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Investigations of the properties of blockpolymerized and injection-moulded PLLA

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The blockpolymerization and injection-moulding procedure are two main techniques used to produce PLLA for medical devices. Until now there has been no comparison of the well known data of blockpolymerized material and data of injection-moulded material. Test rods (2 × 3 × 25 mm) were made from block polymerized balls by the injection-moulding procedure. The rods were incubated in tris-buffer-saline for different periods (0, 2, 4, 6, and 8 weeks) at a pH of 7.4 and a temperature of 37 °C. The test methods we used were the three-point-bending, the fatigue behaviour and the calculation of the decrease of molecular weight. Both materials under investigation are chemically similar but show very different mechanical properties, in particular the injection moulded material has a very decreased behaviour and a very low loss of molecular weight. Blockpolymerized PLLA rods show a very fast lost bending strength and after 6 weeks a low resistance against cyclic loads in the fatigue behaviour test. Injection moulded PLLA will be used in future for internal fixation of fractures.

1. Introduction

In orthopedics and traumatology the use of PLLA as a material for internal fixation of fractures or reconstructive operation is of great importance [1, 2]. The well-known requirements for the use of polymers in medicine are satisfactorily fulfilled by PLLA.

Investigations of this material have mostly been carried out with blockpolymerized material. Now the difficult injection moulding procedure is available and will be the standard procedure in future. Until now there has been no comparison of the well-known data of blockpolymerized material and the newly gained data of injection moulded material.

2. Material and methods

Test rods ($2 \times 3 \times 25\ mm^3$) were made from blockpolymerized balls (blockpolymerized PLLA = BP) with cutting tools under compressed air cooling (Jugenddorf in Köln-Frechen (Bachem)). The injection moulding procedure was carried out by an injection moulding machine (Klöckner Ferromatik Desma FX 25). A special tool was constructed as shown in Fig. 1 in order to produce PLLA with high (IMH) and low (IML) molecular orientation, respectively [4]. Altogether 400 test rods ($2 \times 3 \times 25\ mm^3$) were tested. The test rods were incubated in tris-buffer-saline (0.1 M) for different periods (0, 2, 4, 6, and 8 weeks). All the solutions had a pH of 7.4, a temperature of 37 °C and were renewed after 48 h.

The three-point bending test was carried out on a computerized test machine (UTS 10). With a force-controlled traverse of 2 N/s and a span of 20 mm the rods were bent to their breakpoint or to a maximum deflection of 6 mm. An integrated computer calculated the bending strength, deflection, and modulus of elasticity.

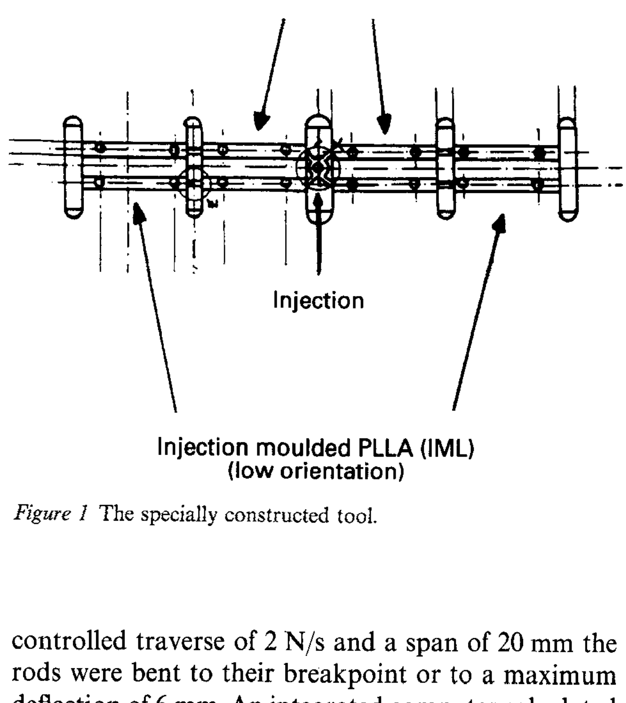

Figure 1 The specially constructed tool.

The fatigue behaviour was tested with a test machine especially constructed for this purpose (Fig. 2). Eleven test rods were stressed simultaneously under a cyclic rectangular flexural stress in an aqueous solution at 37 °C. At a frequency of 1 Hz the number of stress cycles was registered by a counter until the

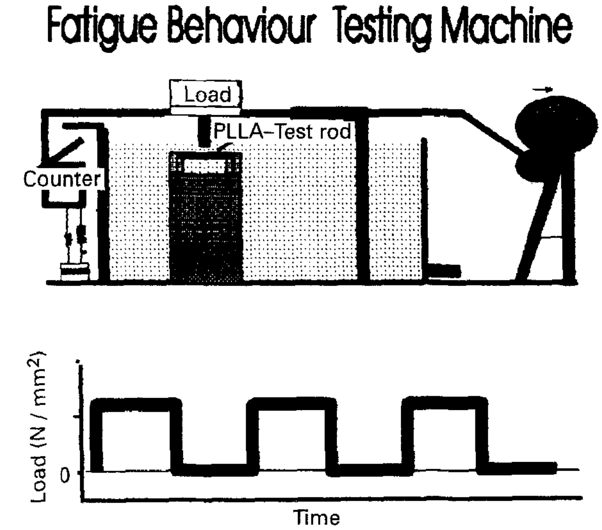

Figure 2 Fatigue behaviour testing machine.

break. The span was 20 mm and four different stresses were adjusted by strain gauge technique (Hottinger Baldwin). First, 35 and 30 N/mm^2 stresses were used, and after 6 weeks the stresses were changed to 25 and 12.5 N/mm^2 because of loss in stability. The analysis of the decrease in molecular weight was carried out by Fa. Boehringer Ingelheim KG [6] by measurement of intrinsic viscosity, and calculations using the Mark–Houwink equation:

$$[n] = K * M^{a}_{(\text{vis})}$$

$k = 1.29*10^{-4}$ dl/g, $c = 0.1$ g/dl (polymer in chloroforme), $a = 0.82$
Juggenddorf in Köln-Frechen (Bachem)

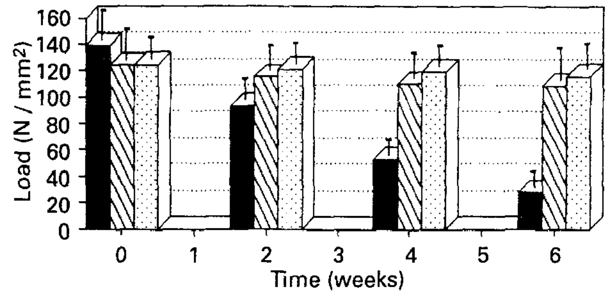

Figure 3 Bending strength (■ BP; □ IML; □ IMH).

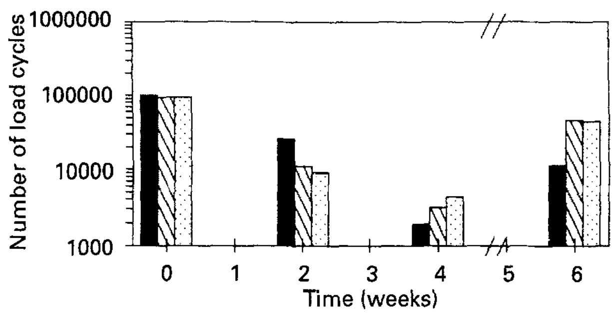

Figure 4 Fatigue behaviour (■ BP; □ IML; □ IMH).

3. Results

The results are shown in Tables I to III.

4. Discussion

The two materials (blockpolymerized and injection moulded) under investigation are chemically similar

TABLE I Bending strength, N/mm^2 ([standard deviation]; (n))

Material	0	Time 2 weeks	4 weeks	6 weeks	8 weeks
BP	139.12 [11.80] (20)	93.52 [9.09] (15)	52.36 [6.93] (15)	27.89 [5.33] (15)	20.92 [1.69] (15)
IML	124.58 [15.56] (20)	115.72 [14.48] (15)	110.12 [12.03] (15)	108.99 [19.91] (15)	114.2 [10.70] (15)
IMH	124.78 [10.79] (20)	121.38 [8.24] (15)	119.40 [8.25] (15)	115.79 [13.31] (15)	108.38 [11.53] (15)

[(BP 8 W.: 20.92 [1.69] (15); IML 8 W.: 114.2 [10.70] (15); IMH 8 W.: 108.38 [11.53] (15)]

TABLE II Modulus of elasticity, kN/mm^2 ([standard deviation]; (n))

Material	0	Time 2 weeks	4 weeks	6 weeks	8 weeks
BP	3.19 [0.37] (20)	2.79 [0.24] (15)	2.72 [0.20] (15)	2.72 [0.39] (15)	2.37 [0.36] (15)
IML	2.61 [0.19] (20)	2.56 [0.17] (15)	2.52 [0.18] (15)	2.46 [0.16] (15)	2.54 [0.19] (15)
IMH	2.81 [0.16] (20)	2.65 [0.15] (15)	2.65 [0.13] (15)	2.59 [0.15] (15)	2.73 [0.13] (15)

(BP 8 W.: 2.37 [0.36] (15); IML 8 W.: 2.54 [0.19] (15); IMH 8 W.: 2.73 [0.13] (15))

TABLE III Fatigue behaviour, stress cycles ([standard deviation]; (n))

Material		Time and stress		
	$t = 0$ 30 N/mm^2	2 weeks 30 N/mm^2	4 weeks 30 N/mm^2	6 weeks 12.5 N/mm^2
BP	100000 [0] (20)	26458 [8149] (11)	1918 [309] (11)	11095 [2580] (11)
IML	92476 [9282] (13)	10991 [3462] (12)	3112 [939] (12)	47481 [6170] (6)
IMH	93183 [9342] (12)	9098 [4180] (12)	4328 [1028] (7)	44666 [9213] (12)
		Time and stress		
	$t = 0$ 35 N/mm^2	2 weeks 35 N/mm^2	4 weeks 35 N/mm^2	6 weeks 25 N/mm^2
BP	100000 [0] (20)	20374 [3120] (10)	624 [366] (10)	1000 [627] (10)
IML	87152 [11354] (20)	6485 [2917] (10)	895 [199] (10)	9051 [1460] (10)
IMH	84677 [14169] (20)	7278 [1877] (10)	1094 [235] (10)	9582 [4076] (10)

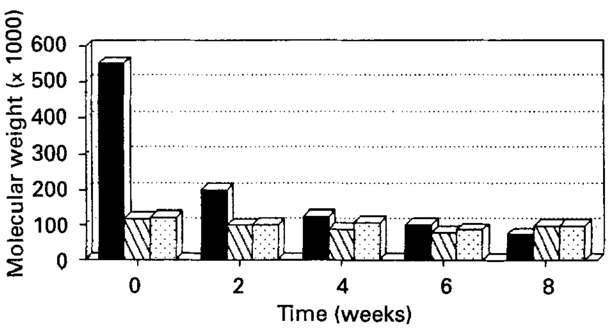

Figure 5 Molecular weight (■ BP; □ IML; □ IMH).

but show very different mechanical properties, in particular the injection moulded material has a very decreased degradation behaviour (Figs 3–5). Also the initial molecular weight is about 30% of the block-polymerized material (Fig. 5). After 6 weeks the block-polymerized PLLA had nearly the same molecular weight as the injection moulded PLLA, but a great difference in stability.

The difference between the high and low orientated injection moulded material is only 5.17 N/mm^2 but this is significant (MANOVA, $p = 0.001$). This will have vast clinical consequences. Undoubtedly, injection moulded material of high molecular weight and of high orientation will soon be available for internal fixation. The exact extent of degradation (i.e. complete or incomplete) remains to be studied.

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