Polymer Vol. 39 No. 2, pp. 467–473, 1998
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0032-3861/97/$17.00+0.00

PII: S0032-3861(97)00293-0

Rubber toughened linear and star-shaped poly(d,l-lactide-*co*-glycolide): synthesis, properties and *in vitro* degradation

C.A.P. Joziasse, H. Veenstra, M.D.C. Topp, D.W. Grijpma and A.J. Pennings*
Department of Polymer Chemistry, University of Groningen, Nijenborgh 4,
9747 AG Groningen, The Netherlands
(Received 20 December 1996; revised 20 March 1997)

Blends of D,L-lactide/glycolide copolymers were synthesized and their properties and *in vitro* degradation behaviour were evaluated as a function of chain architecture and blend composition. Tensile and impact properties of the blends are hardly influenced by matrix composition and chain architecture, but predominantly vary with the amount of rubber. *In vitro* degradation showed that hydrolytic degradation is enhanced by the incorporation of glycolide into the poly(D,L-lactide) matrix. Surprisingly, blends based on 6-arm star-shaped poly(D,L-lactide-*co*-glycolide) retain their mechanical properties for a longer period than blends with linear matrices of comparable composition. Physical aging of the linear copolymers is more severe and faster than that of star-shaped copolymers. © 1997 Elsevier Science Ltd.

(Keywords: D,L-lactide/glycolide copolymers; rubber toughening; star-shaped polymers)

INTRODUCTION

Nowadays, poly(L-lactide) (PLLA) and its copolymers are subject of substantial research efforts, aiming at applications like biodegradable biomaterials and environmentally acceptable (compostable) packing materials and disposables. Poly(lactide)s are conveniently synthesized to high molecular weights and in high yields from lactides, which are derived from lactic acid, a renewable and abundantly available carbon source.

In the human body, poly(lactide) bioresorbable devices, like osteosyntheses[1–4], hydrolyse to lactic acid which is a natural human metabolite. With the use of a degradable osteosynthesis problems associated with permanent metallic devices, like a second surgical procedure to remove the implant and stress-shielding of the healing bone are avoided. A bioresorbable osteosynthesis should retain its mechanical properties for a period of about 8 weeks, after which the healed bone has sufficient load-bearing capacity. From this point on a gradual deterioration of the mechanical properties of the implant and onset of resorption are desired.

High molecular weight semi-crystalline poly(lactide)s have excellent mechanical properties, but exhibit long degradation periods up to 8 years and may induce long term complications *in vivo*[4]. On the other hand, low molecular weight amorphous D,L-lactide stereo-copolymers fully degrade in about 20 weeks[5], but suffer from poor mechanical properties.

So, for osteosyntheses, high molecular weight amorphous poly(lactide)s are preferred. Their degradation rate may be tuned by random copolymerization of D- and L-lactide with small amounts of glycolide. In this way a more hydrophilic copolymer is obtained that is more prone to hydrolytic chain scission and consequently has a higher degradation rate[6] in combination with sufficient initial tensile strength.

High molecular weight amorphous D,L-lactide/glycolide copolymers are intrinsically brittle[7], but their toughness can be improved by rubber modification[8–14]. We have reported on blends of poly(D,L-lactide-*co*-glycolide)s (PDLLGAs) with a biodegradable poly(trimethylene-*co*-ϵ-caprolactone) (poly(TMC-*co*-ϵCL)) rubber, which have much improved impact resistance[14]. Super tough materials were obtained, that did not break in Izod notched impact testing at rubber contents slightly higher than 20 wt%.

Rubber toughening is achieved by phase separation in the blend, which yields discrete rubber particles dispersed in a continuous matrix phase[15]. Star-shaped structures display enhanced phase separation[16]. Therefore, the use of star-shaped poly(lactide)s in blends might result in better performance of our rubber modified systems.

Furthermore, branched and star-shaped polymeric structures possess a lower melt viscosity than linear polymers due to a smaller radius of gyration of the polymer chains in the melt at comparable molecular weights[17,18]. Branched polymers can be processed at lower temperatures than their linear counterparts, which could be advantageous, especially in the processing of thermo-labile polymers like poly(lactide)s[19].

Branched and star-shaped macromolecules have a different entanglement structure and possess a higher density of chain-ends than linear chains of comparable molecular weight. This could affect mechanical properties, degradation behaviour and physical aging. Thermodynamically glassy polymers are in a non-equilibrium state at temperatures below their glass transition temperature (T_g). They can be regarded as solidified super-cooled liquids, whose volume, enthalphy and entropy are larger than their respective equilibrium values. Even below T_g polymeric chains retain some mobility, resulting in a slow progression

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* To whom correspondence should be addressed

towards the equilibrium state, the process which is referred to as physical aging[20]. A convenient technique to reveal physical aging is differential scanning calorimetry (DSC), where the reduction of enthalpy H from the aging process is recorded as a recovery peak most commonly superimposed on the specific heat jump (ΔC_p) at T_g. Physical aging should be distinguished from chemical aging, like hydrolysis, which in the context of biodegradable polymers is commonly referred to as "aging".

The synthesis of well-defined high molecular weight star-shaped poly(lactide)s requires well controlled reaction conditions and highly pure monomers, initiators and catalysts to avoid contamination of the star-shaped polymer sample with linear polymeric structures. Hydroxyl-functions serve as initiating species for the ring-opening polymerization of cyclic esters, like lactide, glycolide and lactones. Indeed, a large number of polyols, like glycerol[21], pentaerythritol[22], inositol[23] and other sugar derivatives are readily available as initiators. In this study, the polymerization of 6-arm star-shaped D,L-lactide/glycolide copolymers was initiated by dipentaerythritol and catalyzed with freshly prepared and purified stannous acetylacetonate ($\mathrm{(Sn(acac))_2}$)[24] instead of tin(II) 2-ethyl hexanoate (stannous octanoate, $\mathrm{Sn(oct)_2}$). For ring-opening polymerizations $\mathrm{Sn(oct)_2}$ is commonly applied, but inevitably contains mono-functional impurities[25].

Altogether, it is important to investigate the influence of chain architecture on mechanical properties, *in vitro* degradation behaviour and thermal properties of lactide/glycolide copolymers and their blends with poly(TMC-*co*-ϵCL) rubber.

In this paper the synthesis of linear and 6-arm star-shaped poly(D,L-lactide-*co*-glycolide)s (PDLLGAs) with glycolide contents 0–12 wt% is described. From these copolymers blends were prepared with 0–30 wt% high molecular weight linear poly(TMC-*co*-ϵCL) and their mechanical properties were evaluated. In the second part of this paper data on the *in vitro* degradation of these blends are presented. Finally, thermal properties and physical aging of PDLLGAs and their blends will be described.

EXPERIMENTAL

Materials

Monomers L- and D-lactide, glycolide (Purac, The Netherlands) and trimethylene carbonate (TMC, Boehringer, Germany) were purified by recrystallization under dry N_2 from sodium dried toluene, toluene/dimethoxy ethylene glycol mixture or *o*-xylene, respectively. ϵ-Caprolactone (ϵCL, Janssen, Belgium) was dried on $\mathrm{CaH_2}$ and purified by vacuum distillation. Dipentaerythritol (Janssen, Belgium) was used as received and kept over $\mathrm{P_2O_5}$ under vacuum.

Bulk polymerizations were carried out in vacuum sealed silanized glass ampoules at 130°C for 4 days using stannous octanoate ($\mathrm{Sn(oct)_2}$) or stannous acetylacetonate ($\mathrm{Sn(acac)_2}$) as a catalyst. $\mathrm{Sn(acac)_2}$ was prepared according to Wakeshima et al.[24] and administered into the ampoules with an oven dried glass syringe as a solution in sodium dried pentane.

High molecular weight linear D,L-lactide/glycolide copolymers and poly(TMC-*co*-ϵCL) rubber were polymerized without the addition of initiator, while the polymerization of star-shaped D,L-lactide-glycolide copolymers was initiated with a calculated small amount of dipentaerythritol. Low molecular weight poly(D,L-lactide) was synthesized with 1-hexanol initiator.

Blends of matrix polymer and rubber were prepared by precipitating a 2% solution of matrix polymer and rubber in chloroform into ethanol (96%). The precipitation was vacuum dried at 40°C to constant weight.

Samples for mechanical testing and degradation studied were moulded at 130°C (PHI-instruments, 40 × 10^3 lb. laboratory press) in stainless steel moulds between Teflon® sheets.

Characterization

Polymerization conversion and blend composition were measured by ^{1}H-NMR (Varian 200 MHz). Molecular weights were determined in tetrahydrofuran or chloroform with SEC (Spectra Physics, Styragel® columns; Shodek RI-71, Viskotek H502 and DAWN MALLS-detectors) relative to narrow poly(styrene) standards.

Thermal properties of the polymers and blends were measured with an indium calibrated DSC-7 (Perkin Elmer) on 5–10 mg samples at a heating rate of 10°C/min. Enthalpy relaxation (ΔH_r) of the polymers was calculated by subtraction of the DSC-trace of quenched material from that of the aged sample. First a DSC-sample was quenched from 150°C and its DSC-trace recorded at a scanning rate of 20°C/min. Again the sample was quenched and then kept at 37°C in the DSC apparatus or in an oven for the desired aging time. After quenching from 37°C the DSC trace of the aged sample was recorded. Quenching was performed by submersion of the sample in liquid nitrogen under stirring.

Micro-tensile specimens (ASTM D1708) were tested at a crosshead speed of 10 mm/min with an Instron 4301 tensile tester. Although ASTM D1708 does not give an absolute measure for E_y, the data obtained may be used for comparison between samples.

Impact tests were performed according to Izod notched (ASTM D256-56) and Dynstat unnotched (DIN 53453) specifications (Zwick pendulum impact tester).

***In vitro* hydrolytic degradation**

Samples for *in vitro* degradation were weighed (original mass, m_0), their dimensions were recorded (tensile specimen typically measured 60 × 4 × 2 mm and Dynstat 15 × 10 × 2 mm) and then were placed in vials containing phosphate buffer (pH = 7.0). The vials were placed in a stirred water bath controlled at 37°C. After a scheduled *in vitro* degradation period, duplicate samples were collected from the vials, dipped dry with a soft tissue, weighed (wet mass: m_w) and measured again. After subsequent mechanical testing the samples were dried in a vacuum stove at 40°C to constant weight (dry mass: m_d). Mass loss (ML) and water uptake (%$\mathrm{H_2O}$) were calculated from:

(1) mass loss = $(m_0 - m_d)/m_0 \cdot 100\%$
(2) water uptake = $(m_w - m_d)/m_d \cdot 100\%$

The surface morphology of the dried degradation samples was analyzed after gold sputtering by scanning electron microscopy (SEM) with an ISI-DS 130 microscope operated at 20 kV. Further characterization of the degraded samples included ^{1}H-NMR, DSC and SEC as described before.

RESULTS AND DISCUSSION

The first part of this section describes the preparation of linear and 6-arm star-shaped lactide/glycolide copolymers

Table 1 Composition, weight average molecular weight (M_w) and glass transition temperature (T_g) of poly(D,L-lactide-*co*-glycolide)s, bulk polymerized under dry N_2/vacuum at 130°C using indicated catalyst. Optionally, an initiator with functionality (*f*) was applied

Polymer	*f* (-)	Initiator	Catalyst	Composition[a] (wt%) L-lac	D-lac	glyc	M_w (10^3)	T_g (°C)
P1	1	1-hexanol	$Sn(oct)_2$	85	15	—	64	54
P2	1	-	$Sn(oct)_2$	85	15	—	400	57
P3	1	-	$Sn(oct)_2$	50	50	—	400	53
P4	1	-	$Sn(oct)_2$	74	20	6	520	53
P5	1	-	$Sn(oct)_2$	73	15	12	390	53
P6	6	dipentaerythritol	$Sn(acac)_2$	80	15	5	450	55
P7	6	dipentaerythritol	$Sn(acac)_2$	79	10	11	340	55

[a] lac = lactide, glyc = glycolide

and their blends with poly(TMC-*co*-εCL) rubber. The physical properties of these materials are presented and discussed with respect to chemical composition and chain architecture of the poly(D,L-lactide-*co*-glycolide).

The second part of this section deals with the *in vitro* degradation behaviour of rubber modified poly(D,L-lactide-*co*-glycolide)s. Data on the deterioration of tensile and impact strength with ongoing mass loss and water absorption as a function of degradation time are presented and the influence of chain architecture and glycolide content are discussed. *In vitro* degradation of the blends is carried out in a buffer solution at 37°C to mimic the hydrolytic cleavage of ester links in the polymer backbone at body temperature. This aging temperature (T_a) is 17°C below the glass transition temperature ($T_g = 55$°C) of the poly(D,L-lactide-*co*-glycolide) matrix. Under these conditions physical aging is known to be appreciably fast[20] and may very likely influence the properties of the degrading material. Until now, no information concerning this phenomenon is available from literature, so physical aging of the lactide/glycolide matrix copolymers was studied with DSC, the results of which are described in the last part of this section.

Synthesis and properties of lactide/glycolide copolymers and blends

D- and L-lactide and glycolide (0–12 wt% glycolide) were melt-polymerized at 130°C to high molecular weight amorphous copolymers in high yields (> 98%). To obtain 6-arm star-shaped macromolecules dipentaerythritol was used as an initiator. If dipentaerythritol was applied, polymerisations were catalysed with $Sn(acac)_2$ instead of $Sn(oct)_2$. Low molecular weight poly(85L/15D-lactide) was synthesized using 1-hexanol initiator. High molecular weight poly(TMC-*co*-εCL) rubber was polymerized without the use of initiator with $Sn(oct)_2$ catalyst. All polymers had polydispersity index in the range 2.1–2.3, which is appropriate for polymers prepared by ring-opening polymerization.

Table 1 summarizes data on polymerization conditions, thermal properties and molecular weights (M_w) of PDLLGA's that were used in the blends for the *in vitro* degradation study.

The T_g of the lactide/glycolide copolymers decreases by a few degrees with increasing glycolide content, which is readily explained by the fact that homopolymer poly(glycolide) has a lower glass transition temperature ($T_g = 36$°C [26]) than amorphous poly(D,L-lactide). Furthermore, *Table 1* indicates that low molecular weights (P1) and increasing D-lactide contents (P3) result in a lowering of T_g[7]. The T_g (−45°C) of the high molecular weight ($M_w > 500 \times 10^3$) poly(TMC-*co*-εCL) rubber used in the blends is in good agreement with previously reported values[8–14].

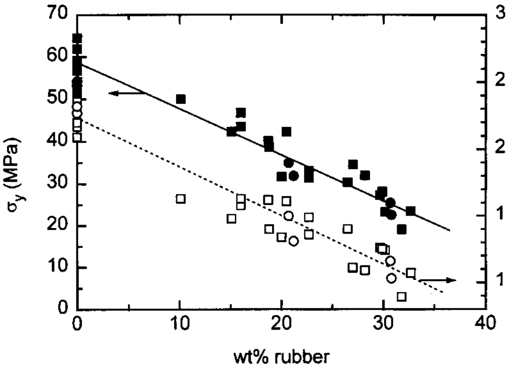

Figure 1 Tensile properties of PDLLGA blends as a function of poly(TMC-co-εCL) rubber content; (■) linear and (●) star-shaped matrices (0–12 wt% glycolide); closed symbols: yield strength σ_y, open symbols: Young's modulus E_Y

High molecular weight amorphous PDLLGAs were blended with poly(TMC-*co*-εCL) rubber (0–30 wt% rubber). A comparison between linear and 6-arm star-shaped lactide/glycolide copolymers was made in order to evaluate the influence of chain architecture on mechanical the properties of the blends.

Figure 1 shows that the tensile yield strength (σ_y) and Young's modulus (E_Y) decrease linearly with increasing rubber content of the blend. Surprisingly, the mechanical properties of blends obtained from linear and 6-arm star-shaped PDLLGA are very much comparable. Since star-shaped polymers possess a higher number of end-groups it would be expected that they have slightly lower T_g and lower E_Y. Apparently this effect, if present at all, is obscured by the high molecular weight of the PDLLGA. DSC-traces and dynamic mechanical thermal spectra of all blends revealed well separated T_g for rubber and matrix, indicating good phase separation. Furthermore, the influence of glycolide content (0–12 wt%) on the mechanical properties of the blends was also found to be negligible.

Table 2 provides an overview of composition and initial mechanical properties of some blends that were selected for the *in vitro* degradation study (see next section).

Rubber toughening results in a marked change of the deformation behaviour of the lactide/glycolide copolymers from brittle to ductile. Strain at break (ϵ_b) increased dramatically from a few percent for the pure matrix polymer

Table 2 Blend composition and initial mechanical properties of rubber toughened PDLLGAs used in the *in vitro* degradation study (yield strength σ_y and Izod notched impact strength (Izod I.S.)). The poly(TMC-co-ϵCL) rubber used in the blends had $M_w > 500 \times 10^3$

Blend	Matrix[a]	Rubber content (wt%)	σ_y (MPa)	Izod I.S. (J/m)
	linear			
B1	P2	20.4	32	250
B2	P5	22.7	31	360
B3	P5	30.8	28	n.b.[b]
	Star-shaped			
B4	P6	20.2	35	200
B5	P6	30.7	25	n.b.[b]
B6	P7	21.2	32	370

[a] for sample codes see *Table 1*
[b] n.b. = no break

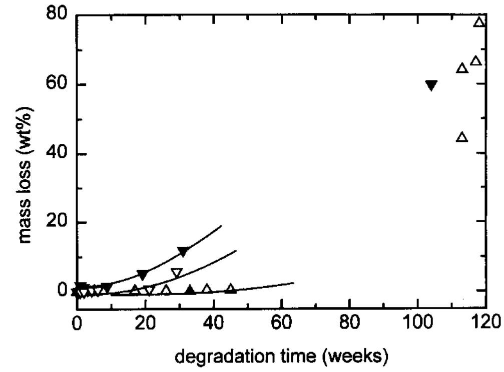

Figure 2 Mass loss as a function of *in vitro* degradation time at 37°C for amorphous PDLLA: (▲) P2: high MW PLA85 and (△) B1: blend with 20 wt% poly(TMC-co-ϵCL) rubber, (▼) P1: low MW PLA85, (▽) P3: high MW PLA50

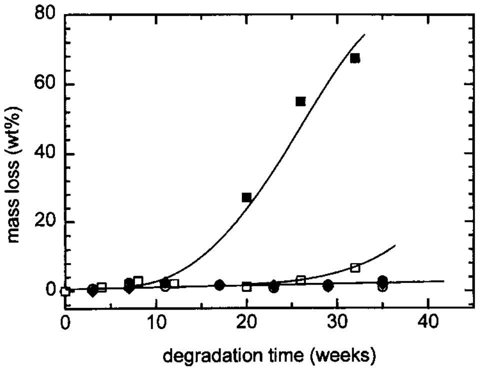

Figure 3 Mass loss as a function of *in vitro* degradation time at 37°C for amorphous PDLLGA blends with poly(TMC-co-ϵCL) rubber: linear matrix (■) B2 and (□) B3, 6-arm star-shaped matrix (●) B4, (○) B5 and (◆) B6

to more than 200% for blends containing 20 wt% rubber or more. This indicates that during deformation in a large amount of strain energy can be dissipated, resulting in enhanced toughness. *Table 2* shows that all blends with approximately 20 wt% rubber have excellent toughness as indicated by their high Izod notched impact strength (Izod I.S.) values, ranging from 200 to 370 J/m, while blends with 30 wt% rubber did not break in Izod testing[14].

In vitro degradation

The degradation of PDLLGA blends with poly(TMC-*co*-ϵCL) rubber was investigated by *in vitro* hydrolysis of moulded samples at 37°C. Mass loss, water uptake and mechanical properties were recorded as a function of hydrolysis time.

In the blends linear and star-shaped lactide/glycolide copolymers were used as the matrix to study the influence of chain architecture on the degradation behaviour. Additionally the influence of glycolide content in the poly(lactide/glycolide) matrix and the poly(TMC-*co*-ϵCL) rubber content of the blend were studied.

Mass loss and water uptake. The tuning of mass loss with degradation time is an important factor in the design biodegradable implants. *Figure 2* shows long-term mass loss data as a function of *in vitro* degradation time for amorphous unmodified high molecular weight poly(85L/15D-lactide) (PLA85, P2) and a blend of this PLA85 with 20 wt% poly(TMC-*co*-ϵCL) rubber (B1). This blend has been tested clinically with promising results[27]. PLA85 and its blend are resorbed 60–80 wt% in 2 years, which is rather slow.

Also included in *Figure 2* are data for low molecular weight PLA85 (P1) and a poly(50L/50D-lactide) (P3), which indicate that a lower molecular weight or an increasing D-lactide content increase the resorption rate of D,L-lactide copolymers.

The degradation rate of poly(lactide) blends was successfully increased by the incorporation of glycolide units into the poly(lactide) matrix, which is clear from comparison of *Figures 2 and 3*. Blends based on linear lactide/glycolide copolymers (B2 and B3) show onset of mass loss at 10 resp. 25 weeks, compared to 50 weeks for blend B1. Furthermore, *Figure 3* shows the influence of chain architecture on degradation behaviour. Over a degradation period of 35 weeks mass loss of blends based on 6-arm star-shaped PDLLGA (B4-B6) is restricted to only a few percent. On this time scale no significant differences are observed between the matrices with 5 and 11 wt% glycolide.

In *Figure 4*, water uptake of the PDLLGA blends is plotted as a function of degradation time.

Figure 4 shows that after a certain induction period water uptake of the remaining material increases significantly (B2 and B3). For the hydrolytic cleavage of ester bonds diffusion of water into the glassy polymeric samples is necessary. In turn, hydrolysis generates an increasing number of carboxylic functions as the molecular weight decreases. So, the material becomes more hydrophilic, which results in an increased water uptake.

The onset of water uptake and mass loss (see also *Figure 3*) coincide at a certain degradation period when M_w of the PDLLGA matrix has dropped considerably to a value

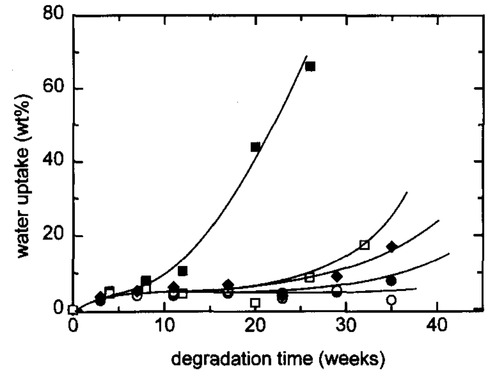

Figure 4 Water uptake as a function of *in vitro* degradation time at 37°C for amorphous PDLLGA blends with poly(TMC-co-εCL) rubber: linear matrix (■) B2 and (□) B3, 6-arm star-shaped matrix (●) B4, (○) B5 and (◆) B6

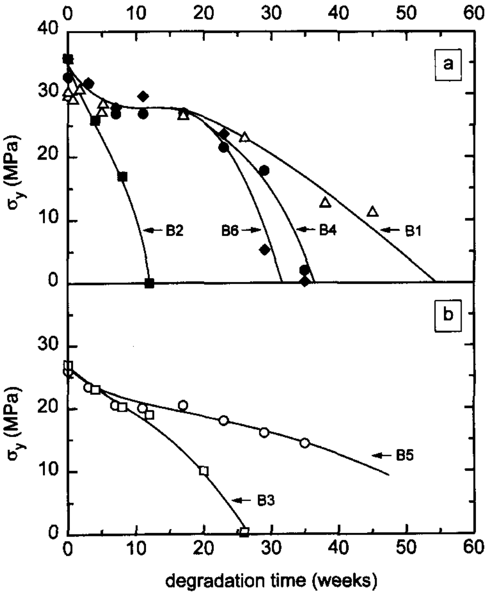

Figure 5 Tensile yield strength (σ_y) of PDLLGA blends as a function of *in vitro* degradation time at 37°C: (a) (△) B1: linear PLA85, (■) B2: linear, (●) B4 and (◆) B6: star-shaped PDLLGA matrix with 20 wt% poly(TMC-co-εCL) rubber; (b) (□) B3: linear and (○) B5: star-shaped PDLLGA matrix with 30 wt% poly(TMC-co-εCL) rubber

in the order of magnitude 10^4, as was established with SEC.

Water uptake is calculated with respect to the dry mass (m_d) for the remaining material and should therefore not be confused with excessive swelling of the samples, as has been reported elsewhere for unmodified poly(lactide)s[5]. Monitoring the dimensions of the degrading samples showed a maximum increase of 5% after 35 weeks, which corresponds to an expansion on volume of approximately 15%.

Mechanical properties. For blends based on linear and star-shaped PDLLGA, containing 0–12 wt% glycolide (B1-B6, see *Table 2*) data on tensile yield strength (σ_y) during *in vitro* hydrolytic degradation are compiled in *Figure 5a* and *b*.

In general, with increasing *in vitro* degradation time, σ_y of the blends decreases, which is caused by a lowering of the molecular weight of the PDLLGA matrix due to hydrolysis. A higher glycolide content in the matrix copolymer results in an increased rate of degradation as is shown by the tensile data for blends containing 20 wt% rubber (B1/B2 and less pronounced B4/B6). Another important observation from *Figure 5* is that the decrease of σ_y with degradation time is different for blends with a different chain architecture of the matrix. The blend with a linear glycolide containing matrix (B2) shows a rapid decrease of σ_y, while the blend of comparable chemical composition with a star-shaped matrix (B6) retains appreciable σ_y up to 25 weeks. This is in agreement with the results for mass loss and water uptake.

Comparison of *Figure 5a* and *b* shows that the highest rates of degradation are observed at the lowest rubber contents in the blend (B2/B3 and B4/B5).

For all blends the decrease of σ_y was accompanied by a reduction of strain at break (ϵ_b), indicating that the toughness of the blends also decreased during degradation. To establish how severely the toughness of the materials is affected by hydrolysis, Dynstat unnotched and Izod notched impact strength (I.S.) of the degrading blends was measured.

Up to 11 weeks none of the blends with star-shaped matrices (B4-B6) showed break of the Dynstat specimens in impact testing, followed by a decrease in impact strength from week 17 on for blends with 20 wt% rubber. The Dynstat specimens of the blend B5 containing 30 wt% rubber did not break until after 35 weeks. Impact strength of blends with linear PDLLGA matrices began to decrease much earlier (4–8 weeks).

In notched Izod impact testing of the blends with star-shaped matrices (B4 and B6) containing 20 wt% rubber still did not break after 23 weeks of degradation. This compares favourably with the blend with linear PDLLGA matrix containing 30 wt% rubber (B3), which showed 'hinge fracture' after a degradation period of only 20 weeks.

Morphology. SEM-analysis of the surfaces of the degraded specimens revealed that in all samples a porous-like surface texture developed with increasing degradation time, as is shown in *Figure 6*.

This effect is less pronounced for sample B5 (*Figure 6c*), which was degraded for 17 weeks. Indeed, sample B5 retained its tensile strength much longer than sample B3 (*Figure 6b*), which shows a sponge-like surface in SEM after only 12 weeks, with pore diameters in the micrometer range.

Some initial surface roughness can be discerned in the non-degraded sample (*Figure 6a*, B3) and is presumably caused by the moulding procedure. Increasing surface porosity has also been reported for the PLA85/poly(TMC-*co*-εCL) blend (B1) during *in vivo* degradation[27]. It remains unclear whether porosity is caused by leaching-out of the rubber from the blend, by mass loss of the blends as a whole or by more complex mechanisms like phase-inversion of the blend during degradation.

General. Summarizing, blends based on star-shaped PDLLGA show a better retention of mechanical properties during *in vitro* degradation. At 130°C glycolide has a higher reactivity[28], which in bulk polymerizations leads to a gradual compositional change of the growing chain. The core of a star-shaped polymer near the initiating hydroxyl functions will be rich in glycolide, while at high conversions the branch-ends will be rich in D,L-lactide. In this way, the more hydrolytically sensitive glycolide units could be shielded by lactide-rich sequences. Furthermore, in the core of a star-shaped macromolecule the segment density is higher than in the branches[29–31], which hinders the

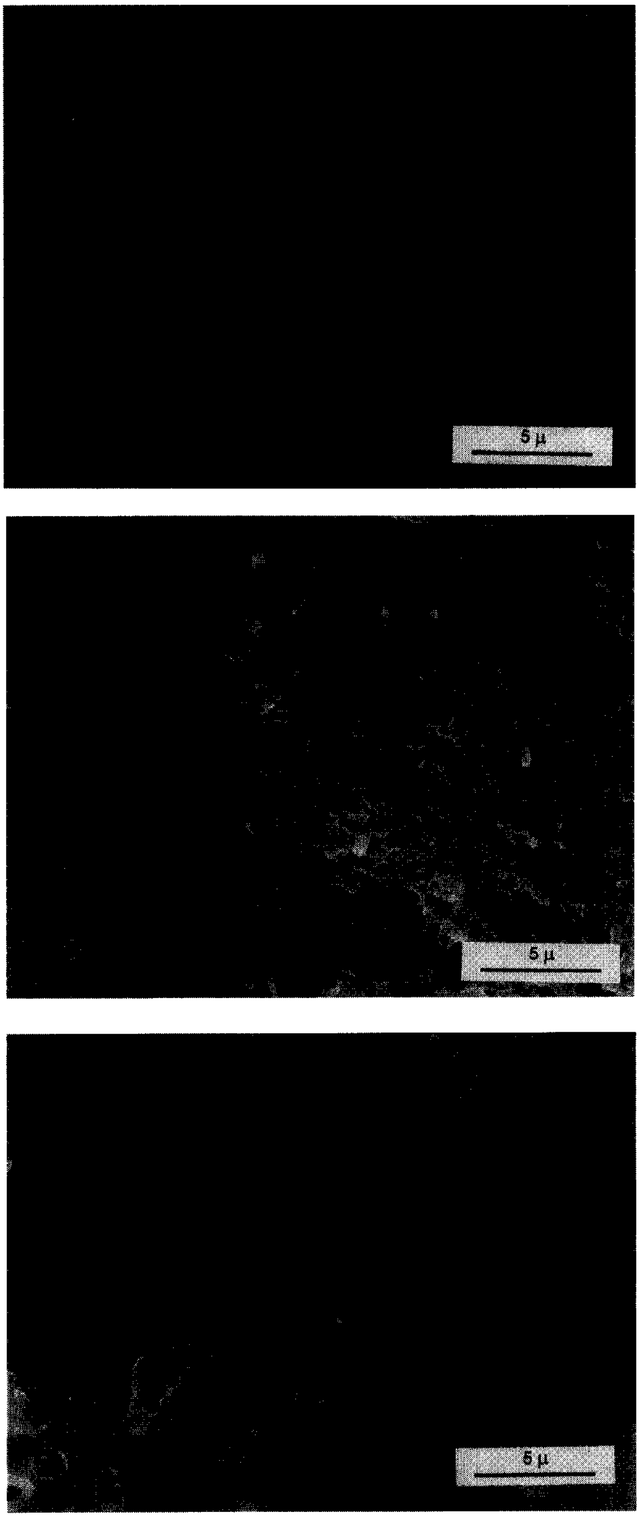

Figure 6 SEM images of PDLLGA blends degraded *in vitro* at 37°C containing 30 wt% poly(TMC-co-ϵCL) rubber: blend B3 at (A) t = 0 and (B) after 12 weeks, (C) blend B5 after 17 weeks

diffusion of water molecules locally and would enhance the aforementioned shielding.

In a rubber modified polymer, rubber particles prevent catastrophic crack growth during deformation by tip blunting of growing cracks[15]. Hypothetically the same toughening mechanism could prevent stress-cracking during hydrolytic degradation, resulting in a longer retention of tensile properties of the poly(D,L-lactide-*co*-glycolide) blends at higher rubber contents.

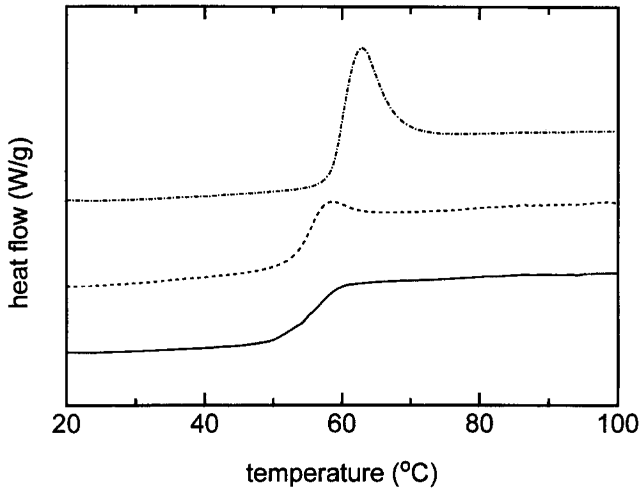

Figure 7 DSC-traces of star-shaped PDLLGA (P6) aged at 37°C: (—) quenched from 150°C in liquid N_2, aged for (– — –) 40 min and (— - -) 45 h (scanning rate 20°C/min)

SEC on the degraded specimens showed a peak for the poly(TMC-*co*-ϵCL) rubber that only slowly shifts to lower molecular weights. Indeed, poly(TMC-*co*-ϵCL) rubber has been shown to degrade relatively slowly[32] when compared to the PDLLGA matrix. An enrichment of the remains of the blends with poly(TMC-*co*-ϵCL) rubber was confirmed by ^{1}H-NMR.

Thermal properties

As an illustrative example, *Figure 7* presents the DSC-traces of a PDLLGA-sample after quenching from the melt and after aging at 37°C. A large enthalpy recovery peak on T_g is observed after an aging time (t_a) of only 45 hours. Indeed, *in vitro* degraded samples of the blends displayed comparable DSC-traces around T_g of the PDLLGA matrix.

To study the effect of chain architecture on physical aging linear and 6-arm star-shaped PDLLGAs (P4-P7) were aged at 37°C ($T_g - T_a = 170$°C). In *Figure 8a* and *b* enthalpy relaxation (ΔH_r) as a function of t_a is compared for two sets of PDLLGA with 5–6 and 11–12 wt% glycolide content.

At all aging times ΔH_r of the linear PDLLGA's is larger than that of the 6-arm star-shaped PDLLGAs, indicating a higher degree of physical aging for the linear lactide/glycolide copolymers. This could mean that the overall structure of the star-shaped copolymers is more dense, thus reducing the difference with the thermodynamical equilibrium state, which is most dense.

Furthermore, the slope of the curves tends to be somewhat steeper for the linear PDLLGA, which indicates that linear chains relax faster than star-shaped ones, i.e. the mobility of star-shaped macromolecules in the glassy state is lowered by a large number of entanglements per chain molecule.

A more dense structure of star-shaped poly(D,L-lactide-*co*-glycolide)s in the glassy state might implicate a reduced penetration of water into the samples, which would explain the improved retention of mechanical properties that has been observed for blends based on star-shaped polymers. If linear PDLLGAs age faster, these matrices will become more brittle in a shorter time span, possibly resulting in a faster deterioration of impact strength, even though poly(TMC-*co*-ϵCL) rubber is present as a modifier.

Matters are complicated by the fact that T_g of the samples is not constant during degradation and so $T_g - T_a$ is constant

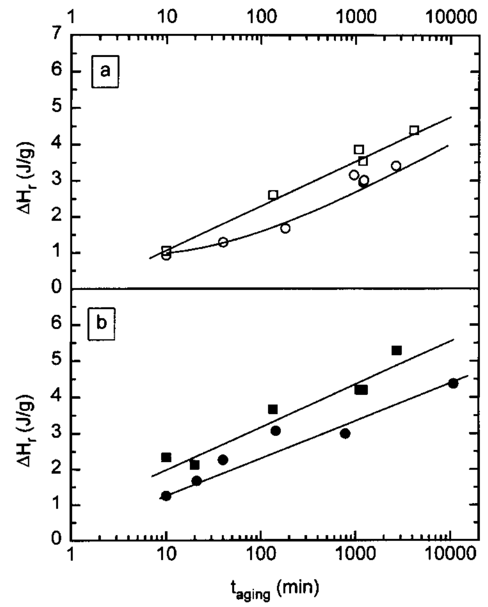

Figure 8 Physical aging of linear and 6-arm star-shaped PDLLGAs at 37°C, measured as the enthalpy relaxation (ΔH_r) of aged samples: *a*) (□) P4: linear and (○) P6: star-shaped, *b*) (■) P5: linear and (●) P7: star-shaped

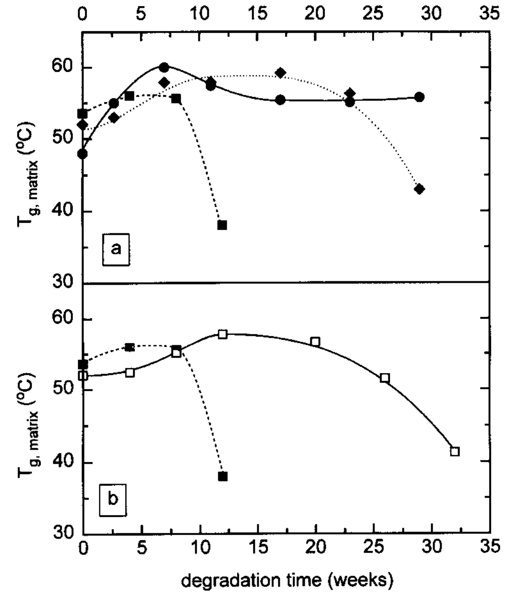

Figure 9 Glass transition temperature (T_g) of the PDLLGA matrix in blends during *in vitro* degradation at 37°C: (a) (■) B2, (●) B4 and (◆) B6: PDLLGA blends with 20 wt% poly(TMC-co-∊CL) rubber; (b) (■) B2: 20 wt% and (□) B3: 30 wt% poly(TMC-co-∊CL) rubber

neither. Due to the decrease of molecular weight and the uptake of water T_g of the PDLLGA matrix eventually decreases significantly as is shown in *Figure 9*. As soon as T_g drops to 37°C or lower, PDLLGA becomes fully relaxed, since then the matrix enters the rubbery state. Figure 9 shows the same trends for T_g as observed earlier for the mechanical properties during degradation. A higher glycolide content of the PDLLGA matrix results in an early drop of T_g, while a higher rubber content of the blend slows down the degradation process. Eventually, the T_g of the matrix broadens and becomes practically indiscernible from the T_g of the rubber component.

It is clear that the physical aging of linear and star-shaped PDLLGAs is different. So far it remains unclear how this influences the degradation behaviour of PDLLGA blends. In lactide/glycolide copolymers physical aging and hydrolytic degradation ('chemical aging') act simultaneously and probably influence each other, the mechanisms of which we have only just begun to understand.

CONCLUSIONS

Amorphous linear and 6-arm star-shaped poly(D,L-lactide-*co*-glycolide)s that were rubber toughened with poly(TMC-*co*-∊CL) rubber have excellent mechanical properties that are very little affected by the composition and chain architecture of the matrix, but mainly depend on the amount of rubber in the blend.

In vitro degradation showed that tough blends of 6-arm star-shaped poly(D,L-lactide-*co*-glycolide) retain their mechanical properties, like tensile strength and impact resistance, for a longer period than the corresponding blends with linear matrices. The incorporation of increasing amounts of glycolide in the matrix speeds up degradation, while higher rubber contents delay the deterioration of mechanical properties.

Blends with star-shaped matrices containing 5 wt% glycolide have a degradation pattern which makes them suitable for application in dynamically loaded resorbable osteosyntheses. These results substantiate the belief of the authors that the optimum properties and degradation pattern of lactide based blends can be obtained by further tuning of composition and chain architecture.

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