

Effect of Process Parameters on Properties of Wet-Spun Poly(L,D-lactide) Copolymer Multifilament Fibers

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ABSTRACT: Poly(L,D-lactide) [P(L,D)LA], L/D ratio 96/4, and poly(L,DL-lactide) [P(L,DL)LA], L/DL ratio 70/30, multifilament fibers were prepared by wet-spinning and the effects of the spin draw ratio and the coagulant on the morphological, thermal, and mechanical properties of the filaments were studied. The hydrolytic degradation of filaments was studied *in vitro*. The filament diameter and the mechanical properties of filaments were highly dependent on the spin draw ratio, whereas the coagulant had no or minor effect. The filament diameters were in the range of 11–36 μm and the maximum tenacity of 150 MPa was obtained at the spin draw ratio of 7.0 for both copolymers. The copolymer had the main importance on

the crystallinity of filaments, but it was also affected by the duration of the coagulation process. The crystallinities of P(L,D)LA 96/4 filaments were in the range of 5–16%, whereas P(L,DL)LA 70/30 filaments were totally amorphous. The degree of crystallinity had effect on the hydrolytic degradation of filaments. The tenacity loss of P(L,D)LA 96/4 filaments was about 10% and that of P(L,DL)LA 70/30 filaments was as high as 50% after 24 weeks *in vitro*. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 2683–2692, 2009

Key words: biopolymers; crystallization; degradation; fibers; mechanical properties

INTRODUCTION

Poly(lactide) is a bioresorbable polymer which is widely used for medical purposes. It is produced by the ring-opening polymerization of lactide into high-molar-mass polymers. Lactide is the cyclic dimer of lactic acid and exists in three stereoisomeric forms: D,D cyclic dimer (D-lactide), L,L cyclic dimer (L-lactide), and D,L cyclic dimer (mesolactide). D-Lactide and L-lactide are partially crystalline polymers, whereas DL-lactide is an amorphous polymer. The degradation of enantiomerically pure poly(lactides) is very slow, depending on the purity of the polymer, the molecular weight and its distribution, the crystallinity, the shape of sample, and the processing conditions (mechanical and thermal). The complete degradation time of enantiomerically pure poly(lactide) could be many years.¹ In many medical applications, such a long degradation time is not necessary; a shorter degradation time is enough for tissue

repair. The degradation rate of poly(lactides) can be controlled through the copolymerization of L-lactide with a different ratio to D-lactide or DL-lactide.² When a more rapid degradation rate is needed, it is possible to use poly(L,D-lactide) [P(L,D)LA] or poly(L,DL-lactide) [P(L,DL)LA] copolymers to fulfil the requirements for tissue repair.

Poly(lactide) filaments are possible to manufacture by wet, dry, or melt-spinning processes. In the wet-spinning process the polymer is dissolved in solvent. Then the polymer solution is pumped through a spinneret into a spin bath, where the polymer is precipitated and the filaments are reeled. The spin bath includes polymer nonsolvent and possible additives.³ The wet-spinning of poly(L-lactide) [P(L)LA] filaments has been studied as early as 1966.⁴ The low mechanical strength of filaments is one reason why the wet-spinning method has not been studied widely after those days. The wet-spun filaments have lower mechanical strength compared to dry-spun and melt-spun filaments. This is due to the high concentration of voids in the filament structure. The voids are formed during the diffusion of solvent and nonsolvent in the spin bath.⁵ Nelson et al.⁶ have reported the ultimate stress values of wet-spun filaments between 30 and 120 MPa.

In the dry-spinning, the polymer is also dissolved in solvent and extruded through the spinneret. The

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polymer solution is flowed into an evaporation tunnel where solvent evaporates from the polymer jets and the filaments solidify.³ Pennings and coworkers^{7,8} have reported as high as 2.3 GPa tenacity values to dry-spun and subsequent hot-drawn P(L)LA filaments ($M_v = 9.1 \times 10^5$). The filaments were extruded from chloroform/toluene solution at 60°C. The research group used high drawing temperature (190–200°C) which enabled high draw ratios and tensile strengths. The crystallinity of filaments was about 53%. They⁹ have also studied dry-spinning and subsequent hot-drawing (at 145°C) of P(L,D)LA 95/5 stereocopolymer filaments. The tensile strength of filaments was 0.95 GPa and Young's modulus was 9.2 GPa. The crystallinity of filaments was about 20%. Fambri et al.¹⁰ reported the dry-spinning at room temperature and subsequent hot-drawing (at 200°C) of P(L)LA ($M_v = 6.6 \times 10^5$) from chloroform solution. The maximum tensile strength was 1.1 GPa, Young's modulus 9.6 GPa, and the crystallinity of filaments about 19%. Gupta et al.^{11,12} have studied the dry-jet-wet-spinning of P(L)LA ($M_v = 1.5 \times 10^5$). The polymer was dissolved in chloroform and extruded through the spinneret and the air gap to the methanol containing spin bath. Afterwards the filament was drawn and heat-set. The maximum tensile strength of the filament was 0.6 GPa, Young's modulus 8.2 GPa, and crystallinity about 40%.

In the industrial-scale production the recovery of solvent used for dissolving the polymer is important to the economics of dry-spinning. The recovery equipment increases the cost of the investment and it decreases the popularity of the dry-spinning method. This could be one reason why the studies of the polylactide filament manufacturing have been concentrated on the melt-spinning process.

The melt-spinning process is the main production method of thermoplastic polymer filaments. The polymer is heated until it melts, and the molten polymer is then forced through the spinneret holes. When the polymer jets emerge from the spinneret, they are cooled and solidified with air. Melt-spun filaments can be produced at high spinning velocities. The drawback of melt-spinning method is that during the melt-spinning the polymer is subjected to elevated temperature, which can cause the thermal degradation indicated by the decrease in molecular weight.³

The mechanical strength of melt-spun filaments has been lower compared to the dry-spun filaments because the number of entanglements in polymer melt was higher compared to polymer solution and it reduced the stretchability in drawing.¹³ Fambri et al.¹⁴ have studied the two-stage melt-spinning and hot-drawing of P(L)LA ($M_v = 3.3 \times 10^5$). The mechanical strength of filaments was 0.87 GPa, Young's modulus

9.2 GPa, and the crystallinity up to 65%. The minimum diameter of filaments was 48 μm . Yuan et al.¹⁵ have studied also the two-stage melt-spinning and hot-drawing of P(L)LA ($M_v = 2.6 - 4.9 \times 10^5$). The tenacities were between 0.3 and 0.6 GPa, Young's modulus values between 3.6 and 5.4 GPa, and diameters between 110 and 160 μm after the hot-drawing. The crystallinities were between 50 and 64%. Fambri et al.¹⁶ have studied the melt-spinning of [P(L,DL)LA] 70/30. The maximum tenacity was 0.18 GPa and Young's modulus 4.1 GPa. The diameter of the thinnest filaments was about 50 μm . Cicero and Dorgan¹⁷ have studied the two-step melt-spinning and cold-drawing of standard-fiber-grade P(L,D)LA 98/2 ($M_w = 0.99 - 1.1 \times 10^5$). The maximum tensile strength was 0.38 GPa and Young's modulus 3.2 GPa. The crystallinity was around 50%.

The high-speed melt-spinning, which is economically and commercially more attractive, is also widely studied. Mezhani and Spruiell¹⁸ have studied the high-speed melt-spinning of P(L)LA ($M_w = 2.1 \times 10^5$). The maximum crystallinity (about 40%), tenacity (0.38 GPa), and Young's modulus (6 GPa) were reached at spinning velocities between 2000 and 3000 m/min. The filament diameter was as low as 12 μm at spinning velocity of 5000 m/min. Schmack et al.¹⁹ have studied the high-speed melt-spinning of P(L,D)LA ($M_v = 2.1-4.1 \times 10^5$). The spinning speeds were up to 5000 m/min. The orientation increased the crystallinity, and it reached up to 40% with the low D-content (1%) polymers. The orientation-induced crystallinity increased only to the level of 10% with high D-content (8%) polymer. The maximum tenacity was 0.3 GPa and Young's modulus 6.8 GPa.

Despite the advantages of the melt-spinning process, we wanted to use spinning method which does not need an elevated temperature. Most of the possible end-uses of dry-spun and melt-spun polylactide filaments have been bioresorbable sutures or implants, and in these end-uses very high mechanical strength during the healing process is important. Our goal was to manufacture filaments for non-woven production, and therefore the moderate tensile strength is sufficient. In the previous wet-spinning studies P(L)LA filaments have been produced by a syringe.^{6,20} In this study, we produced P(L,D)LA stereocopolymer filaments by a gear pump and a 20-hole spinneret. The purpose was to manufacture fine multifilaments which have a shorter degradation time than the enantiomerically pure polylactide has. We²¹ have studied the phase separation of P(L,D)LA stereocopolymers by cloud point titration and found that methanol and ethanol had similar precipitation properties. The earlier studies^{11,12,20} have used only methanol in the spin bath, but this time we also used ethanol for comparison.

TABLE I
Tested Copolymers and their IVs, Molecular Weights and Spin Dopes

Copolymer	Material type	IV (dL/g)	M_v (g/mol)	Spin dope concentration (%)	Spin dope viscosity (cP)
P(L,D) LA 96/4	Granulate	2.2	93 700	–	–
	Filament	–	97 800	15	1720
P(L,DL) LA 70/30	Granulate	3.1	167 200	–	–
	Filament	–	167 100	10	1660

EXPERIMENTAL

Materials

The two tested medical grade polylactide stereocopolymers were supplied from Purac Biochem by (Gorinchem, The Netherlands). The copolymers were P(L,D)LA, L/D ratio 96/4, and P(L,DL)LA, L/DL ratio 70/30. The viscosity-average molecular weight (M_v) values were determined by gel permeation chromatography,²² and the inherent viscosities (IVs) were reported by the polymer supplier. The intrinsic viscosities and viscosity-average molecular weights of copolymers are given in Table I.

Spin dope preparation and wet-spinning

The polymer was dissolved in dichloromethane (analytical grade) in a conical flask covered by a glass stopper at room temperature. A magnetic stirrer was used for the dissolution until the solution was clear. The spin dope concentrations were calculated from the volume of the solvent. The viscosities of polymer solutions were measured by Brookfield-viscometer. The spin dope concentrations and viscosities are given in Table I.

The polymer solution was pumped by Zenith gear pump (Allweiler AG, Radofzell, Germany) through the spinneret (20 holes, hole diameter 0.1 mm; Enka Tecnica GmbH, Heinsberg, Germany) into the spin bath. The used precipitants were methanol or ethanol (analytical grade). The filaments were reeled to a bobbin (diameter 87 mm). The schematic drawing of the wet-spinning equipment is presented in Figure 1. The utilized spin draw ratios (SDR) were from 1.4 (low) to 9.8 (high), and they were calculated from the ratio of the final velocity (reeling velocity) and the initial velocity (spinneret velocity). The coagulation time was calculated by dividing the length of the coagulation (0.9 m) by the average velocity of the filaments. The spinneret velocities were in the range of 7–22 m/min and the reeling velocities were between 10 and 70 m/min.

The filaments were evacuated in a vacuum oven at 40°C overnight to eliminate chemical residues.²³ The filaments were stored in a desiccator until their testing to avoid the moisture intake.

Characterization of filaments

A scanning electron microscope (SEM) (Jeol JSM-T100, Jeol Ltd., Tokyo, Japan) was used to characterize the filament surface. An optical microscope was used to determine the filament diameter. The mean of diameter was calculated from 50 individual filaments.

A heat-flux type differential scanning calorimeter (DSC) 821TM from Mettler Toledo Inc. was used to measure the thermal behavior of the copolymer granulates and filaments. Two to four parallel sets of samples (about 5 mg) were heated from –10 to 250°C in standard 40 μ L aluminium sample crucibles. Data were taken from the first heating scans. The glass transition temperatures (T_g), the peak melting temperatures (T_m), the crystallization enthalpies (H_c), and the melting enthalpies (H_m) were measured at a heating rate of 10 K min⁻¹. The degree of crystallinity (X) was calculated using the H_m value of 93.7 J/g for the totally crystallized P(L)LA crystal.²⁴

The breaking force and elongation at break were tested from 50 individual filaments using the tensile testing machine (VibroDYN by Lenzing AG, Lenzing, Austria). The gauge length was 20 mm, the testing

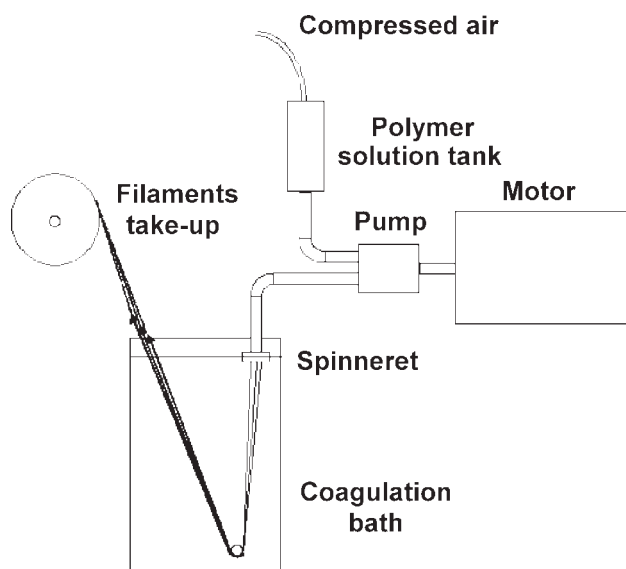


Figure 1 Schematic drawing of wet-spinning equipment.

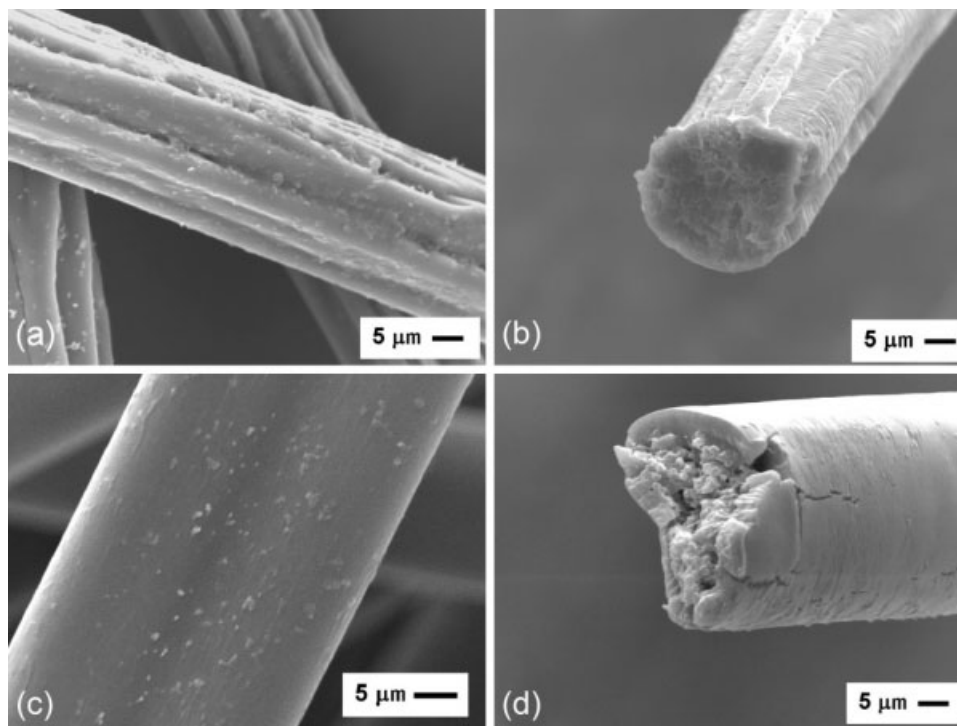


Figure 2 SEM-images of filaments (SDR 1.4). Coagulation time (a,b) 5.6 s; (c,d) 1.9 s. Polymer: P(L,D)LA 96/4; coagulant: ethanol.

speed was 20 mm/min, and the maximum force of the load cell was 100 cN. If the elongation at break was over 200% the gauge length was changed to 10 mm and speed to 10 mm/min. Because the diameters of filaments differed from each other the breaking force was converted to the tenacity.

For *in vitro* degradation tests the filament bundles were placed in test tubes and the tubes were filled (about 10 ml) with soaking solution (phosphate buffer solution).²⁵ The filled test tubes were kept at constant temperature (37 ± 1)°C. The soaking solution was changed during the testing time to maintain a pH of 7.4 ± 0.2 . At each data point the filaments were taken out from the test tube, and the breaking forces of 20 wet filaments were measured. The data points were 0, 2, 4, 6, 8, 12, 16, 20, and 24 weeks. The breaking force values were also converted to the tenacities.

RESULTS AND DISCUSSION

Wet-spinning

The viscosity-average molecular weight of P(L,DL)LA 70/30 remained same before and after the wet-spinning as shown in Table I. The molecular weight of P(L,D)LA 96/4 slightly increased after the wet-spinning. Probably the dissolution process had an effect on the polymer chains because the polydispersity (PD) value slightly decreased ($PD_{\text{polymer}} = 1.8$; $PD_{\text{filament}} = 1.7$) after spinning. Because our wet-spun fila-

ments were processed at room temperature the polymer did not degrade as in the melt-spinning process. Since melt-spun filaments are processed at elevated temperature the molecular weight can decrease significantly due to the thermo-oxidative degradation caused by direct heating, conversion of mechanical energy related to screw speed and torque, and the residence time.²⁶ The reported molecular weight decreases have been, for example, 40% to poly(D-lactide) ($M_v = 2.80 \times 10^5$),²⁷ 50% to P(L)LA ($M_v = 42 \times 10^5$) and P(L,D)LA 30/70 ($M_v = 1.6 \times 10^5$), 60% to P(L,DL)LA 80/20 ($M_v = 2.1 \times 10^5$),²⁸ and even 70% to P(L)LA ($M_v = 3.3 \times 10^5$).¹⁴ Respectively, during the dry-spinning the decrease of molecular weight has been lower. It has reported 25% reduction in the molecular weight of P(L)LA ($M_v = 9.1 \times 10^5$)²⁹ and 6% reduction also to P(L)LA ($M_v = 6.6 \times 10^5$).¹⁰ The dry-jet-wet spinning has decreased the molecular weight of P(L)LA ($M_v = 1.5 \times 10^5$) only about 5%.¹¹ The length of the dissolution time has had an effect on the reduction of the molecular weight. The time has been one week for the dry-spun filaments and 24 h for the dry-jet-wet-spun filaments. Respectively, our dissolution times were only 1–2 h.

Surface structure

In the previous studies^{11,20} the wet-spun filaments have been shown a porous structure, which can be seen also in our filaments with the low SDR [Fig. 2(a–d)]. The skin structure on the surface and the

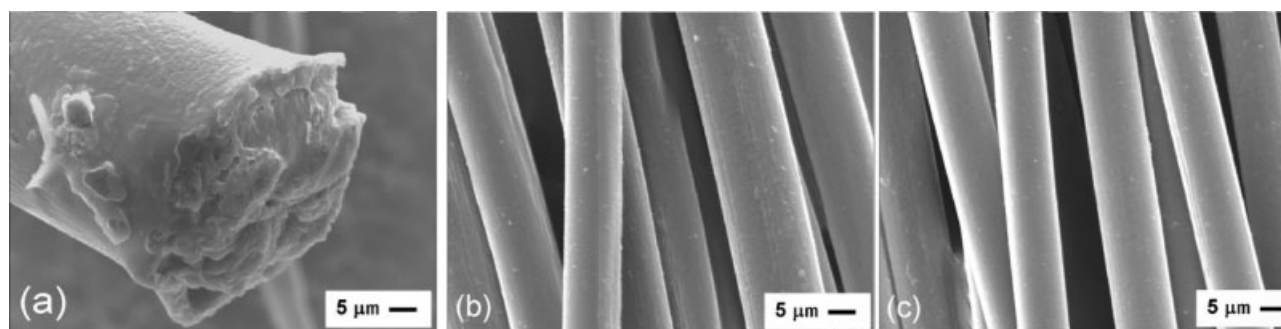


Figure 3 SEM-images of filaments (a) SDR 1.4; (b) SDR 7.0; and (c) SDR 9.8. Polymer: P(L,DL)LA 70/30; coagulant: ethanol.

porous structure inside the filament can be seen in the cross-section [Fig. 2(b,d)]. The porous structure was formed during the coagulation process. The surface of filament was solidified immediately and the skin, thus, was formed first. Solvent and nonsolvent were trapped inside the filament. The porous structure was formed when solvent and nonsolvent were evaporated from the filament after the solidification. In our previous study,²¹ we found that the coagulation rate of P(L,D)LA 96/4 was faster than that of P(L,DL)LA 70/30. If the solidification process is fast the high number of pores is formed. Respectively, the slow solidification rate decreases the formation of pores.⁵ Although we did not measure the porosity of our filaments, P(L,DL)LA 70/30 filaments could be less porous based on the solidification rate [Fig. 3(a)].

The surfaces of the high SDR filaments (7.0 and 9.8) were smooth [Fig. 3(b,c)]. The filament drawing orientated the molecular structure and this can be seen in the smooth surface. Similar appearance was formed with both tested nonsolvents.

The coagulation time had an effect on the surface of P(L,D)LA 96/4 filaments, as shown in Figure 2(a,c). A long coagulation time (5.6 s) produced filaments with longitudinal striations, whereas a short time (1.9 s) coagulated filaments had smoother surface. A collapsed, serrated cross-section was formed when the solidifying outer skin was rigid and more solvent exited the filament than nonsolvent entered. When the coagulation time was longer the volume of solvent diffusing out was greater and the filaments collapsed more. Because the coagulation rate of P(L,DL)LA 70/30 was slower the solidifying outer skin was softer and more deformable, and the cross-section of filaments became more circular, as shown in Figure 3(a).

Crystallinity and thermal behavior

The crystallinity of filament has an effect on its degradation rate. During the hydrolytic degradation of polylactide water diffuses first into amorphous

regions of polymer. The degradation rate of amorphous polymers is therefore faster than that of semi-crystalline polymers. The crystallinity value is one way to predict the degradation rate of polymer, and therefore we measured the crystallinities of polymers.

The crystallinity of P(L,D)LA 96/4 copolymer granulates was about 40%, T_m was 157.3°C, and T_g in the range from 65.1 to 67.9°C, as shown in Table II. The wet-spinning decreased crystallinities of filaments, as shown in Table II and Figure 4. The post-crystallization, i.e. cold-crystallization (X_{cc}),^{6,30,31} was observed in the temperature range from about 75 to 120°C with a peak temperature (T_{cc}) of about 89°C slightly above T_g , that took place with an enthalpy relaxation (an endothermic peak), as shown in Figure 4. Very closely spaced T_g and cold-crystallization has been observed in a 1 : 1 blend of P(L)LA and P(D)LA.³² The X_{cc} of 12% and the X_c of 28% were obtained with both coagulants. Therefore, the wet-spun P(L,D)LA 96/4 copolymer filaments were partially crystalline with the degrees of initial crystallinity ($X = X_c - X_{cc}$) of 16% coagulated either in methanol or ethanol, as shown in Table II. Our wet-spun filaments were more amorphous than the melt-spun filaments ($X = 29\%$) which have been made from a similar copolymer.³³

The wet-spun P(L,D)LA 96/4 filaments were modified using longer coagulating time (5.6 s) in ethanol (Fig. 4 and curve 4). The elongation at break was higher (235%), Table III, and the greater X_{cc} (17%) was observed during the heating in DSC, as shown in Figure 4. Hence, the initial crystallinity of wet-spun filament was only 5%. In other words, the longer coagulation time produced more amorphous wet-spun P(L,D)LA 96/4 filaments.

The T_m values of the partially crystalline wet-spun P(L,D)LA 96/4 filaments remained practically unchanged when the SDR was increased from 1.4 to 9.8, as shown in Table II and Figures 5 and 6. The methanol coagulated P(L,D)LA 96/4 wet-spun filaments lost 2% of their crystallinity at the SDR of 7.0 and 2% more at the SDR of 9.8. The crystallinity of

TABLE II
Glass Transition Temperatures (T_g), Melting Peak Temperatures (T_m) and Crystallinities of Original Copolymer Granulates, and the Corresponding Filaments Coagulated in Methanol (Met-OH) and Ethanol (Et-OH) with Different Spin Draw Ratios (SDR)

Curve number	Material	SDR	T_g (°C)	T_m (°C)	Crystallinity(%)
P(L,D)LA 96/4					
1	Granulate	–	65.1 – 67.9	157.3	40 ± 0
2	Filament, Met-OH	1.4	65.8 ± 0.5	156.9	16 ± 1
8	Filament, Met-OH	7.0	69.9 ± 0.0	156.3	14 ± 2
9	Filament, Met-OH	9.8	70.0 ± 0.0	157.1	12 ± 2
3	Filament, Et-OH	1.4	66.4 ± 0.2	156.8	16 ± 2
4	Filament, Et-OH ^a	1.4	66.3 ± 0.1	155.4	5 ± 1
10	Filament, Et-OH	7.0	69.2 ± 0.0	156.4	12 ± 3
11	Filament, Et-OH	9.8	70.0 ± 0.1	156.4	12 ± 2
P(L,DL)LA 70/30					
5	Granulate	–	59.6 – 61.7	121.5	14 ± 0
6	Filament, Met-OH	1.4	62.3 ± 0.1	–	–
12	Filament, Met-OH	7.0	64.5 ± 0.0	–	–
7	Filament, Et-OH	1.4	62.4 ± 0.2	–	–
13	Filament, Et-OH	7.0	63.5 ± 0.0	–	–

^a The curve 4 has been measured with a filaments that had an elongation at break of 235% and curve 3 that of 59%.

ethanol coagulated fibers decreased by 4%, when the SDR was increased from 1.4 either to 7.0 or to 9.8. The drawing orientates the filaments, and the crystals become thinner, which can be seen as a decreased crystallinity.^{11,34} The increase of the SDR from 1.4 to 9.8 increased T_g about 4°C with both coagulants, and the T_g was 70.0°C at the SDR of 9.8. The increase of draw ratio increased the orientation of the amorphous zones and the number of intermolecular bonds, and this can be seen as an increasing T_g .^{11,33} The cold-crystallization started earlier when the SDR increased which can be seen as the decrease of the T_{cc} . It decreased about 7°C with the methanol coagulated filaments and about 5°C with ethanol coagulated filaments when the SDR increased from 1.4 to 9.8.

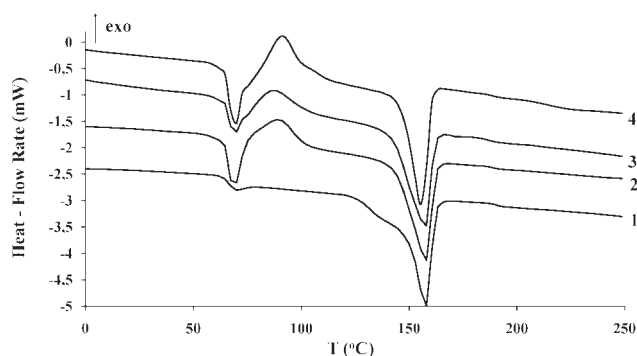


Figure 4 DSC curves of P(L,D)LA 96/4 copolymer: (1) granulate; (2) filament, SDR 1.4, coagulated in methanol, coagulation time 1.9 s; (3) filament, SDR 1.4, coagulated in ethanol, coagulation time 1.9 s; and (4) filament, SDR 1.4, coagulated in ethanol, coagulation time 5.6 s. The curves have been shifted by an arbitrary amount for clarity.

Crystallinity of the original partially crystalline P(L,DL)LA 70/30 granulates was about 14%, T_m was 121.5°C, and T_g in the range from 59.6 to 61.7°C with an enthalpy relaxation (an endothermic peak) based on DSC measurements, as shown in Table II. The crystallinity of the P(L,DL)LA 70/30 filaments was lost and the filaments were amorphous, as shown in Figure 7. There was no cold-crystallization during the heating process of P(L,DL)LA 70/30 in the DSC. The amorphous nature of the P(L,DL)LA 70/30 filaments did not change by increasing the SDR or by changing the coagulant, as shown in Table II and Figure 7.

Mechanical properties

The filament diameter was controllable by the SDR. It was possible to spin very fine filaments when the SDR was high. The diameters of the obtained wet-spun filaments were between 11 and 36 μm as shown in Table III. The methanol coagulated P(L,D)LA 96/4 filaments with the short coagulation time had larger diameter than other filaments manufactured by otherwise similar process parameters. As reported earlier the precipitation rate of P(L,D)LA 96/4 was faster than that of P(L,DL)LA 70/30, and methanol and ethanol had similar coagulation properties in low polymer concentrations (< 6%).²¹ In the present study, the spin dope concentration was 15%, and the diffusion of nonsolvent was more difficult caused by higher density of polymer solution. Methanol is a smaller molecule than ethanol and it can diffuse easier into the polymer solution. The volume of methanol diffusing in was greater than the

TABLE III
Spinning Parameters, Diameters and Mechanical Properties of Wet-Spun Filaments

SDR	Pump velocity (m/min)	Reeling velocity (m/min)	Coagulation time (s)	Diameter (μm)	Tenacity (MPa)	Young's modulus (GPa)	Elongation (%)
Methanol coagulated P(L,D)LA 96/4							
1.4	21.4	30	1.9	36 \pm 3	49 \pm 4	0.7 \pm 0.1	92 \pm 13
7.0	7.1	50	1.7	18 \pm 1	80 \pm 8	1.0 \pm 0.1	67 \pm 3
9.8	7.1	70	1.2	14 \pm 1	94 \pm 8	1.3 \pm 0.1	47 \pm 3
Ethanol coagulated P(L,D)LA 96/4							
1.4	7.1	10	5.6	26 \pm 3	77 \pm 7	1.2 \pm 0.1	235 \pm 15
1.4	21.4	30	1.9	30 \pm 7	53 \pm 5	1.2 \pm 0.2	59 \pm 16
4.2	7.1	30	2.6	17 \pm 2	125 \pm 10	1.5 \pm 0.1	105 \pm 9
7.0	7.1	50	1.7	13 \pm 2	148 \pm 10	1.7 \pm 0.2	70 \pm 8
9.8	7.1	70	1.2	12 \pm 2	113 \pm 12	1.6 \pm 0.1	42 \pm 6
Methanol coagulated P(L,DL)LA 70/30							
1.4	7.1	10	5.6	29 \pm 3	45 \pm 5	0.8 \pm 0.1	231 \pm 13
1.4	21.4	30	1.9	32 \pm 5	55 \pm 6	0.7 \pm 0.1	105 \pm 14
4.2	7.1	30	2.6	17 \pm 2	103 \pm 10	1.0 \pm 0.1	94 \pm 4
7.0	7.1	50	1.7	13 \pm 2	148 \pm 12	1.3 \pm 0.1	59 \pm 4
9.8	7.1	70	1.2	11 \pm 1	126 \pm 14	1.3 \pm 0.1	41 \pm 3
Ethanol coagulated P(L,DL)LA 70/30							
1.4	7.1	10	5.6	27 \pm 3	56 \pm 6	0.9 \pm 0.1	211 \pm 19
1.4	21.4	30	1.9	27 \pm 6	98 \pm 12	1.4 \pm 0.2	92 \pm 17
4.2	7.1	30	2.6	18 \pm 2	105 \pm 13	0.9 \pm 0.1	82 \pm 13
7.0	7.1	50	1.7	14 \pm 1	146 \pm 18	1.3 \pm 0.2	47 \pm 5
9.8	7.1	70	1.2	12 \pm 1	135 \pm 17	1.3 \pm 0.1	34 \pm 5

volume of dichloromethane diffusing out, and the filament solidified in the swollen state.

Compared with earlier studies our filaments were relatively fine (11–14 μm at the SDR 9.8). For example, in the earlier studies filaments with diameters between 28–550 μm have been produced by the wet-spinning method.^{6,35} Respectively, Gupta et al. have produced the jet-wet-spun filaments, whose minimum diameter was about 50 μm .¹¹ They have manufactured filaments with the syringe pump and the

nozzle with one hole. In our study the gear pump and the 20-hole-spinneret (hole diameter 0.1 mm), which is normally used in the textile filament wet-spinning production, were used. This enabled thinner diameter of the filaments.

The filament tenacity was also controllable by the SDR. Tenacities of methanol coagulated P(L,D)LA 96/4 filaments were between 49 and 94 MPa and that of ethanol coagulated filaments between 53 and 148 MPa, as shown in Table III. Respectively, the

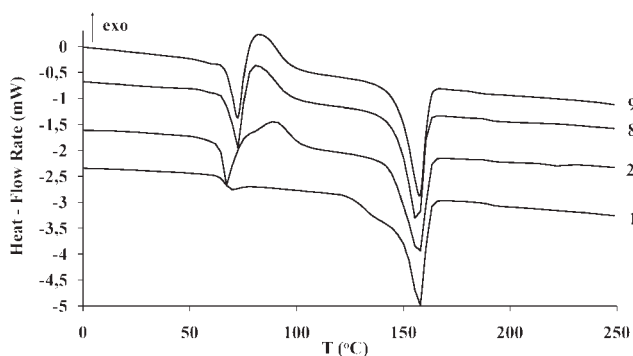


Figure 5 DSC curves of P(L,D)LA 96/4 copolymer: (1) granulate; (2) filament, SDR 1.4, coagulated in methanol, coagulation time 1.9 s; (8) filament, SDR 7.0, coagulated in methanol; and (9) filament, SDR 9.8, coagulated in methanol. The curves have been shifted by an arbitrary amount for clarity.

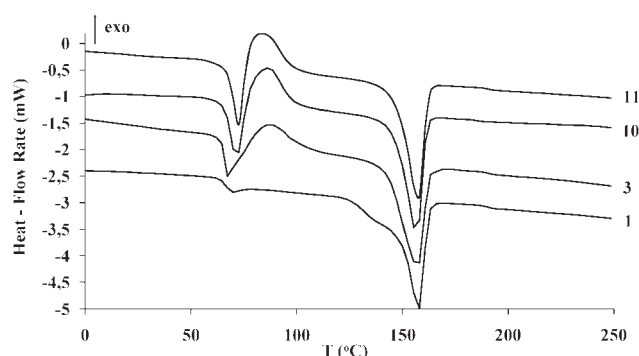


Figure 6 DSC curves of P(L,D)LA 96/4 copolymer: (1) granulate; (3) filament, SDR 1.4, coagulated in ethanol, coagulation time 1.9 s; (10) filament, SDR 7.0, coagulated in ethanol; and (11) filament, SDR 9.8, coagulated in ethanol. The curves have been shifted by an arbitrary amount for clarity.

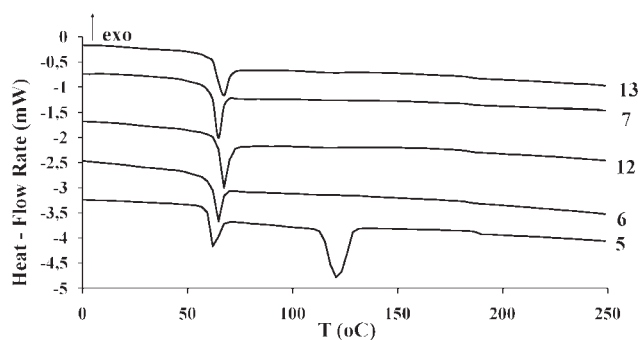


Figure 7 DSC curves of $P_{(L,DL)}LA$ 70/30 copolymer: (5) granulate; (6) filament, SDR 1.4, coagulated in methanol; (12) filament, SDR 7.0, coagulated in methanol; (7) filament, SDR 1.4, coagulated in ethanol; and (13) filament, SDR 7.0, coagulated in ethanol. The curves have been shifted by an arbitrary amount for clarity.

Young's modulus values were between 0.7 and 1.3 GPa for the methanol coagulated filaments and between 1.2 and 1.7 GPa for the ethanol coagulated filaments. Because the ethanol coagulated filaments were thinner and the tenacity depends on the filament diameter, the ethanol coagulated filaments were stronger than the methanol coagulated filaments. Also the coagulation properties could have effect on the mechanical properties. The high efficient coagulant, as methanol in our study, can form the high number of pores and capillaries inside the filament, and thus reduce the mechanical strength.⁵

The tenacities of the methanol coagulated $P_{(L,DL)}LA$ 70/30 filaments were between 45 and 126 MPa and that of the ethanol coagulated filaments between 56 and 135 MPa, as shown in Table III. Respectively, the Young's modulus values were between 0.7 and 1.3 GPa and between 0.9 and 1.4 GPa. The tenacity and the Young's modulus values were quite similar with both coagulants. The precipitation rate of $P_{(L,DL)}LA$ 70/30 was slower,²¹ and in the present study the tested coagulants had similar coagulation properties to $P_{(L,DL)}LA$ 70/30. Hence, both coagulants produced similar mechanical properties.

The highest tenacity values were obtained at the SDR of 7.0. The increase of the SDR to 9.8 caused the overstretching of molecular chains, and this can be seen as the decrease of tenacity.

The coagulation time had effect on the elongation at break of filaments. We tested two different coagulation times at low SDR. The long coagulation time (5.6 s) ensured the long elongation at break (more than 200%). If the coagulation time was short (1.9 s) at the same SDR the elongation at break values were smaller (59 – 105%).

The stress–strain curves of $P_{(L,D)}LA$ 96/4 filaments are presented in Figure 8 and those of $P_{(L,DL)}LA$ 70/30 filaments in Figure 9. The beginning of curves

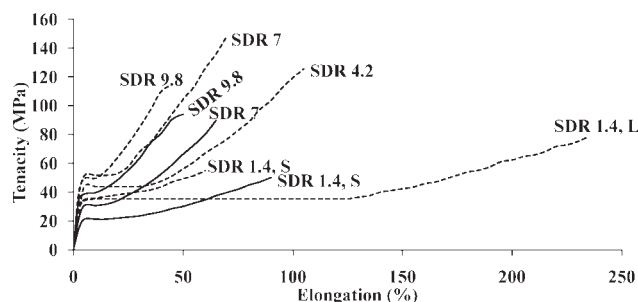


Figure 8 Tenacities of $P_{(L,D)}LA$ 96/4 filaments: (—) methanol coagulated filaments and (---) ethanol coagulated filaments. L: long coagulation time (5.6 s); S: short coagulation time (1.9 s). Mean of 50 measurements.

was a linear Hookean region. In this region the molecular chains started to stretch and the molecules straightened in the amorphous region of the filament, and the intermolecular bonds strained. Yield stresses of $P_{(L,DL)}LA$ 70/30 filaments with the low SDR were smaller compared with $P_{(L,D)}LA$ 96/4 filaments, and therefore the chain molecules and intermolecular bonds in $P_{(L,DL)}LA$ 70/30 were easier to strain compared to $P_{(L,D)}LA$ 96/4 filaments. At the high SDR the yield stresses of both stereocopolymers were similar. After the linear Hookean region came a region of easier extension. At the low SDR this region was very long, whereas at the high SDR it was practically disappeared. In this region the highly strained bonds in the amorphous area broke because they could not withstand the force applied to them. The molecules straightened further and the load increased to the other bonds. Therefore, the extension became easier. After the region of easier extension came the region of increasing slope. In this region some of the molecules were fully straightened and further extension became more difficult. The increasing strain affected on the bonds and molecules, and finally the filament broke.³⁶

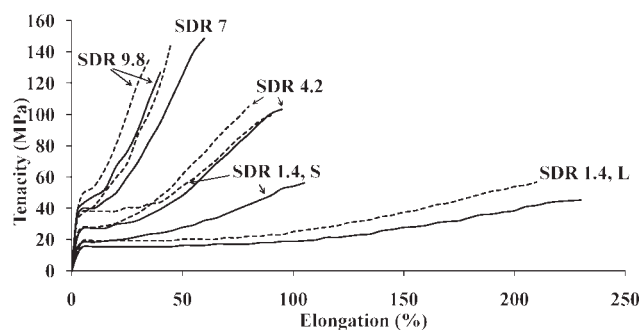


Figure 9 Tenacities of $P_{(L,DL)}LA$ 70/30 filaments: (—) methanol coagulated filaments and (---) ethanol coagulated filaments. L: long coagulation time (5.6 s); S: short coagulation time (1.9 s). Mean of 50 measurements.

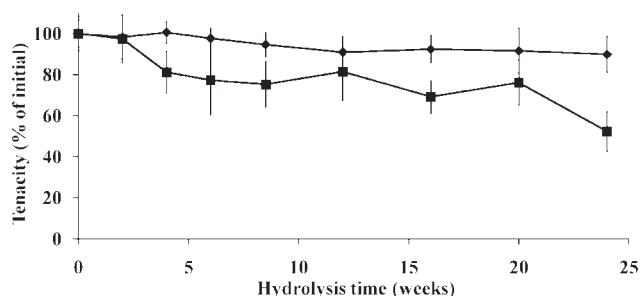


Figure 10 Retention of tenacity *in vitro* for wet-spun filaments. Filaments: (◆) P(L,D)LA 96/4 and (■) P(L,DL)LA 70/30. Coagulant: methanol. Mean of 20 measurements.

In vitro degradation

The *in vitro* hydrolytic degradation results are presented in Figure 10. The filament, which were tested, were spun at the low SDR (1.4) and the coagulation time was short (1.9 s). Those spinning parameters gave about 16% crystallinity to the P(L,D)LA 96/4 filaments and the P(L,D)LA 70/30 filaments were amorphous. As already mentioned the crystallinity has influence on the hydrolysis properties of polylactide. During the hydrolytic degradation water diffuses into the amorphous regions of polymer and causes the breakage of the ester bonds which initiates a reduction in molecular weight and later on a reduction in mechanical strength. After amorphous regions the hydrolytic degradation occurs in the crystalline regions leading to increased mass loss and finally to complete resorbtion.³⁷ Because our P(L,DL)LA 70/30 filaments were totally amorphous, the tenacity loss occurred earlier compared to the P(L,D)LA 96/4 filaments, as shown in Figure 10. The tenacity loss started after 2 weeks. After 24 weeks the tenacity loss of P(L,DL)LA 70/30 filaments was about 50% from the initial tenacity. Respectively, it was about 10% with the P(L,D)LA 96/4 filaments.

The degradation rate of enantiomerically pure polylactide is slow. Suuronen et al.¹ have studied the biodegradation of semi-crystalline self-reinforced (SR) P(L)LA plates ($X = 53\%$). After five years *in vivo*, small particles of polymers still existed but the mechanical strength of material was lost. The degradation of P(L,D)LA copolymers is faster. Kallela et al.³⁸ have studied the use of totally amorphous SR P(L,DL)LA 70/30 screws, and after 24 weeks *in vivo*, there were cracks, clefts and fragmentation in some screws. Under *in vitro* hydrolysis the material lost its mechanical strength after 48 weeks. Although it is not possible to fully compare the degradation of screws and our filaments, the degradation rate of our filaments is in accordance with the earlier studies.

CONCLUSIONS

Our study showed that it is possible to prepare fine polylactide copolymer multifilaments by the wet-spinning method. Because there was no need to use elevated temperature during the spinning process, the molecular weight of copolymer remained similar before and after spinning. However, the degree of crystallinity decreased due to wet-spinning. The P(L,D)LA 96/4 filaments were semicrystalline with the remaining degree of crystallinity from 5 to 16%. Respectively, P(L,DL)LA 70/30 filaments were amorphous. The degree of crystallinity had an influence on the hydrolytic degradation rate. P(L,DL)LA 70/30 filaments biodegraded faster than P(L,D)LA 96/4 filaments. Hence, the use of P(L,DL)LA 70/30 filaments is recommendable when shorter degradation time is needed.

The spin draw ratio had effect on the mechanical properties of filaments. The optimum spin draw ratio was observed to be 7.0 to get the tenacity of 150 MPa. It is high enough, for example, to the non-woven production. The coagulant had no or minor effect on the mechanical properties and thus methanol and ethanol are both suitable coagulants for the spin bath. However, the use of ethanol is recommendable in the laboratory scale because of its lower toxicity.

References

1. Suuronen, R.; Pohjonen, T.; Hietanen, J.; Lindqvist, C. *J Oral Maxil Surg* 1998, 56, 604.
2. Kellomäki, M.; Pohjonen, T.; Törmälä, P. In *Biodegradable Polymers*; Arshady, R., Ed.; Citus: London, 2003; Chapter 7.
3. Fournier, F. *Synthetic Fibers—Machines and Equipment Manufacture, Properties*; Hanser: Munich, 1999.
4. Kulkarni, R. K.; Pani, K. C.; Neuman, C.; Leonard, F. *Arch Surg* 1966, 93, 839.
5. Frushour, B. G.; Knorr, R. S. *Handbook of Fiber Chemistry*; Lewin, M., Ed.; CRC: Boca Raton, FL, 2007; Chapter 12.
6. Nelson, K. D.; Romero, A.; Waggoner, P.; Crow, B.; Borneman, A.; Smith, G. M. *Tissue Eng* 2003, 9, 1323.
7. Leenslag, J. W.; Pennings, A. J. *Polymer* 1987, 28, 1695.
8. Postema, A. R.; Pennings, A. J. *J Appl Polym Sci* 1989, 37, 2351.
9. Penning, J. P.; Dijkstra, H.; Pennings, A. J. *Polymer* 1993, 34, 942.
10. Fambri, L.; Pegoretti, A.; Mazzurana, M.; Migliaresi, C. *J Mater Sci Mater Med* 1994, 5, 679.
11. Gupta, B.; Revagade, N.; Anjum, N.; Atthoff, B.; Hilborn, J. *J Appl Polym Sci* 2006, 100, 1239.
12. Gupta, B.; Revagade, N.; Anjum, N.; Atthoff, B.; Hilborn, J. *J Appl Polym Sci* 2006, 101, 3774.
13. Eling, B.; Gogolewski, S.; Pennings, A. J. *Polymer* 1982, 23, 1587.
14. Fambri, L.; Pegoretti, A.; Fenner, R.; Incardona, S. D.; Migliaresi, C. *Polymer* 1997, 38, 79.
15. Yuan, X.; Mak, A. F. T.; Kwok, K. W.; Yung, B. K. O.; Yao, K. *J Appl Polym Sci* 2001, 81, 251.
16. Fambri, L.; Bragagna, S.; Migliaresi, C. *Macromol Symp* 2006, 234, 20.

17. Cicero, J. A.; Dorgan, J. R. *J Polym Environ* 2001, 9, 1.
18. Mezghani, K.; Spruiell, J. E. *J Polym Sci B: Polym Phys* 1998, 36, 1005.
19. Schmack, G.; Tändler, B.; Optiz, G.; Vogel, R.; Komber, H.; Häußler, L.; Voigt, D.; Weinmann, S.; Heinemann, M.; Fritz, H.-G. *J Appl Polym Sci* 2004, 91, 800.
20. Gao, H.; Gu, Y.; Ping, Q. *J Contr Release* 2007, 118, 325.
21. Rissanen, M.; Puolakka, A.; Nousiainen, P.; Kellomäki, M.; Ellä, V. *J Appl Polym Sci* 2008, 110, 2399.
22. Ellä, V.; Kellomäki, M.; Törmälä, P. *J Mater Sci Mater Med* 2005, 16, 655.
23. Chen, J.; Wang, C.; Dong, X.; Liu, H. *J Polym Res* 2006, 13, 515.
24. Fischer, E. W.; Sterzel, H. J.; Wegner, G. *Kolloid Z Z Polym* 1973, 251, 980.
25. Shah, S. S.; Chay, Y.; Pitt, C. G. *J Control Release* 1992, 18, 261.
26. Wang, Y.; Steinhoff, B.; Brinkmann, C.; Alig, I. *Polymer* 2008, 49, 1257.
27. Weiler, W.; Gogolewski, S. *Biomaterials* 1996, 17, 529.
28. Ferguson, S.; Wahl, D.; Gogolewski, S. *J Biomed Mater Res* 1996, 30, 543.
29. Postema, A. R.; Luiten, A. H.; Oostra, H.; Pennings, A. J. *J App Polym Sci* 1990, 39, 1275.
30. Cao, X.; Mohamed, A.; Gordon, S. H.; Willett, J. L.; Sessa, D. J. *Thermochim Acta* 2003, 406, 115.
31. SolarSKI, S.; Ferreira, M.; Devaux, E. *Polymer* 2005, 46, 11187.
32. Sarasua, J.-R.; Rodriguez, N. L.; Arraiza, A. L.; Meaurio, E. *Macromolecules* 2005, 38, 8362.
33. Ellä, V.; Gomes, M. E.; Reis, R. L.; Törmälä, P.; Kellomäki, M. *J Mater Sci Mater Med* 2007, 18, 1253.
34. Turner Ii, J. F.; Riga, A.; O'connor, A.; Zhang, J.; Collis, J. *J Therm Anal Calorim* 2004, 75, 257.
35. Ngo, T.-T. B.; Waggoner, P. J.; Romero, A. A.; Nelson, K. D.; Eberhart, R. C.; Smith, G. M. *J Neurosci Res* 2003, 72, 227.
36. Morton, W. E.; Hearle, J. W. S. *Physical Properties of Textile Fibres*; Textile Institute: Manchester, 1997.
37. Vert, M.; Li, S. M.; Spenlehauer, G.; Guerin, P. *J Mater Sci Mater Med* 1992, 3, 432.
38. Kallela, I.; Tulamo, R.-M.; Hietanen, J.; Pohjonen, T.; Suuronen, R.; Lindqvist, C. *J Craniomaxillofac Surg* 1999, 27, 124.