

High impact strength as-polymerized PLLA

D. W. Grijpma, A. J. Nijenhuis, P. G. T. van Wijk, and A. J. Pennings*

Department of Polymer Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

Summary

As-polymerized poly(L-lactide), (PLLA), has a much higher impact strength than after compression moulding. Several routes have been explored to further increase the impact strength of nascent PLLA. First results on the preparation of composites with carbon fibres, the copolymerization with trimethylene carbonate and ϵ -caprolactone, the block copolymerization with rubbers and the plasticization with ethyl acetate indicate possibilities to prepare much more impact resistant as-polymerized PLLA materials.

Introduction

In the development of (degradable) materials for use in orthopaedic applications such as bone fracture fixation devices, much attention is focused on improving the tensile strength and modulus of these materials (1,2). Higher tensile strengths would increase the range of applications, the percentage of successful stabilizations and perhaps even allow the fixation of fractures in stressed parts of the skeleton. In addition, a matching of the material's Young's modulus with that of bone would minimize stress shielding and bone resorption. But it should be kept in mind however, that the actual forces acting across the fracture and on the bone, as well as stress concentrations, depend on the dimensions and shape of the applied fixation device.

On the other hand many problems related to the brittleness of the used materials still need to be recognized and solved (3,4,5,6). The failure of resorbable screws below the head is an often occurring and major complication (7,8) which limits the use of such devices. New screw designs attempt to overcome these less adequate material properties (7,8,9,10). We believe that high impact resistance is essential in the successful application of degradable materials in fracture fixation and any other use where dynamic loading takes place.

It has already been shown (11), that as-polymerized PLLA shows high values of impact strength when compared to compression- or injection moulded PLLA. It is our objective to further improve the impact strength of the as-polymerized PLLA. In this paper we wish to report preliminary results.

Experimental

Fibre composites: In situ polymerizations of L-lactide were carried out in the presence of carbon fibres. Strands of carbon fibres, (GRAFIL, Courtaulds Ltd., Coventry, England) were aligned in a small glass cylinder open at both ends. The filled tube was then placed in one leg of an "inverted Y"-shaped polymerization vessel. In the other leg, L-lactide and catalyst were brought in. After evacuation, the L-lactide was melted in an oil bath and poured over the fibres by tipping the polymerization vessel. The space between fibres was

*Corresponding author

filled by applying N₂ pressure (1 atm). Polymerizations were carried out in the presence of Sn-octoate at 120 °C for 5 days. Dynstat impact strength specimens (15x10x3 mm) were machined from the as-polymerized composite. Experiments with PET and PLLA fibres were also carried out.

Copolymers: Copolymers of L-lactide and ϵ -caprolactone (ϵ -cl) or trimethylene carbonate (TMC) were prepared in the melt at 110 °C with stannous octoate as the catalyst (12,13). The polymerization time was 10 days. TMC was prepared by depolymerization of low molecular weight poly(trimethylenecarbonate) (14), and purified by recrystallization from sodium dried *o*-xylene. Copolymer composition was determined by 300 MHz ¹H NMR.

Blockcopolymers: As-polymerized blocky copolymers of 50/50 L-lactide/ ϵ -caprolactone rubbers and L-lactide were prepared in "inverted Y"-shaped polymerization vessels. In one leg of the polymerization vessel a 50/50 mixture of L-lactide and ϵ -caprolactone was polymerized with stannous octoate for a period of 3 hrs at 100 °C. At this point the rubber was still fluid and could be mixed with the molten L-lactide from the other leg of the vessel. Polymerization was continued at different temperatures until complete conversion. Rubber fractions were 30% by mass.

Plasticization: Specimens of 15x10x2 mm machined from a block of as-polymerized PLLA were placed in excess ethyl acetate for 2 days at room temperature. The swollen samples (14 mass % ethyl acetate absorbed) were then dried at 40 °C in vacuo for varying periods of time. The possibility of plasticization by water was also verified.

Compression moulding and materials testing: Sheets of L-lactide homo- and copolymers (2x15x100 mm) were produced by compression moulding the as-polymerized material at 210 °C for 5 min and rapidly cooling down to room temperature. Unnotched impact strength measurements were carried out according to ASTM D256-78 (Izod) and DIN 53453 (Charpy and Dynstat) specifications. Sample sizes of compression moulded and as-polymerized specimens for Izod, Charpy and Dynstat tests were respectively 60x12.7x4 mm, 50x6x4 mm and 15x10x2 mm.

Tensile testing was done on an Instron 4301 tensile testing at a crosshead speed of 10 mm/min. The dimensions of the samples were 50x6x4 mm.

Results and Discussion

A favoured method of manufacturing articles from thermoplastic materials is by compression- or injection moulding. Although this technique allows the mass production of objects of many sizes and shapes, it will alter the original morphology, structure and properties of the nascent bulk synthesized poly(L-lactide) (12).

Table 1:
Mechanical properties of poly(L-lactide).

preparation method	tensile strength (MPa)	bending modulus (GPa)	impact strength	
			Charpy (kJ/m ²)	Dynstat (kJ/m ²)
as-polymerized	60	5	47	11-13
compression moulded	65	4	12	2-4

In Table 1 it can be seen that for very high molecular weight PLLA tensile strength and modulus remain more or less unchanged after processing, while impact strength decreases dramatically after compression moulding.

Apart from this loss in impact strength, other material properties will be affected by injection moulding. The high melting temperature of PLLA requires the material to be moulded at 200 °C or more, making it susceptible to thermal and hydrolytic degradation. Crystallization of PLLA in the cooling period of the processing cycle may lead to shell-core effects and also induce stresses in the material. Crystallinity might also change during storage of the object after production, leading to variations of mechanical and thermal properties in time.

In the case of L-lactide bulk polymerization, crystallization of PLLA takes place at elevated temperatures over relatively long polymerization (and annealing) times. The above mentioned difficulties will therefore not arise. Advantage of this stability and of the superior impact properties may be taken when bone fixation plates and screws are machined from a block of as-polymerized poly(L-lactide). Reaction injection moulding (RIM) is of course another, industrially perhaps more attractive, method of manufacturing as-polymerized PLLA objects.

We explored a number of approaches to further improve the impact strength of as-polymerized PLLA:

Fibre composites

The preparation of composite materials in order to improve mechanical properties of materials has been widely investigated and described (15). Compression moulding of PLLA/PGA fibre systems and sintered PGA and PLLA fibres result in high strength and modulus materials with improved impact strength (3,4,16,17). Polymerization of L-lactide in the presence of high strength fibres will result in a composite material consisting of fibres embedded in an as-polymerized PLLA matrix.

Although they are not degradable, carbon fibres were first used in a model study to reinforce as-polymerized PLLA. Complete filling of the space between the fibres with the monomer melt was accomplished by the method explained in the experimental section.

Table 2:

Influence of molecular weight and carbon fibre reinforcement on the impact strength of as-polymerized PLLA.

\bar{M}_v ($\times 10^{-5}$)	C-fibres (weight %)	Impact Strength (Dynstat) (kJ/m ²)
0.5	0	1.9
1.0	35	6.2 ± 0.6
3.1	0	10.8 ± 0.7
3.3	0	10.8 ± 2.0
3.3	34	21.8 ± 4.5
5.1	0	12.1 ± 2.4
5.1	36	62.8 ± 1.9
7.7	0	12.7 ± 1.5
7.8	0	11.4

From the results presented in Table 2, it can be seen that several factors greatly influence the impact strength of the material. High molecular weight of the matrix polymer results in the highest values of impact strength. Incorporation of 35 % by weight of long parallel carbon fibres oriented perpendicular to the direction of impact greatly increases the impact strength. A maximum value of 63 kJ/m^2 was obtained for a matrix molecular weight of 5×10^5 . In the presence of voids in the matrix or in the case of incomplete filling, much lower values are obtained.

Figure 1 is an SEM micrograph of the fracture surface after impact testing of the most impact resistant sample containing 36 % carbon fibres. It can be observed that the fibres are well embedded in the polymer matrix. The fibre surface is well wetted, and voids are not present. During fracture of the sample, matrix debonding and carbon fibre pull-out has taken place. Crack tip blunting and frictional energy dissipation account for the high impact resistance (15).

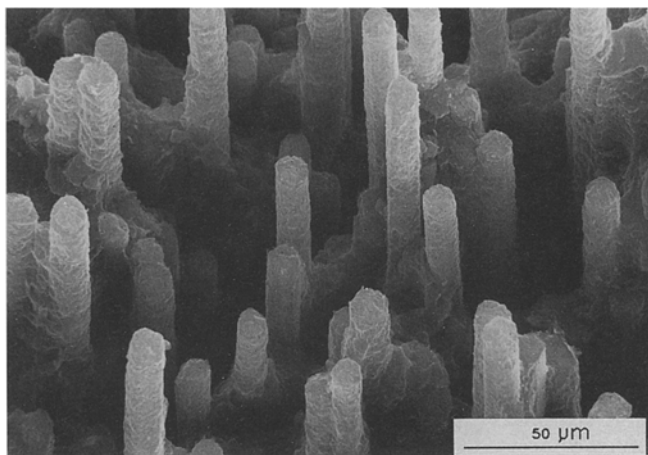


Figure 1: SEM micrograph of the fracture surface after impact testing of an as-polymerized PLLA/carbon fibre composite.

These results indicate that L-lactide polymerization in the presence of carbon fibres is quite successful, and leads to composite materials with excellent material properties. Degradable fibres are currently being tested in these applications. Hot drawn, high strength PLLA fibres may also be used for this purpose, as it was found that at temperatures below 120°C the fibres were insoluble in the L-lactide melt (11,18).

Copolymerization

Copolymerization of L-lactide with ϵ -caprolactone results in a decrease in crystallinity and melting temperature in comparison to the homo poly(L-lactide) (19). Also the ductility of the polymer increases; a higher impact strength, higher elongation at break and a lower yield- and tensile strength were observed (19). Unnotched Izod impact strengths of these compression moulded samples showed values of 0.34 ftlb/in (18.1 J/m) for 3%

ϵ -caprolactone to 4.1 ftlb/in (219 J/m) for 10% ϵ -caprolactone containing copolymers.

In order to compare the data with our results, we performed the same unnotched Izod impact tests with as-polymerized copolymers and found much higher impact resistance. The as-polymerized PLLA homo polymer had an impact strength of 575 J/m and a 6.9 % ϵ -caprolactone copolymer a value of 809 J/m. Specimens with higher ϵ -caprolactone contents absorbed 1000 J/m and did not break, as the apparatus could not be fitted with a hammer exceeding 4J. Intrinsic viscosities in chloroform at 25 °C of our as-polymerized copolymers were in the range of 7-10 dl/g.

Figure 2 shows the dependence of the Dynstat unnotched impact strength on the ϵ -caprolactone percentage in the copolymer. Both as-polymerized and compression moulded samples were tested. It can be seen that for a given composition the as-polymerized material has a much higher impact strength than after moulding.

At low ϵ -caprolactone contents impact strength increases slightly with comonomer content. It can be seen that impact strength does not continue to increase as more ϵ -caprolactone is copolymerized although yield stress, crystallinity, melting temperature and glass transition temperature decrease. It is not until the T_g of the material approaches room temperature, that very high impact strengths can be measured. At this point the material has low modulus and yield stress (20).

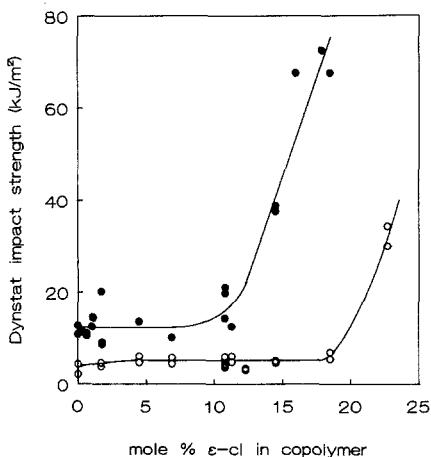


Figure 2:

Influence of L-lactide and ϵ -cl copolymer composition on impact strength. ● as-polymerized, ○ compression moulded.

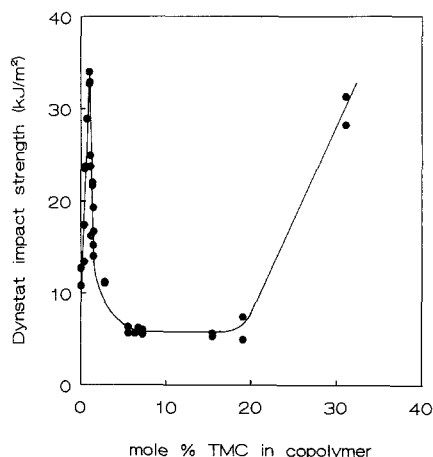


Figure 3:

Influence of as-polymerized L-lactide and TMC copolymer composition on impact strength.

The case is different when L-lactide is copolymerized with trimethylene carbonate. Copolymers with intrinsic viscosities in the range of 8-10 dl/g were prepared. In Figure 3 it can be seen that apart from high impact strengths at high TMC contents when T_g approaches room temperature, a very sharp maximum in impact strength of 34 kJ/m² at 1.0 mole % TMC concentration can be observed. The nature of this effect is not clear, but could be related to the morphology of the copolymer. As-polymerized samples with this high

impact strength were found to be macroscopically very homogeneous. At these low amounts of TMC in the copolymer, the tensile properties are hardly affected and remain as high as those of the as-polymerized homo poly(L-lactide) (20).

Compression moulded samples are again much more brittle.

Blockcopolymers

Extensive craze formation and/or shear banding throughout the volume of the polymer account for the very large increase in impact strength in glassy polymers where a separate phase of dispersed rubber particles is present (21).

A two-phase system comprising of a rubber phase dispersed in a PLLA matrix may be obtained when a rubberblock is copolymerized with L-lactide. 50/50 copolymers of L-lactide and ϵ -caprolactone have low glass transition temperatures (13) and can be block copolymerized with L-lactide by first preparing the 50/50 rubberblock, and subsequently adding and polymerizing L-lactide.

Table 3:

Mechanical properties of blocky L-lactide/ ϵ -caprolactone and L-lactide copolymers.

50/50 L-lac/ ϵ -cl rubber fraction (%)	polymerization temperature	σ (MPa)	ϵ (%)
29.7	100	29.7	90
32.6	100	29.8	150
30.0	110	24.9	180
29.4	120	30.7	250
34.0	140	30.8	1500

Table 3 shows that it is possible to prepare very ductile copolymers in this way. Relatively low tensile strengths but very high elongations at break of up to 1500 % have been found. Charpy impact testing of the samples in Table 3 did not lead to fracture. Although the tensile strengths are lower than that of our poly(L-lactide), it has been shown that successful stabilization of mandibular fractures in dogs occurred with PLLA of tensile strength 37 MPa (22).

In order to ensure homogeneous mixing of the rubber with the molten L-lactide, the viscosity of the rubber could not be too high. It was necessary to add the L-lactide after the rubber had polymerized for a period of 3 hours at 100 °C. It should be noted that because of the difference in reactivity between L-lactide and ϵ -caprolactone (23), at this moment only a fraction of the ϵ -caprolactone had been converted.

Control of the molecular weight of the rubberblock by addition of small amounts of hydroxylgroup containing compounds, or the use of TMC in the preparation of the rubber block may lead to better properties. Other means of homogeneously mixing the rubber with L-lactide are also under investigation.

Plasticization

Previously it was shown that extraction of PLLA with ethyl acetate resulted in the formation of a more ductile material (24). In comparison to the untreated as-polymerized PLLA the tensile strength was lowered and the elongation at

break greatly increased (45 MPa and 105 % respectively). Also the rate of hydrolytic degradation and strength loss was strongly reduced. This can be attributed to the removal of unreacted L-lactide, as was also shown by others (25).

Impact strength values of ethyl acetate extracted PLLA samples depend on the residual amounts present in the material. Table 4 shows that high impact strengths are obtained when 3 % or more ethyl acetate remains in the sample. Further removal does not lead to higher impact strength. The tensile strength of a sample containing 3.2 % ethyl acetate was 28.8 MPa, the elongation at break was 19.6 %.

The possibility of plasticization of PLLA by water was also explored. However the data in Table 5 show that water absorption does not lead to plasticization and an increase in impact resistance of PLLA.

Table 4:

Plasticization of PLLA by ethyl acetate after an immersion period of two days, followed by drying in vacuo.

drying time (days)	residual ethyl acetate (mass %)	Dynstat Impact Strength (kJ/m ²)
untreated	untreated	10.8
0.5	3.4	23.2
1	3.0	16.5
4	2.2	-
5	2.0	11.1
16	1.6	10.8
27	1.6	8.9

Table 5:

Effect of water absorption on the impact strength of PLLA at room temperature.

absorption time (days)	water in PLLA (mass %)	Dynstat Impact Strength (kJ/m ²)
0	0	10.8
1	1.1	8.9
2	1.8	7.7

Conclusions

As-polymerized PLLA shows a much greater impact strength than compression moulded poly(L-lactide). The impact strength of as-polymerized PLLA can be further increased by polymerizing L-lactide in the presence of strong and stiff fibres. Copolymers with trimethylene carbonate show a very sharp maximum in impact strength when 1.0 mole% TMC is built into the L-lactide polymer chain. Block copolymerization of L-lactide with rubberblocks and plasticization with ethyl acetate also lead to high impact strength as-polymerized poly(lactides).

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