JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE **10** (1999) 659–662

Fibers by bioresorbable poly(ester-ether-ester)s as potential suture threads: a preliminary investigation

G. D. GUERRA* P. CERRAI, M. TRICOLI
Centro di Studi sui Materiali Macromolecolari Polifasici e Biocompatibili, CNR, Via Diotisalvi 2, I-56126 Pisa, Italy

S. MALTINTI, I. ANGUILLESI, N. BARBANI
Dipartimento di Ingegneria Chimica, Chimica Industriale e Scienza dei Materiali, Università di Pisa, Via Diotisalvi 2, I-56126 Pisa, Italy
E-mail: guerra@ing.unipi.it

Fibers made by a bioresorbable poly(ε-caprolactone)-*block*-poly(oxyethylene)-*block*-poly(ε-caprolactone) copolymer, having a number average molecular mass of about 200 000 Da and an average molar composition of 66% oxycaproyl units and 34% oxyethylene units, were melt-spun, with the aim at using them as suture threads. Their properties were investigated by the stress-strain test and by differential scanning calorimetry (DSC). The results obtained show that the properties of this material depend very strongly on the alignment of its macromolecules. In particular, the only partial alignment, obtainable by a relatively moderate drawing just after the extrusion, leads to values of elongation at break too high for use of the fibers as suture threads. The DSC analysis reveals interesting properties of the material, but also confirms their strong dependence on the extrusion procedure and on the mechanical treatment. In conclusion, the results of this preliminary study show that the spinning technique must be improved, and that further investigations are necessary to ascertain the possibility of using these poly(ester-ether-ester)s for the fabrication of suture threads.

---

1. Introduction

Synthetic bioresorbable homo- and copolymers, mainly aliphatic polyesters, have been widely used for the fabrication of absorbable suture threads since the early 1970s [1, 2]. The class of poly(ester-ether-ester)s offers the possibility of modulating the bioresorption time by varying the lengths of both the hydrophilic polyether blocks and of the hydrophobic polyester ones [3].

The non-catalyzed synthesis of such copolymers, developed by us by thermally polymerizing cyclic esters onto preformed poly(ethylene glycol) chains (PEG) [3–5], permits to solve the problem of the commonly used Sn catalysts, potentially toxic when not completely removed. Threads made by a bioresorbable poly(ε-caprolactone)-*block*-poly(oxyethylene)-*block*-poly(ε-caprolactone) copolymer (PCL-POE-PCL) were melt-spun; their properties were investigated by the stress–strain test and by differential scanning calorimetry (DSC). Different screw rotations and drawing speeds have been chosen with the aim at testing the best extrusion conditions to obtain fibers having the most appropriate mechanical properties for use as suture threads.

2. Materials and methods

2.1. Copolymer synthesis and characterization

The material was synthesized, according to the mechanism shown in Fig. 1, by polymerizing ε-caprolactone (Janssen Chimica) onto a PEG of 35 000 Da average molecular mass (Merck), under vacuum at 185 °C, without any catalyst. The reactants were purified according to the previously reported procedure [4].

DSC was carried out with a Perkin Elmer DSC 7 apparatus, in the temperature range from 20 to 150 °C. The measurements were made on the copolymer as such and on two fibers, both as such and after mechanical strain, at 10 °C min^{-1} scanning speed. At the end of each scan, the sample was rapidly quenched, and a second run was carried out at 20 °C min^{-1} in the same temperature range.

---

*Author to whom correspondence should be addressed.

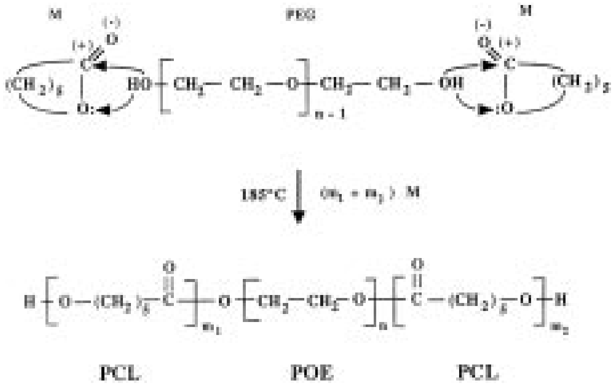

Figure 1 General scheme of reaction for the chemical synthesis of the PCL-POE-PCL block copolymers and composition of the copolymer synthesized. *M* ε-caprolactone; average $(m_1 + m_2)$ 1480; average *n* 790.

2.2. Fiber melt-spinning and mechanical testing

Preliminary melt-spinning tests were carried out by a Mac.gi screw-extruder, having a 1.1 mm strainer and four heating sections with temperatures of 67, 73, 80 and 82 °C, respectively. Just after the extrusion, the thread was drawn between two belts, moving at controlled speed. Five fibers were extruded, using the screw rotations and thread-drawing speeds reported in Table I.

The stress–strain tests were carried out by an Instron 1185 apparatus, with a 10 mm min^{-1} cross-head speed.

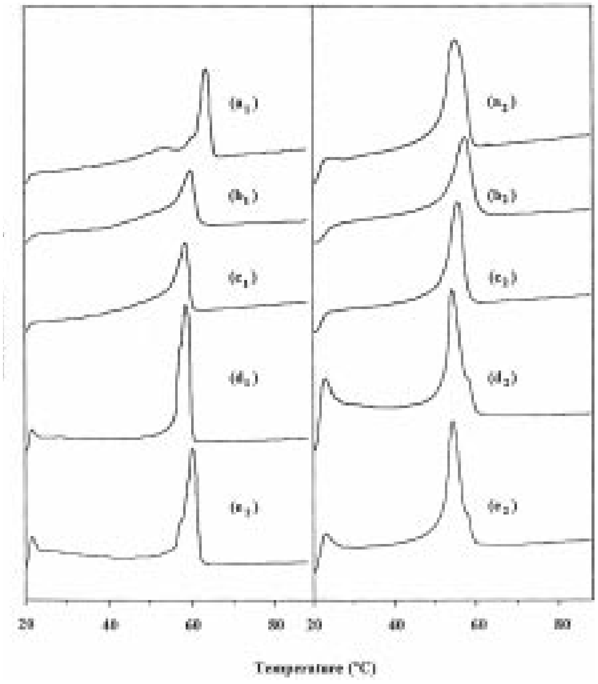

Figure 2 DSC thermograms of the following specimens: (a_1) non-extruded copolymer; (b_1) Fiber 3 in Table I, as such; (c_1) Fiber 5 in Table I, as such; (d_1) Fiber 3 in Table I, after mechanical strain at 10 mm min^{-1} speed; (e_1) Fiber 5 in Table I, after mechanical strain at 10 mm min^{-1} speed. Temperature range 20.00–150.00 °C; scanning speed 10.00 °C min^{-1}. Curves (a_2) to (e_2): the same specimens, second runs after quenching. Temperature range 20.00–150.00 °C; scanning speed 20.00 °C min^{-1}.

3. Results

The copolymer has a number average molecular mass of about 200 000 Da and an average molar composition of 66% oxycaproyl units and 34% oxyethylene units. The DSC analysis of the material shows a non-single endothermic melting peak, having a maximum at 63.7 °C, as shown in Fig. 2, curve (a_1), which becomes a single peak in a second run after quenching, as shown in Fig. 2, curve (a_2).

The mean diameters of the fibers extruded at the same screw rotation diminish with increasing the thread-drawing speed, as shown in Table I. All the fibers show similar behavior in the stress–strain tests, as can be expected for specimens obtained by different extrusion conditions, but made with the same material. The following mechanical properties are typical of all the specimens: yield stress: $16\,\text{MPa} \le \sigma_y \le 20\,\text{MPa}$; deformation at yield: $\varepsilon_y \cong 8\%$; elongation at break: $\varepsilon_r > 300\%$.

Figs 3 and 4 show the typical stress–strain behavior of two fibers, both melt-spun with the screw rotating at 7 r.p.m., which seems to be the speed more suitable for a good extrusion. Fig. 3 shows the behavior of Fiber 3 (see Table I), drawn at a medium speed (1.4 m min^{-1}); Fig. 4 shows the behavior of Fiber 5, drawn at the maximum speed (2.8 m min^{-1}).

The DSC analysis of the fibers shows the structural changes of the materials, induced by extrusion and by mechanical strain. In Fig. 2, (b_1) and (c_1) curves are the DSC thermograms of Fiber 3 and Fiber 5 as such; (d_1) and (e_1) curves are the thermograms of the same fibers after mechanical strain. Curves (b_2) to (e_2) are the thermograms of the same specimens carried out after quenching. The melting peak temperatures and the ΔH values found in the DSC tests are reported in Table II.

4. Discussion

All the results reported show that the characteristics of the material are strongly dependent on its processing. The material is a linear copolymer with long chains of

TABLE I Experimental melt-extrusion conditions and measured mean fiber diameters

Fiber	Screw rotation (r.p.m.)	Thread-drawing speed (m min^{-1})	Mean fiber diameter (mm)
1	2	1.7	0.47
2	7	0.7	0.51
3	7	1.4	0.385
4	7	2.1	0.35
5	7	2.8	0.22

Strainer diameter: 1.1 mm. Temperatures of the heating sections: 67, 73, 80 and 82 °C.

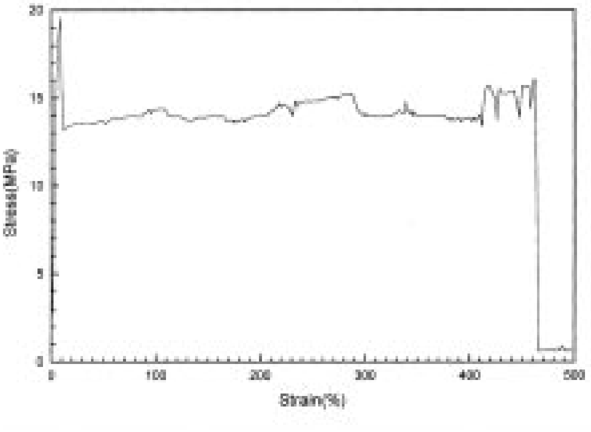

Figure 3 Typical stress–strain behavior for Fiber 3 in Table I.

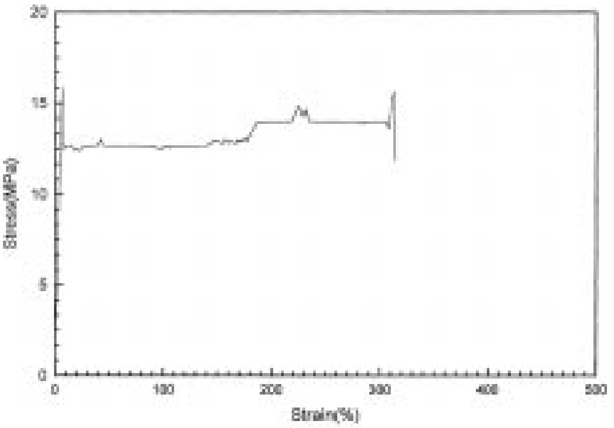

Figure 4 Typical stress–strain behavior for Fiber 5 in Table I.

nearly 13 000 atoms each (see Fig. 1), which can undergo dipole–dipole interactions, which are progressively enhanced as the chains are aligned. A moderate alignment is caused by the drawing of the fibers just after the extrusion, as shown by the diminishing of their mean diameters with increasing thread-drawing speeds (see Table I).

The stress–strain plots show that all the fibers exhibit the typical behavior of a ductile polymer, giving σ_y values varying in quite a short range with the extrusion conditions, a quite constant ε_y and very high elongation at break. Such behavior is likely due to the nature of the material, as well as to the procedure of its extrusion in fibers. The macromolecular chains, having the length and the chemical composition shown in Fig. 1, undergo only ‘‘random’’ dipole–dipole interactions, when arranged in a poorly ordered structure. When the fibers are drawn, an alignment of the macromolecules occurs, so enhancing both the interactions between the chains and the mechanical properties of the material; however, the relatively moderate drawing made just after the extrusion is likely not sufficient to align the macromolecular chains completely. Such a phenomenon makes it impossible to compare our fibers with the commercial suture threads commonly used in surgery, which give much higher strength (450–910 MPa) and much lower elongation (18–30%) values [1, 2, 6].

When the fibers are submitted to the stress–strain test, two subsequent phenomena occur: first, a total alignment of the macromolecular chains; second, the true mechanical strain of the material. This behavior produces the great elongation measured in the test. In Fig. 3 we can see that Fiber 3, drawn at 1.4 m min^{-1}, breaks at $\varepsilon_r \cong 465\%$; in Fig. 4 we can see that Fiber 5, drawn at a double speed, breaks at $\varepsilon_r \cong 310\%$; clearly, such a stronger drawing enhances the alignment of the macromolecules, so reducing the elongation at break.

Such an explanation is well consistent also with the behavior of the non-drawn fibers, made with a PCL-POE-PCL, of similar molecular mass and different $(m_1 + m_2)$ and *n* values (see Fig. 1) than that studied here. Such non-drawn fibers show [4] an elongation at break of about 700%, higher than that shown in Fig. 3.

The calorimetric analysis gives further information about the structure of the material and its modification by extrusion and mechanical strain. As regarding the non-extruded copolymer, in the curve (a_1) of Fig. 2 a weak transition is present before the main melting peak, likely due to the melting of some less ordered crystals. The quenching of the melt causes, as shown by curve (a_2), a rearrangement of the copolymer in a more homogeneous and less crystalline structure; the corresponding T_m and ΔH values, reported in Table II, show that, after quenching, the copolymer structure is on the whole ‘‘less organized’’, with less ordered (lower T_m) and less numerous (lower ΔH) crystals, as expected for a material having the structure and composition shown in Fig. 1. As concerning the two fibers examined, in the DSC thermograms of the fibers as such, a ‘‘shoulder’’ at temperatures lower than the main peak, due to the melting of less ordered crystals, indicates that the crystalline structure is not fully homogeneous. In the curves (d_1) and (e_1), which are the thermograms of the mechanically strained fibers, a sharp melting peak appears; in Table II, the corresponding enthalpies of

TABLE II Main melting peak temperatures (T_m) and enthalpies of fusion (ΔH) from the DSC thermograms in Fig. 2

Sample	First run		Second run after quenching	
	T_m	ΔH	T_m	ΔH
	(°C)	(J g^{-1})	(°C)	(J g^{-1})
(a)	63.7	86.6	55.3	74.6
(b)	58.9	85.1	57.3	53.8
(c)	58.5	84.5	54.3	62.3
(d)	58.5	90.7	55.7	52.8
(e)	60.0	86.9	54.3	60.8

Samples: (a) Non-extruded copolymer; (b) Fiber 3 in Table I, as such; (c) Fiber 5 in Table I, as such; (d) Fiber 3 in Table I, after mechanical strain at 10 mm min^{-1} speed; (e) Fiber 5 in Table I, after mechanical strain at 10 mm min^{-1} speed.

fusion are greater than those of the non-strained fibers, which are not substantially different from that of the copolymer as such. It seems particularly significant that the enhancement of ΔH after mechanical strain is greater for Fiber 3, drawn at $1.4\,\mathrm{m\,min^{-1}}$, than for Fiber 5, drawn at $2.8\,\mathrm{m\,min^{-1}}$, so reflecting the differences in the elongation at break. As regarding the thermograms carried out after quenching, (b_2) and (c_2) curves show only single peaks at lower T_m and ΔH values; on the contrary, (d_2) and (e_2) curves, the ''second run'' thermograms of the mechanically strained fibers, show, after a main peak at lower T_m and ΔH, a ''tail'' at about the same temperature as the unquenched samples. This fact is attributable to some ''crystalline structure memory'', maintained by the strained material also after melting. On the whole, the DSC analysis confirms that the properties of the fibers depend strongly on the alignment of the macromolecules.

5. Conclusions

This study is still preliminary, and further research has to be carried out to ascertain the possibility of using PCL-POE-PCL block copolymers for the fabrication of suture threads.

Both the stress–strain tests and the DSC analysis show the interesting properties of the material; however, they also clearly indicate that the extrusion technique used is not sufficient as such to obtain threads with mechanical properties comparable with those of the commercial sutures. Consequently, the fibers so extruded need a further cold stretch at controlled speed, to align completely the macromolecules; alternatively, we could experiment with some different extrusion technique.

The investigation for a fiber fabrication technique able to obtain threads, having the best mechanical properties related to the copolymer structure, is still in progress. However, the most promising aspect of this research is the possibility, if such a technique were found, of producing suture threads with different bioresorption times, simply by varying the relative lengths of the polyether and polyester blocks of the same copolymer [3].

References

1. S. VANIONPÄÄ, P. ROKKANEN and P. TÖRMÄLÄ, *Prog. Polym. Sci.* **14** (1989) 679.
2. P. TÖRMÄLÄ, T. POHJONEN and P. ROKKANEN, *Proc. Instn. Mech. Engrs. Part H* **212** (1998) 101.
3. R. SBARBATI DEL GUERRA, C. CRISTALLINI, N. RIZZI, R. BARSACCHI, G. D. GUERRA, M. TRICOLI and P. CERRAI, *J. Mater. Sci.: Mater. Med.* **5** (1994) 891.
4. P. CERRAI, G. D. GUERRA, L. LELLI, M. TRICOLI, R. SBARBATI DEL GUERRA, M. G. CASCONE and P. GIUSTI, *ibid.* **5** (1994) 33.
5. R. SBARBATI DEL GUERRA, P. GAZZETTI, G. LAZZERINI, P. CERRAI, G. D. GUERRA, M. TRICOLI and C. CRISTALLINI, *ibid.* **6** (1995) 824.
6. D. P. MUKHERJEE, in ''Encyclopedia of polymer science and engineering'', 2nd edn, edited by H. F. Mark, N. M. Bikales, C. G. Overberger and G. Menges (J. Wiley & Sons, New York, 1985–1989) vol. 16, p. 473.

Received 1 December 1998
and accepted 9 April 1999