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Poly-L-lactic acid braided fibres produced by melt spinning: characterization and *in vitro* degradation

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Bioabsorbable fibres showing stress at break of 500 MPa and modulus of 10 GPa, have been obtained through a melt-spinning, hot-drawing process. Multifilament braids present the characteristic S-shaped stress–strain curve of human ligaments. Mechanical behaviour is affected by twisting and braiding such that stiffness can vary from 0.8 GPa to 6.2 GPa, covering the whole ligament physiologic range, reported to be $\simeq$ 1.5 GPa, according to age and sport activity. A cyclic tension load applied for 2×10^6 cycles lead to initial mechanical improvement and causes no creep. During degradation *in vitro*, yield stress increases continuously while the ultimate tensile strength (UTS) starts to decrease after 5 weeks. After 13 weeks degradation, strength loss amounts to 6% of the initial UTS. At this time the surface of the fibres shows isolated longitudinal cracks.

1. Introduction

Since polyglycolic acid was introduced as a biodegradable suture [1], many other bioresorbable polymers have been studied for an increased number of medical applications [2–5]. In orthopaedic surgery, where good mechanical performance and long resorption time are prerequisites, poly-L-lactic acid (PLLA) seems to be the choice.

PLLA has been suggested for bioabsorbable pins and rods in orthopaedics and maxillo-facial surgery [6–10]; some authors have reported on the ability of PLLA to be spun into fibres [11–17]. As often happens, literature data are difficult to compare because of the lack of test normalization and incomplete parameter reports. Although PLLA suits several orthopaedic applications, its long lifetime *in vivo* may become disadvantageous. In known cases, a second operation has been required almost 3 years after implantation, in order to remove it [6, 7]

The present work is part of a larger investigation of PLLA fibres [18–21]. In previous studies we have set up a melt-spinning/hot-drawing process. Although the molecular weight underwent a great loss, it was possible to produce fibres with high strength and moduli, 1 GPa and 10 GPa, respectively. Such high values for melt-spun fibre have never been reported.

Mechanical properties [19] and *in vitro* degradation behaviour [20] for single fibres have been reported elsewhere.

This communication reports the characterization of braided fibres and their *in vitro* degradation data. Their possible application as a biodegradable ligament augmentation device (LAD) is considered.

2. Experimental procedure

2.1. Materials

Fibres were produced by melt-spinning PLLA flakes (M_w = 480 000) supplied by Purac, Gorinchem. The raw material had a melting point of 184.9 °C and crystallinity content of 66%, as detected by differential scanning calorimetry (DSC) analysis referring to 93.6 J/g enthalpy of fusion [22].

Fibres were produced through a two-stage process, i.e. melt spinning and hot drawing, reported elsewhere (19)

In the present study melt-spun filaments were drawn at 100 °C under flushing nitrogen up to a draw ratio of 6. The final average diameter was 140 μm. Fibres had a molecular weight of 70 000 and crystallinity content of 47%.

Bundles of 16 fibres 1 m long were twisted to a twist density of 0, 4.5 and 9 rpc (round per centimetre). Three twisted bundles were then braided at a constant braid density of 1.3 braids/cm to produce a homogeneous braid from which 10 cm samples were cut (Fig. 1).

2.2. Characterization

Mechanical properties were measured at room temperature using an Instron tensile tester mod. 4502 at room temperature and with a crosshead speed of 12 mm min^{-1} and gauge length of 7 cm. Special

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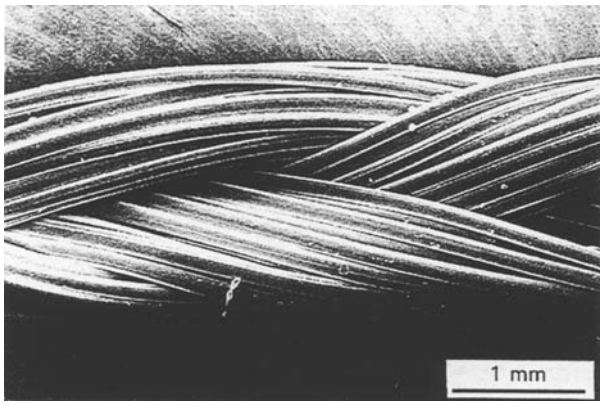

Figure 1 PLLA braided fibres. Twist density 0 rpc.

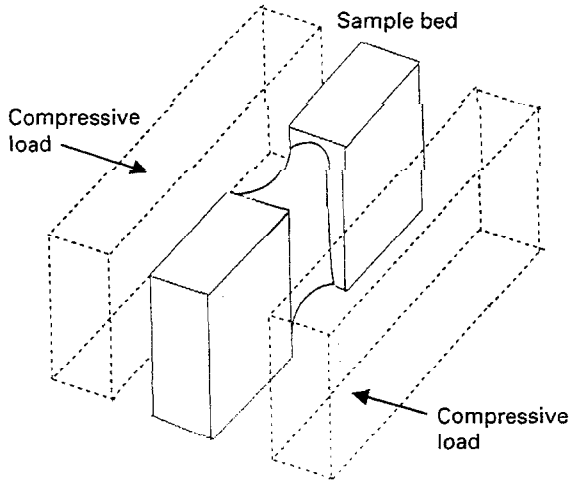

Figure 2 Aluminium clamps specially designed for tensile test of sample braids.

aluminium clamps were used to avoid squeezing the samples at their extremities (Fig. 2).

Fatigue tests were performed with an apparatus built in the laboratory. A sinusoidal tension force, variable between 1 and 3 N with a frequency of 10 Hz, was applied.

Degradation tests were performed by immersing the braids in Ringers saline solution at 37 °C, renewed monthly. Each sample was mechanical characterized in the wet state, at room temperature.

Molecular weight was calculated from intrinsic viscosity of diluted chloroform solution measured in a Ubbelhode viscosimeter, type 0C, using the following equation [23]:

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

Surface images at different degradation times were collected with a scanning electron microscope, Cambridge Stereoscan 200.

3. Results

Braided PLLA fibres were mechanically characterized before fatigue, after fatigue and during hydrolytic degradation.

The braided fibre axis does not exactly coincide with the braid axis, so the first mechanical reaction is

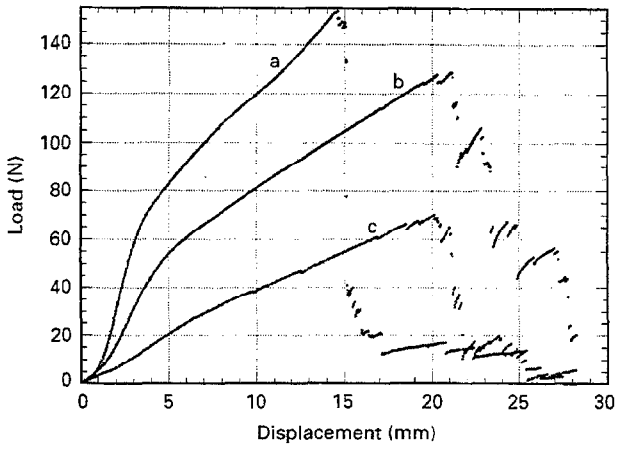

Figure 3 Stress–strain curve for PLLA braided fibres with different twist density: (a) 0 rpc; (b) 4.5 rpc; (c) 9 rpc.

TABLE I Mechanical properties of PLLA braided fibres

Twist (rpc)	Youngs modulus (%)	UTS (%)	Load-at-Break (%)
0	100	100	100
4.5	58	45	85
9	15	35	46

governed by fibre displacement and alignment, which gives rise to the characteristic "toe" of the stress–strain curve (Fig. 3).

When uniaxiality between fibres and load is reached, stress rises almost linearly with deformation; this slope is the elastic modulus of the specimen. At higher stress, linearity is lost and the polymer undergoes yielding until failure.

Twisting has the ability to lower braid rigidity, thus controlling the mechanical response, as shown by stress–strain curves for three twisted braids reported in Fig. 3. Young's modulus, calculated from the slope of the linear part of the $\sigma(\varepsilon)$ curve, is 6.2 GPa for 0 rpc twist density, and decreases to 0.8 GPa when twist density is raised to 9 rpc. Load-at-break also is affected, being 85% and 46% for the 4.5 and 9 rpc, respectively, relative to the untwisted material. This is likely due to pre-tension and enlargement of surface microdefects caused by twisting. In Table I elastic moduli, ultimate tensile strength and load-at-break, for the three geometries considered, are reported in percentages referred to the untwisted braid. Ultimate tensile strength appears to be even more sensitive to twisting than load-at-break. This is likely due to the angular displacement of the fibre cross-sectional area from the load axis, due to high roll up. This causes the stress to be calculated over a larger area than is actually effective.

The S-shaped curve exhibited by braided fibres is similar to the stress-strain curve of human ligament [24]. Up to now there has not been an artificial device able to mimic perfectly physiological behaviour [25, 26]. This is difficult because physiological properties change according to the age of the patient and the

anatomical site. However, most permanent implants cannot withstand fatigue. When possible, homoimplant as the medial third of patellar tendon is preferred. To allow early mobilization, an augmentation device is inserted, which is required to bear most of the load initially, but to a decreasing extent as the healing process takes place. A bioresorbable implant would suit, provided that it has enough initial strength and rigidity with controlled decrease of these machanical properties with time. The idea is not new and PDS LAD is already commercially available. Although its rigidity is very similar to that of human tissue, it does not show any increasing modulus behaviour, its strength is low and strength retention is too short [26].

The anterior cruciate ligament (ACL) has been widely studied but available data are scattered as a consequence of different test practices [26–29]. ACL is reported to have load-at-break within the range 350–2100 N with strain–at–break of 30–44%. Cross-sectional area varies from 44.7 mm^2 in young people, to 57.5 mm^2 in older people [26–29]. Ultimate tensile strength is reported to be between 40 and 147 MPa [30, 31]. Linear behaviour starts at 3–6% deformation and the elastic modulus is $\simeq$ 1.5 GPa [32]. When walking, the ACL is subjected to loads in the range 30–60 N, while jogging exerts loads of about 730 N [33]. Deformation never exceeds 8% [27]. Under normal living conditions therefore, ACL works in the low elastic modulus range.

When an intra-articular implant is performed, new ligamentous tissue starts to be thick enough after 4 weeks, and perfect healing is achieved in 20 weeks if an augmentation device is used [34, 35]. In ligament reconstruction the LAD is positioned parallel to the omoimplant and load sharing is determined by relative rigidity. PLLA melt-spun fibre braids can be twisted in order to provide stiffness within the physiological range (Fig. 4).

The present untwisted braid UTS is 460 MPa, well over the maximum value reported for human anterior cruciate ligament.

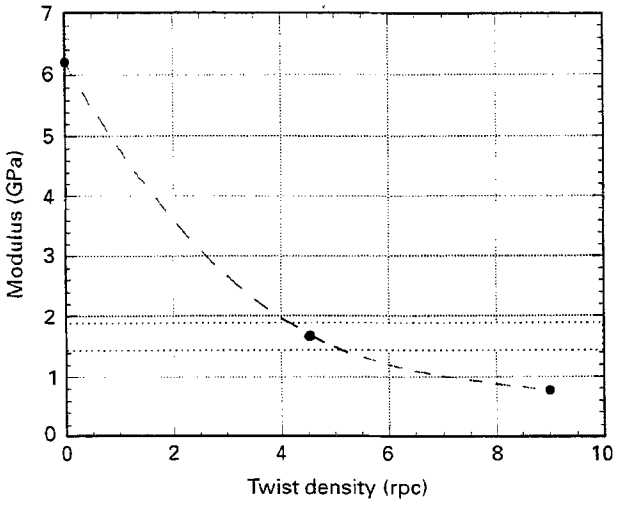

Figure 4 Young's modulus for PLLA braided fibers with different twist density. Grey area shows the physiological range.

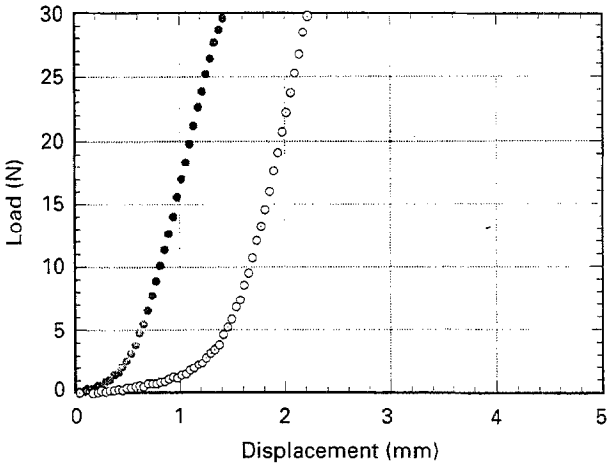

Figure 5 Effect of 1 week degradation on the linear part of the mechanical response: (●) original; (○) after 1 week in saline solution.

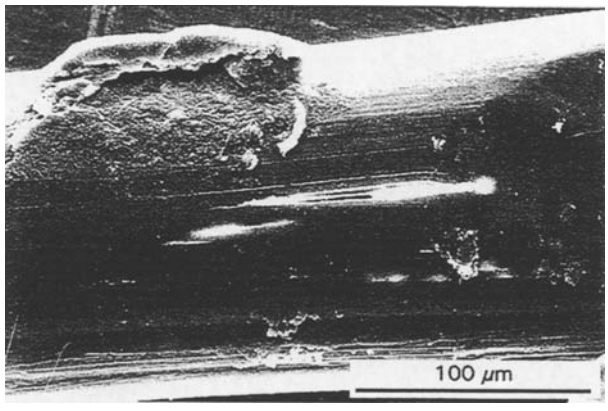

Figure 6 Fibre lateral surface after 13 weeks in saline solutions at 37 °C.

In vitro degradation tests have been performed in saline solution at 37 °C. Initially water absorption causes the linear part of the stress–strain curve to shift towards higher deformation (Fig. 5). During this initial period, strength also appears to increase. The same has been observed for single PLLA fibres (21). In 8 weeks this effect is no longer detectable and braid strength starts to decrease. At this time brittleness induced by degradation opposes plasticity and the toe region of the stress–strain curve agrees exactly with the initial undegraded part. At 13 weeks only 6% of the original UTS is lost despite a halving of molecular weight.

Fibre surfaces present some longitudinal cracks and few spots of preferential hydrolitic attack (Fig. 6).

In the present experimental trial, PLLA braids have high strength but only 153 N load-at-break, 1/15 of the highest value reported for human ACL [27–29]. However, it must be considered that the small number of fibres employed in each braid, giving a load-resisting cross-section of 0.3 mm^2, is almost 1/170 of the 44–57 mm^2 reported for human ACL [27–29].

Fatigue tests were performed by imposing a cyclic tensile load of 1–3 N at a frequency of 10 Hz. The maximum load of 3 N was chosen by considering that the present PLLA braids withstand only 1/15 of

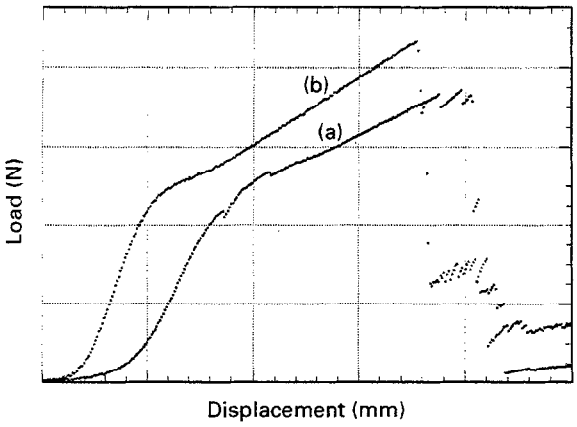

Figure 7 Stress–strain curve for PLLA braided fibres before (a) and after (b) fatigue test.

TABLE II Final modulus increase after 3 months fatigue

Twist density (rpc)	Final modulus increase (%)
0	247
4.5	112
9	61

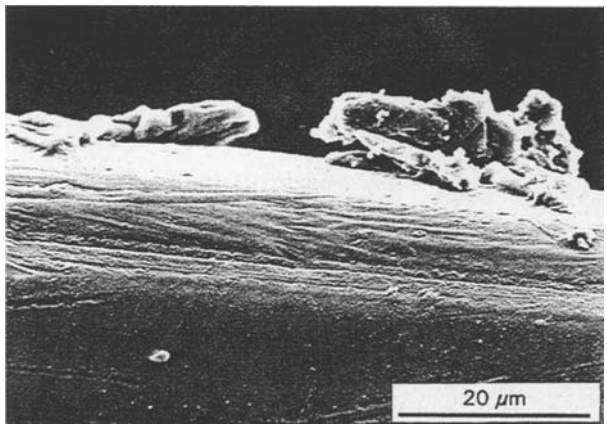

Figure 8 PLLA fibre lateral surface after fatigue test.

human ACL load-at-break. To maintain a proportion consistent with the load acting on human ACL during walking, the 45 N [33] has been divided by 15. Braid samples 7 cm long were mounted in an aluminium clamp and tests were run for 2×10^6 cycles. This emulates 3 months of reduced activity, 12 h per day, assuming one movement every 2 s. At the end of the fatigue test, the braids had not lengthened. However, the load applied, although not sufficient for creep, did modify the fibres within the braid. The linear region of the stress–strain curve rose lower deformation and its slope increased with twist density (Fig. 7). It is likely that the low tension lasting for a long period, although insufficient to induce cold drawing, is able to improve molecular and fibre alignment and consequently braid rigidity. The effect is more marked for untwisted braids, where the fibre axis is already close to the load direction, as reported in Table II; the modulus increase is reported in percentage terms relative to the modulus of the braid before fatigue.

The fibre surface is affected by fatigue. After 2×10^6 cycles, fibres show some shredding where filaments have not stood up to the fatigue process (Fig. 8).

4. Conclusions

PLLA fibres were produced by a melt spinning–hot drawing process. Fibres with strength 500 MPa and modulus 10 GPa were twisted in bundles and braided.

The properties of PLLA braids resemble the mechanical behaviour of human ligament, with its nonlinear increasing modulus. They are strong enough to be employed as biodegradable ligament augmentation devices in reconstructive orthopaedic surgery. Device rigidity can be tailored by twisting fibres in order to match biological tissue compliance. Braids with Young's modulus within the range 0.77–6.2 GPa were obtained.

Load proportional to the physiological load during walking was applied for 2×10^6 cycles, and caused no creep or weakening of the braid.

In the process of degradation, braids lose 6% of their initial UTS in 13 weeks, *in vitro*. Although *in vivo* degradation may progress faster, PLLA braid fibres have been shown to be suitable as an augmentation device in ACL reconstructive surgery, assuming a healing period of 20 weeks [35].

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