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Strength retention of self-reinforced poly-L-lactide screws. A comparison of compression moulded and machine cut screws

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The effect of the manufacturing method on the strength retention of self-reinforced poly-L-lactide (SR-PLLA) screws was studied *in vitro* and *in vivo* from 3 up to at least 15 weeks. SR-PLLA screws were manufactured from axially oriented SR-PLLA billets by the conventional compression moulding process and an in-house developed machine cutting technique. New machined SR-PLLA screws (thread diameters 4.5 mm and 3.5 mm) were significantly stronger than older compression moulded SR-PLLA screws (4.5 mm and 3.5 mm) in bending and torque strength tests but significantly weaker in shear strength tests. In pull out tests there were not significant strength differences between the screws. Mechanical analysis and molecular weight measurements confirmed earlier observations that SR-PLLA degrades faster *in vivo* than *in vitro*. These results suggest that the new screws could be suitable for clinical use.

1. Introduction

Compression moulded SR-PLLA screws have been in clinical use in the fixation of ankle fractures at our department since 1988 [1] and have also been extensively studied experimentally [2, 3, 4, 5, 6]. SR-PLLA screws have also been used in the fixation of talocrural arthrodesis [7] and subtalar arthrodesis in children [8] as well as in mandibular condyle osteotomies in sheep [4]. Other authors have described the use of PLA screws in ankle fractures [9, 10] and other fixations [11] but, after mechanical tests, not in horses [12]. Bending and shear strengths of our clinically used compression moulded SR-PLLA screws (Biofix®, Bioscience Ltd, Finland) have not caused any problems in surgery and observation of postoperative clinical courses has shown uneventful healing. However, the lower torque strength of SR-PLLA screws in comparison with metallic screws has necessitated a careful so-called pinch-grip operative technique for the introduction of these screws.

In this study, the mechanical properties of SR-PLLA screws produced by a new manufacturing technique are presented and compared with clinically used compression moulded SR-PLLA screws.

2. Materials and methods

2.1. Manufacturing of implants

Commercial medical grade poly-L-lactide (PURAC biochem b.v., The Netherlands) was used for the manufacture of the screws. Specific details of the raw polymer given in the manufacturer's certificate of analysis are as follows: batch number DB 257 AK, intrinsic viscosity 9.7 and molecular weight 664 000 (according to dilution viscosity in chloroform at 25 °C). Weight and number average molecular weights according to GPC (gel permeation chromatography) analysis were 2 449 000 and 1 813 000, respectively. Specific rotation was − 157° (in chloroform at 25 °C). DSC melting range was 171.6–182.2 °C and heat of fusion was 49.7 J/g. Residual solvent content was 0.03 %.

In order to prevent extensive thermal degradation during processing, water and air were removed from PLLA by vacuum drying at 110 °C and 2 mbar for 1 day. The material was subsequently extruded into cylindrical billets in the melted state which was followed by hot solid-state axial orientation (self-reinforcing) in a die-drawing process. During draw, the extension ratio was adjusted to transform the spherulitic crystalline structure partially or completely into a fibrillar structure [13]. The PLLA billets used for the manufacture of SR-PLLA screws by the new machine cutting technique were partially fibrillated after uniaxial extension by 400%. The material used for the manufacture of old type SR-PLLA screws by the conventional compression moulding process was completely fibrillated after uniaxial extension by 700%. The difference of microstructures between the screws can be seen from scanning electron microscopy

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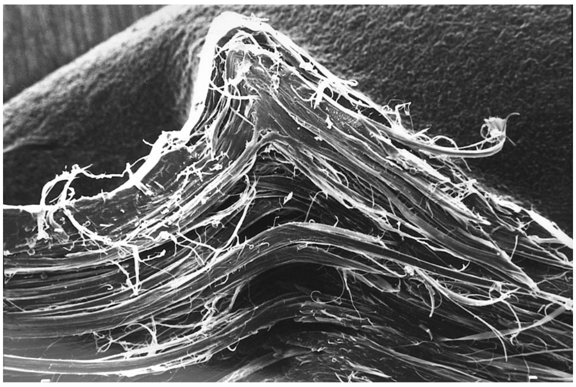

Figure 1 SEM micrograph of the fibre structure at the thread of the compression moulded SR-PLLA screw with thread diameter of 4.5 mm showing the orientation of fibrils according to the shape of the thread. Origitnal magnification 100x.

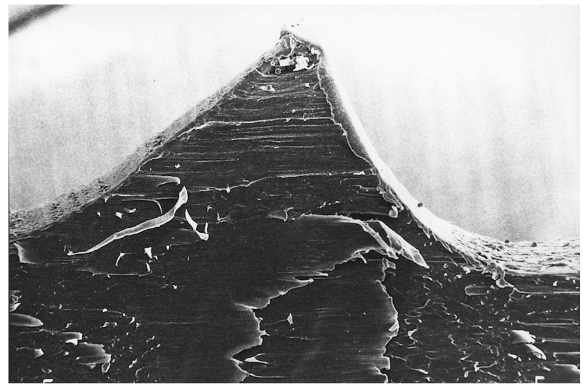

Figure 3 SEM micrograph of the fibre structure at the thread of the turning cut SR-PLLA screw with thread diameter of 4.5 mm showing the parallel orientation of fibrils to the long axis of the screw. Original magnification 100x.

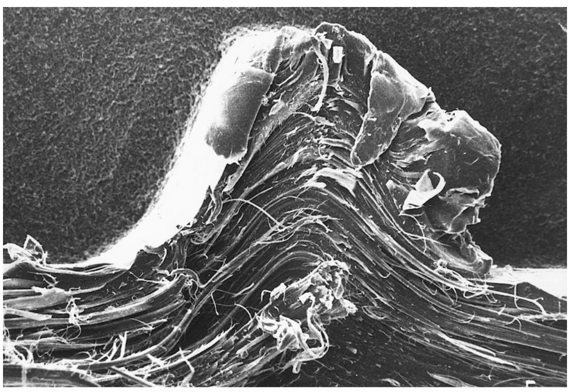

Figure 2 SEM micrograph of the fibre structure at the thread of the compression moulded SR-PLLA screw with thread diameter of 3.5 mm showing the orientation of fibrils according to the shape of the thread. Original magnification 100x.

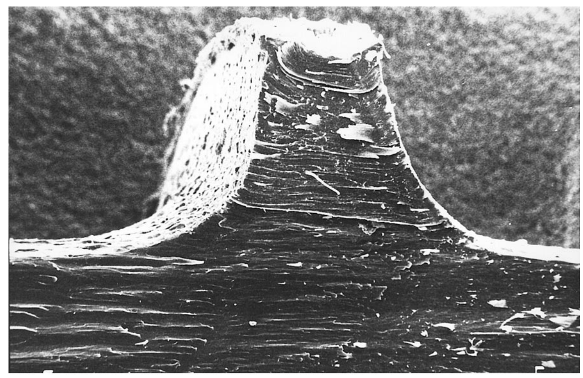

Figure 4 SEM micrograph of the fibre structure at the thread of the turning cut SR-PLLA screw with thread diameter of 3.5 mm showing the parallel orientation of fibrils to the long axis of the screw. Original magnification 100x.

(SEM) micrographs (Figs. 1 and 2, completely fibrillated structure; Figs. 3 and 4, partially fibrillated structure). The maximum thread diameter of the screw was 4.5 mm and the core diameter was 3.5 mm in the first group (Fig. 1). The length of the screws were 50 mm (threadportion and head) in the bending test and 50 mm (threadportion) in pull out test. In the second group, the thread diameter of the screw was 3.5 mm and the core diameter was 2.5 mm. The geometry of the thread (Fig. 2) was also different from that of the first group. The length of the samples were the same as those in the first group.

All screws were sterilized by gamma irradiation at a minimum dose of 25 kGy (actual dose 1.4–1.6 times the specified minimum, Kolmi-Set Ltd, Finland).

2.2. Degradation *in vitro*

The SR-PLLA screws were immersed in NaOH (1.6 g/l)–KH_2PO_4 (6.8 g/l) buffered saline (NaCl 0.9 g/l) at pH 7.4 and 0.24 M and kept at 37 °C. Screw samples were removed at 3, 6, 9, 15 and 26 weeks and changes in mechanical and thermal properties and molecular weight were determined.

2.3. Experimental animals and surgical technique for *in vivo* studies

22 adolescent New Zealand male rabbits with an average weight of 2.6 kg (range 2.4–3.0 kg) were used as experimental animals. They were given 30 min subcutaneous atropin (Atropin®, Finland) 0.5 mg/kg preoperatively as premedication and anesthetized subcutaneously with medetomidine (Domitor®, Finland) 0.3 mg/kg and ketamine hydrochloride (Ketalar®, Parke-Davis, Spain) 30 mg/kg. Intramuscular kefuroxim (Zinacef®, Glaxo, UK) 50 mg/kg was given as a prophylactic measure against infection. They also received methylcellulos (Oftan-MC®, Leiras, Finland) eyedrops to prevent ocular conjuctival drying.

The back skin was shaved and scrubbed with antibacterial and antifungal 60% isopropanol solution (Neo-Amisept®, Lääkefarmos, Finland) and straight incisions were made on the both sides of spine. The first 10 screws were implanted on the left side of the back and 10 on the right side. This proved to be too many, often causing spontaneous perforation of the back skin; later, 5–6 screws were implanted on each side without any problems. After implantation the wound was closed in layers with absorbable 3-0 polyglycolide sutures (Dexon®, Davis & Greek, UK).

Follow-up intervals were 3, 6, 9, 15, and 26 weeks. At removal of screws the rabbits were killed with an overdose of intravenous sodium pentobarbital (Mebunat®, Orion, Finland). The screws were carefully removed, transferred into saline solution and tested wet within 24 h.

2.4. Strength measurements

The bending strength of the intact SR-PLLA screws before and after *in vitro* and *in vivo* exposure were measured by the three-point bending method (Fig. 5), using a Lloyd 6000R Materials Testing Machine (Lloyd Instruments PLC, U.K.) at room temperature (22–23 °C). At least three samples of each screw size and manufacturing method were tested. The measurements were performed on wet samples because drying of the incubated screws led to a decrease in strength. The support spans and the cross-head speeds were 42 mm and 10 mm/min for ∅ 4.5 mm screws and 32 mm and 5 mm/min for ∅ 3.5 mm diameter screws. The radius of the loading nose was 5 mm and the radius of each support was 1.5 mm. The bending strength was calculated using the following equation

$$\sigma_b = \frac{8 \cdot F_{\max} \cdot L}{\pi \cdot d^3}$$

where σ = bending strength (MPa), $F_{\max}$ = maximum bending force (N), L = support span (mm) and d = inner diameter of the screw (mm).

The shear strength of the SR-PLLA screws before and after *in vitro* and *in vivo* exposure was measured by means of a tool constructed by modifying the standard BS (British Standard) 2782, Method 340 B (1978). The tool consisted of two parts which were joined together by the implant (Fig. 6a). The parts were pulled apart during the test using a Lloyd 6000R Materials Testing Machine operating at a cross-head speed of 10 mm/min, such that the implant resting in a drillhole was cut into pieces perpendicular to the long axis of the screw (Fig. 6b). The shear strength was calculated using the following equation

$$\tau_s = \frac{2 \cdot F_{\max}}{\pi \cdot d^2}$$

where τ_s = shear strength (MPa), $F_{\max}$ = maximum force recorded (N) and d = inner diameter of the screw (mm).

The torque strength of the SR-PLLA screws before and after *in vitro* and *in vivo* exposure was measured by means of the tool shown in Fig. 7. The tip of the screw was fixed to a stationary grip while the head of the screw was turned by Biofix® screwdriver fixed to a rotating grip. The torque was transmitted to the screwdriver by means of a rotating wheel and driveshaft mounted to a bearing stand. The test device was installed to a Lloyd 600R Materials Testing Machine and the rotating wheel was turned at a rate of 0.2 r/min by means of a chain attached to the load cell. The load pulling the chain was recorded and used for the calculation of the torque strength according to the equation

$$\tau_t = \frac{16 \cdot F_{\max} \cdot R}{\pi \cdot d^3}$$

where τ_t = torsion strength (MPa), $F_{\max}$ = force at yield (N), (approx. rotation 45°), R = radius of the rotating wheel = 40 mm and d = inner diameter of the screw (mm).

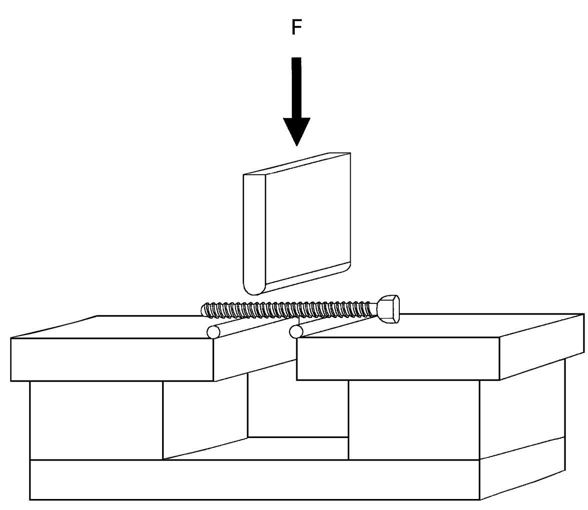

Figure 5 The testing arrangements for the bending strength of SR-PLLA screws.

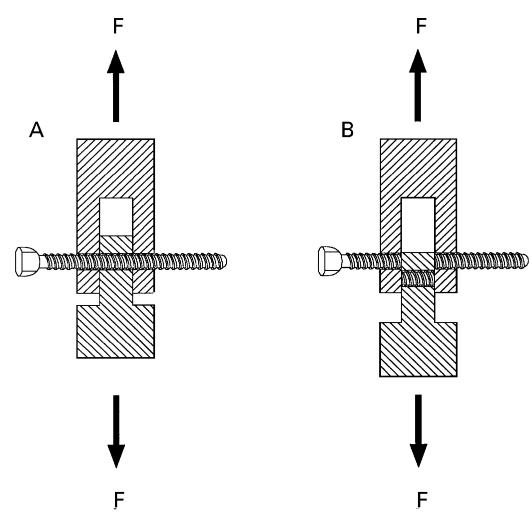

Figure 6 The testing arrangements for the shear strength of SR-PLLA screws.

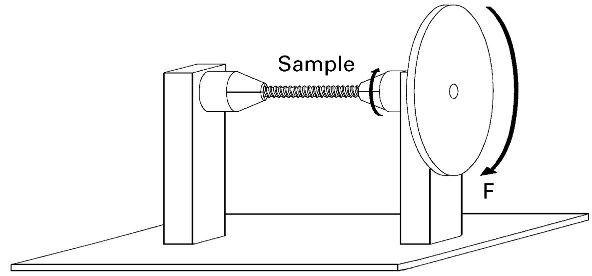

Figure 7 The testing arrangements for the torsional strength of SR-PLLA screws.

The pull out strength of SR-PLLA screws before and after *in vitro* and *in vivo* exposure was measured using the arrangement shown in Fig. 8. In this test, the tip of the screw was turned as deep as three pitches of thread into a tapped jaw mounted into a Lloyd 6000R Materials Testing Machine. The screw was then fixed by the head to the load cell and pulled out at a rate of 10 mm/min. The maximum load to break and the type of fracture were recorded. In most instances, the tensile load carrying capacity of both the screw head and the cross section exceeded that of the three pitches of thread which were cut away.

The arrangement of the tensile test of the screw head was similar to the pull out test except that the screw was turned deeper into the jaw (Fig. 9) such that the load carrying capacity of the thread always exceeded that of the screw head and the cross section. The maximum load to break and the type of fracture were again recorded. In most cases, tensile failure of the cross section occurred. In some cases the head of the screw came off.

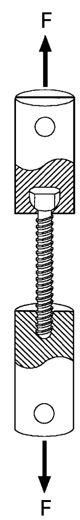

Figure 8 The testing arrangements for the pull out test of SR-PLLA screws.

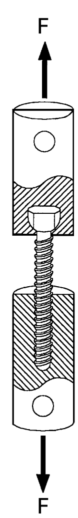

Figure 9 The testing arrangements for the tensile test of the Biofix® screw head.

2.5. Thermal analysis and molecular weight measurements

A DSC-7 differential scanning calorimeter (Perkin–Elmer Co., U.S.A.), calibrated with indium standards, was used to determine the heat of fusion of SR-PLLA screws before and after *in vitro* and *in vivo* exposure. The calorimeter was operated at a heating rate of 20 °C/min. Dry 6 ± 1 mg samples evacuated at room temperature for 3 days were used in each case. The samples were heated in a nitrogen atmosphere from room temperature to 220 °C (about 40 °C above melting temperature to assure melting of all crystallites) and the heat of fusion was estimated from the area enclosed by the calorimeter curve and the baseline [14]. The level of crystallinity was estimated from the heat of fusion, using the figure 93.7 J/g calculated by Fischer *et al.* [15] for perfectly crystalline PLLA. Triplicate samples were used in each case.

The solution viscosities (according to ASTM (American Society for Testing and Materials) 445-88) of SR-PLLA screws before and after *in vitro* and *in vivo* exposure were measured in chloroform at 25 °C with an Ubbelohde capillary viscometer (type 0a according to ASTMD 446). Intrinsic viscosities (η in dl/g) were obtained by linear regression analysis from dilution series (0.1 g/dl, 0.2 g/dl, 0.3 g/dl and 0.5 g/dl) and viscosity-average molecular weights (in g/mol) were calculated using the Mark–Houwink equation and parameters determined by Schindler *et al.* [16]:

$$[\eta] = 5\cdot 45 \times 10^{-4} \cdot M_V^{0\cdot 73}.$$

where $[\eta]$ = intrinsic viscosity (dl/g).

3. Results

The results of the strength measurements are given in tables I–VIII. Machine cut SR-PLLA screws (∅ 4.5 mm and ∅ 3.5 mm) were significantly stronger than older compression moulded SR-PLLA screws (∅ 4.5 mm and ∅ 3.5 mm) in bending and torque tests but significantly weaker in shear tests. In pull out tests there were no significant differences between the screws; however, new machine cut screws were stronger than the older ones in the first group (∅ 4.5 mm). Conversely older type screws were stronger in the second group (∅ 3.5 mm). The results of the tensile test of the screw head did not show differences between the two different screw types. The screws placed *in vivo* showed a faster loss of strength than the screws embedded in the phosphate buffer.

The results of the molecular weight measurements are given in tables IX and X. Although high molecular weight PLLA raw polymer (M_v 664 000) was used for processing of the SR-PLLA screws, the molecular weight of intact screws after gamma irradiation ranged from 43 700 to 61 500. Due to thermal degradation during melt processing the molecular weight decreased to 200 000–250 000 ($\sim$ 38% of initial value). A further decrease in molecular weight took place during compression moulding; however, the most significant decrease took place in gamma irradiation ($\sim$ 8% of initial M_v and $\sim$ 23% of M_v after melt processing). Although machining had no effect on

TABLE I Bending strength (MPa). Variance analysis of the 4.5 mm screws.

In vitro		mean and SD					In vivo		mean and SD				
Weeks	N	Machine cut	N	Compression moulded	N	Total	Weeks	N	Machine cut	N	Compression moulded	N	Total
0	3	243.6	3	190.0	6	216.8	0	3	223.5	3	176.9	6	220.2
		5.8		2.7		29.6			4.1		7.1		26.1
3	3	226.1	3	188.6	6	207.4	3	3	215.5	3	211.2	6	213.4
		3.2		2.9		20.7			2.2		1.9		3.0
6	2	228.4	3	182.5	5	200.8	6	3	222.9	3	178.8	6	200.9
		7.3		5.1		25.6			1.3		7.2		24.6
9	3	232.0	3	189.6	6	209.4	9	3	211.2	3	161.3	6	186.3
		6.3		4.3		25.2			1.1		1.0		27.4
15	3	198.1	3	159.7	6	178.9	15	3	184.0	3	116.5	6	150.3
		3.1		4.7		21.4			13.1		10.0		38.4
26	3	177.6	3	126.2	6	151.9	26	3	77.2	2	30.7	5	58.6
		2.6		8.8		28.8			27.0		3.5		31.9
	17	217.0	18	172.3	35	194.0		18	189.1	17	152.7	35	171.4
		24.1		24.1		32.8			54.3		55.0		56.9

ANOVA horizontal:
T-test: t = 5.490, d.f. = 33
F-test 643.0, d.f. 1; 21 ($p < 0.001$)
HSD 5% = 4.460, HSD 1% = 5.781

ANOVA vertical:
F-test 65.7, d.f. 5; 21 ($p < 0.001$)
HSD 5% = 14.64, HSD 1% = 17.79

Interaction
F-test 2.627, d.f. 10; 21 ($p < 0.05$)

ANOVA horizontal:
F-test 107.0, d.f. 1; 21 ($p < 0.001$)
HSD 5% = 8.902, HSD 1% = 11.537

ANOVA vertical:
F-test 81.7, d.f. 5; 21 ($p < 0.001$)
HSD 5% = 29.22, HSD 1% = 35.51

Interaction
F-test 7.208, d.f. 10; 21 ($p < 0.001$)

HSD = Tukey's Honestly Significant Difference

TABLE II Shear strength (MPa). Variance analysis of the 4.5 m screws.

In vitro		mean and SD					*In vivo*		mean and SD				
Weeks	N	Machine cut	N	Compression moulded	N	Total	Weeks	N	Machine cut	N	Compression moulded	N	Total
0	3	146.8	3	156.0	6	151.4	0	3	148.5	3	161.1	6	155.3
		4.3		3.3		6.1			5.8		7.3		9.5
3	3	143.1	3	163.5	6	153.3	3	3	132.9	3	162.4	6	147.6
		0.6		7.0		12.0			6.4		2.6		16.7
6	2	138.5	3	159.6	5	151.2	6	3	138.2	3	161.0	6	149.6
		4.7		8.0		13.1			2.0		5.5		13.0
9	3	147.1	3	163.3	6	155.2	9	3	137.0	3	158.2	6	147.6
		4.7		1.8		9.4			9.3		4.2		13.3
15	3	134.7	3	152.1	6	143.4	15	3	115.9	3	118.4	6	117.2
		2.5		2.1		9.8			3.2		2.9		3.1
26	3	142.7	3	147.4	6	145.1	26	3	28.5	3	32.4	6	30.5
		7.6		4.0		6.0			10.3		8.0		8.5
	17	142.4	18	157.0	35	149.9		18	116.8	18	132.4	36	124.6
		5.9		7.3		9.9			42.3		48.9		45.8

ANOVA horizontal:
T-test: t = 6.466, d.f. = 33
F-test 75.0, d.f. 1; 21 ($p < 0.001$)
HSD 5% = 4.272, HSD 1% = 5.537

ANOVA vertical:
F-test 2.6, d.f. 5; 21 ($p < 0.05$)
HSD 5% = 14.02, HSD 1% = 17.04

ANOVA horizontal:
F-test 52.2, d.f. 1; 22 ($p < 0.001$)
HSD 5% = 5.460, HSD 1% = 7.076

ANOVA vertical:
F-test 165.5, d.f. 5; 22 ($p < 0.001$)
HSD 5% = 17.92, HSD 1% = 21.78

HSD = Tukey's Honestly Significant Difference

M_v, the molecular weight of the PLLA in the new type screws was slightly higher. The screws placed *in vivo* showed a faster decrease in M_v, confirming the results of mechanical analysis of faster degradation kinetics *in vivo*. There were no significant differences between the molecular weight loss of the two different screw types.

The results of crystallinity measurements by calorimeter are given in tables XI and XII. The measurements revealed an increase in crystallinity of SR-PLLA by 10–14% over time. There were no significant differences between the crystallinities of the two different screw types.

TABLE III Torsional strength (MPa). Variance analysis of the 4.5 mm screws

In vitro	mean and SD						In vivo	mean and SD					
Weeks	N	Machine cut	N	Compression moulded	N	Total	Weeks	N	Machine cut	N	Compression moulded	N	Total
0	3	61.9	3	36.0	6	48.9	0	3	60.5	3	29.6	6	45.1
		0.5		4.8		14.5			1.7		2.3		17.0
3	3	46.5	3	17.6	6	32.1	3	3	48.6	3	26.3	6	37.5
		5.6		5.3		16.5			2.6		2.2		12.4
6	3	39.4	3	15.5	6	27.4	6	3	43.6	3	25.7	6	34.6
		3.2		2.0		13.3			1.6		7.9		11.1
9	3	46.6	3	28.6	6	37.6	9	3	44.3	3	22.6	6	33.4
		2.6		2.3		10.1			0.8		1.8		12.0
15	3	32.9	3	14.2	6	23.5	15	3	35.0	3	16.5	6	25.7
		4.4		10.3		12.5			4.4		0.7		10.5
	15	45.5	15	22.4	30	33.9		15	46.4	15	24.1	30	35.3
		10.5		10.0		15.5			8.9		5.6		13.5

ANOVA horizontal:
T-test: t = 6.163, d.f. = 28
F-test 137.3, d.f. 1; 16 ($p < 0.001$)
HSD 5% = 5.410, HSD 1% = 7.348

ANOVA vertical:
F-test 8.1, d.f. 4; 16 ($p < 0.01$)
HSD 5% = 18.31, HSD 1% = 23.58

ANOVA horizontal:
T-test: t = 8.191, d.f. = 28
F-test 276.1, d.f. 1; 16 ($p < 0.001$)
HSD 5% = 3.678, HSD 1% = 4.996

ANOVA vertical:
F-test 8.7, d.f. 4; 16 ($p < 0.01$)
HSD 5% = 12.45, HSD 1% = 16.03

HSD = Tukey's Honestly Significant Difference

TABLE IV Pull out tests (MPa). Variance analysis of the 4.5 mm screws

In vitro	mean and SD						*In vivo*	mean and SD					
Weeks	N	Machine cut	N	Compression moulded	N	Total	Weeks	N	Machine cut	N	Compression moulded	N	Total
0	2	789.3	3	964.3	5	894.3	0	3	871.3	3	657.9	6	764.6
		71.8		166.8		156.2			66.2		128.7		148.4
3	3	1014.1	3	957.0	6	985.6	3	3	678.0	2	614.6	5	652.6
		34.6		136.9		94.6			105.8		103.0		97.3
6	3	914.0	2	876.9	5	899.1	6	1	849.9	1	856.0	2	853.0
		144.1		4.6		103.9			–		–		4.3
9	2	826.8	3	803.6	5	812.9	9	2	711.9	2	697.9	4	734.9
		261.9		44.8		135.3			32.1		82.9		66.8
15	3	680.4	3	752.4	6	716.4	15	3	373.6	2	353.5	5	365.5
		112.1		20.1		82.1			67.7		19.1		50.1
26	2	690.1	2	582.7	4	636.4							
		42.1		136.2		103.0							
	15	829.2	16	834.4	31	831.9		12	680.2	10	616.2	22	651.1
		164.1		156.1		157.3			208.6		171.6		191.0

ANOVA horizontal:
F-test 0.014, d.f. 1; 17 (ns)

ANOVA vertical:
F-test 2.7, d.f. 5; 17 (ns)

ANOVA horizontal:
F-test 1.937, d.f. 1; 8 (ns)

ANOVA vertical:
F-test 5.2, d.f. 5; 8($p < 0.01$)
HSD 5% = 425.40,HSD 1% = 547.70

HSD = Tukey's Honestly Significant Difference

4. Discussion

Research into and clinical use of absorbable implants and screws have increased rapidly during the past decade. In spite of this, the literature concerning the mechanical properties of the screws used and the clinical results has been limited. The initial strength values of self-reinforced polyglycolide implants were higher than those of SR-PLLA implants, but the values of strength retention were lower [13, 16]. In experimental studies PLA screws were comparable with the metallic screws histologically [17] and biomechanically [18].

Although the shear and bending strengths of SR-PLLA screws are acceptable for the treatment of certain types of bone fractures [1, 7, 8], the torque strength is lower than that of metallic ones. SR-PLLA has excellent shear and bending strengths, which increase almost linearly as a function of draw ratio, but the torque strength starts diminishing after a certain draw ratio when the structure becomes fully fibrillated. The purpose of this study was to develop a manufacturing method which would optimize the strength and productivity of SR-PLLA screws. The results showed that the new manufacturing method

TABLE V Bending strength (MPa). Variance analysis of the 3.5 mm screws

In vitro	mean and SD							*In vivo*	mean and SD						
Weeks	N	Machine cut	N	Compression moulded	N	Total		Weeks	N	Machine cut	N	Compression moulded	N	Total
0	6	221.5	3	140.0	9	194.4		0	6	219.1	3	140.1	9	192.7
		31.0		8.9		47.8				14.2		2.7		41.1
3	5	222.4	3	139.7	8	191.4		3	6	232.3	3	143.0	9	202.5
		23.3		11.4		46.7				27.4		14.6		50.1
6	6	219.8	3	130.9	9	190.2		6	6	184.8	3	111.5	9	160.4
		21.9		3.9		47.8				18.5		0.5		39.4
9	6	222.7	3	143.9	9	196.4		9	6	200.1	3	107.7	9	169.3
		19.1		4.0		42.2				16.8		4.6		48.1
15	6	217.2	3	126.3	9	186.9		15	6	136.9	3	73.7	9	115.8
		21.1		4.1		48.4				23.6		10.6		37.1
26	6	191.0	3	91.3	9	157.7		26	2	99.7	3	29.2	5	57.4
		25.5		7.0		53.9				4.2		1.9		38.7
52	6	18.4	3	14.2	9	17.0								
		6.9		1.8		5.9								
	41	186.7	21	112.3	62	161.5			32	188.7	18	100.9	50	157.1
		74.3		44.7		74.4				44.2		41.1		60.3

ANOVA horizontal:
F-test: 179.7, d.f.1; 41 ($p < 0.001$)
HSD 5% = 12.777, HSD 1% = 16.231

ANOVA vertical:
F-test 31.5, d.f. 6; 41 ($p < 0.001$)
HSD 5% = 52.71, HSD 1% = 62.40

ANOVA horizontal:
F-test: 225.5, d.f.1; 29 ($p < 0.001$)
HSD 5% = 14.209, HSD 1% = 18.416

ANOVA vertical:
F-test 14.4, d.f. 5; 29 ($p < 0.001$)
HSD 5% = 59.65, HSD 1% = 72.51

HSD = Tukey's Honestly Significant Difference

TABLE VI Shear strength (MPa). Variance analysis of the 3.5 mm screws

In vitro	mean and SD							*In vivo*	mean and SD						
Weeks	N	Machine cut	N	Compression moulded	N	Total		Weeks	N	Machine cut	N	Compression moulded	N	Total
0	6	156.0	3	184.0	9	165.3		0	6	149.1	3	170.0	9	156.1
		6.7		11.0		15.9				4.5		12.7		12.8
3	6	146.6	3	177.4	9	156.8		3	6	144.4	3	176.2	9	155.0
		5.1		3.2		16.0				4.3		2.8		16.3
6	6	144.7	3	170.3	9	153.2		6	6	124.7	3	146.3	9	131.9
		7.8		4.1		14.4				2.5		2.4		11.0
9	4	141.2	3	169.2	7	153.2		9	6	131.7	3	156.7	9	140.0
		1.9		13.2		16.8				8.8		3.8		14.4
15	6	145.1	3	169.0	9	153.1		15	6	79.6	3	125.5	9	94.9
		4.5		3.8		12.6				14.3		4.2		25.7
26	6	127.1	3	161.9	9	138.7		26	6	7.0	3	42.4	9	18.8
		14.7		3.5		21.0				2.3		17.8		19.9
51	6	8.8	3	12.7	9	10.1								
		7.0		6.5		6.7								
	40	123.4	21	149.2	61	132.3			36	106.1	18	136.2	54	116.1
		50.0		57.8		53.8				50.9		47.0		51.2

ANOVA horizontal:
F-test: 127.8, d.f.1; 40 ($p < 0.001$)
HSD 5% = 5.287, HSD 1% = 6.717

ANOVA vertical:
F-test 131.3, d.f. 6; 40 ($p < 0.001$)
HSD 5% = 21.81, HSD 1% = 25.82

ANOVA horizontal:
F-test: 133.0, d.f.1; 33 ($p < 0.001$)
HSD 5% = 6.078, HSD 1% = 7.749

ANOVA vertical:
F-test 89.6, d.f. 5; 33 ($p < 0.001$)
HSD 5% = 25.18, HSD 1% = 30.09

HSD = Tukey's Honestly Significant Difference

enabled significant improvement of the torque and bending strengths of SR-PLLA screws while other strength properties remained acceptable. The results are encouraging for the continued use of these screws in the treatment of lightly-loaded bone fractures and in more demanding treatments than they have previously been used.

In this study, the strength loss was faster *in vivo* than *in vitro*, as also found in our earlier studies [19, 20], probably because of the effects of enzymes and other

TABLE VII Torsional strength (MPa). Variance analysis of the 3.5 mm screws

In vitro	mean and SD						*In vivo*	mean and SD					
Weeks	N	Machine cut	N	Compression moulded	N	Total	Weeks	N	Machine cut	N	Compression moulded	N	Total
0	6	48.3	3	20.5	9	39.1	0	6	53.8	3	20.9	9	42.8
		6.1		2.4		14.8			3.0		1.8		16.6
3	6	41.8	3	18.1	9	33.9	3	6	41.5	3	15.7	9	32.9
		4.2		5.2		12.6			2.2		1.6		13.0
6	6	37.2	3	14.5	9	29.6	6	6	36.5	3	11.6	9	28.2
		6.5		2.0		12.5			2.4		3.2		12.7
9	6	35.0	3	8.9	9	26.3	9	6	31.6	3	14.7	9	26.0
		4.8		2.7		13.6			4.8		2.7		9.3
15	6	22.2	3	8.6	9	17.7	15	6	19.4	3	8.8	9	15.8
		6.2		4.0		8.6			4.9		1.0		6.6
	30	36.9	15	14.1	45	29.3		30	36.6	15	14.3	45	29.2
		10.2		5.7		14.0			12.0		4.6		14.6

ANOVA horizontal:
F-test 136.3, d.f. 1; 24 ($p < 0.001$)
HSD 5% = 4.658, HSD 1% = 6.037

ANOVA vertical:
F-test 3.6, d.f. 4; 24 ($p < 0.01$)
HSD 5% = 19.55, HSD 1% = 23.77

ANOVA horizontal:
F-test 310.5, d.f. 1; 24 ($p < 0.001$)
HSD 5% = 3.010, HSD 1% = 3.901

ANOVA vertical:
F-test 12.9, d.f. 4; 24 ($p < 0.001$)
HSD 5% = 12.64, HSD 1% = 15.36

HSD = Tukey's Honestly Significant Difference

TABLE VIII Pull out tests (MPa). Variance analysis of the 3.5 mm screws

In vitro	mean and SD						*In vivo*	mean and SD					
Weeks	N	Machine cut	N	Compression moulded	N	Total	Weeks	N	Machine cut	N	Compression moulded	N	Total
0	6	484.4	3	500.5	9	489.7	0	6	537.4	2	621.4	8	558.4
		87.0		33.7		71.3			89.1		151.6		102.3
3	5	355.4	2	402.8	7	369.0	3	5	272.5	2	418.3	7	314.1
		64.8		69.0		64.2			39.4		41.3		79.9
6	5	304.0	2	394.7	7	329.9	6	6	191.5	3	383.7	9	255.5
		49.0		39.1		61.8			43.8		16.9		102.5
9	5	345.9	3	370.9	8	355.3	9	6	130.8	2	264.0	8	164.1
		77.6		113.0		85.2			23.1		69.4		69.8
15	6	169.6	2	347.5	8	214.1	15	4	121.9	3	294.7	7	195.9
		72.0		14.6		102.5			60.4		31.5		103.4
26	4	271.5	2	227.0	6	256.7							
		87.0		72.8		78.3							
	31	323.8	14	382.7	45	342.1		27	259.5	12	386.9	39	298.7
		123.1		101.4		118.9			168.3		134.8		167.8

ANOVA horizontal:
F-test: 4.6, d.f.1; 24 ($p < 0.05$)
HSD 5% = 64.727, HSD 1% = 83.892

ANOVA vertical:
F-test 3.0, d.f. 5; 24 ($p < 0.05$)
HSD 5% = 271.75, HSD 1% = 330.33

ANOVA horizontal:
F-test: 24.0, d.f.1; 18 ($p < 0.001$)
HSD 5% = 65.874, HSD 1% = 89.473

ANOVA vertical:
F-test 8.1, d.f. 4; 18 ($p < 0.01$)
HSD 5% = 285.23, HSD 1% = 367.23

HSD = Tukey's Honestly Significant Difference

TABLE IX Viscosity average molecular weight (M_v) (g/mol) of 4.5 mm SR-PLLA screws

In vitro	M_v	M_v	*In vivo*	M_v	M_v
Weeks	Machine cut	Compression moulded	Weeks	Machine cut	Compression moulded
0	61650	51050	0	61650	51050
3	55800	46400	3	49650	45950
6	45050	44600	6	46850	37950
9	42800	41450	9	36200	30800
15	34950	34950	15	23650	22150
26	21800	23300	26	14700	11450

TABLE X Viscosity average molecular weight (M_v) (g/mol) of 3.5 mm SR-PLLA screws

In vitro	M_v	M_v	*In vivo*	M_v	M_v
Weeks	Machine cut	Compression moulded	Weeks	Machine cut	Compression moulded
0	56300	43700	0	56300	43700
3	51800	41000	3	49550	38800
6	47000	41450	6	41150	36200
9	38850	34950	9	34850	30350
15	35400	30350	15	16050	23300
26	19200	16750	26	12050	13700

TABLE XI Crystallinities of 4.5 mm SR-PLLA screws

In vitro	(%)	(%)	*In vivo*	(%)	(%)
Weeks	Machine cut	Compression moulded	Weeks	Machine cut	Compression moulded
0	63	65	0	63	65
3	64	72	3	62	66
6	64	67	6	63	68
9	64	69	9	65	72
15	65	71	15	70	71
26	72	73	26	73	74

TABLE XII Crystallinities of 3.5 mm SR-PLLA screws

In vitro	(%)	(%)	*In vivo*	(%)	(%)
Weeks	Machine cut	Compression moulded	Weeks	Machine cut	Compression moulded
0	62	60	0	62	60
3	65	70	3	64	66
6	65	68	6	67	70
9	67	68	9	68	68
15	67	71	15	72	69
26	74	70	26	76	74

biochemical factors on the degradation process. The faster degradation kinetics *in vivo* were confirmed by molecular weight measurements.

The crystallinities of SR-PLLA screws, which were already high before exposure (60–65%), showed only a slight increase (70–76%) during degradation, consistent with the result of Li *et al.* [21] for highly crystalline PLLA.

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