly(lactide)s if they are chemically cross-linked. Due to the presence of chemical cross-links, the polymeric chains can be effectively oriented by hot-drawing, which is not the case for linear amorphous polymers where chain entanglements are the only form of network points present. During drawing of chemically cross-linked networks, however, a substantial amount of bond rupture was found to occur.

Acknowledgement

This study was financially supported by AKZO Polymers and Fibres, The Netherlands

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Received 15 January
and accepted 10 February 1993