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### High impact strength poly(lactide) tough biodegradable materials.

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## SUMMARY

The development of biodegradable polymers for use in surgical applications has received considerable attention in recent years. Especially poly( $\alpha$ -hydroxy-acids) have been utilized in sutures, drug release systems and bone fracture fixation. In load bearing surgical devices like bone plates and screws, good mechanical properties (strength, toughness) of the material are essential if the implants are to be used safely and successfully. In order for the polymer to hydrolyze and degrade *in vivo* without eliciting adverse secondary tissue reactions, low crystalline or amorphous polymers are the preferred materials. This thesis describes the synthesis and properties of several copolymers of L-lactide. The effect of the nature of the comonomer and the copolymer composition on the thermal- and mechanical properties has been evaluated. Furthermore, the low impact resistance of amorphous poly(lactide) can be related to the relatively low entanglement density in the melt. The toughness of these brittle materials can be substantially improved by block copolymerization and blending with biodegradable rubbers.

The preparation of biodegradable elastomeric implant materials is described in **Chapter 2**. High molecular weight copolymers of L-lactide and  $\epsilon$ -caprolactone were prepared in the monomer melt by ring opening polymerization with stannous octoate. The 50/50 mole/mole L-lactide/ $\epsilon$ -caprolactone copolymers show a non-random distribution of monomer sequences, resulting in the presence of crystallizable L-lactide sequences. These crystalline domains account for the good mechanical properties of the material, the tensile strength is 34 MPa and the elongation at break 500 %. These favourable properties make this copolymer a suitable material for use in biomedical applications such as nerve guides, where a degradable, elastomeric implant material is required. The degradation products of these L-lactide/ $\epsilon$ -caprolactone copolymers are non-toxic, in contrast to those of the frequently used medical grade, MDI containing polyurethanes.

In **Chapter 3** the effect of the polymerization temperature on the properties of L-lactide and  $\epsilon$ -caprolactone copolymers is investigated. In the ring opening copolymerization of these lactones, the large difference in reactivity between the monomers leads to tapered copolymers with blocky structures. Less blocky copolymers are formed at higher temperatures due to the increased occurrence of transesterification reactions and a less pronounced difference in reactivity of the monomers. The average monomer sequence lengths, readily measured by  $^{13}\text{C}$  NMR, have a large effect on the thermal- and mechanical characteristics of the copolymers. Copolymers synthesized at 80 °C with relatively long average monomer sequence lengths and pronounced phase separation were much stiffer and stronger than copolymers prepared at 110 °C.

**Chapter 4** deals with routes to improve the impact resistance of as-polymerized poly(L-lactide). It was shown that as-polymerized poly(L-lactide) has a much higher impact strength than after compression moulding and rapidly cooling to below room temperature. The toughness can greatly be increased by bulk polymerizing of L-lactide in the presence of carbon fibres. These model composites possess an unnotched impact strength upto six times higher than nascent poly(L-lactide). As-polymerized copolymers of L-lactide with small amounts of trimethylene-carbonate showed a very sharp maximum in impact strength versus the copolymer composition, most likely related to the homogeneity and morphology of the obtained material. Other means of

toughening, such as block copolymerization of L-lactide with L-lactide/ $\epsilon$ -caprolactone rubbers and plasticization with ethyl-acetate, were also investigated, leading to high impact strength as-polymerized poly(L-lactide).

**Chapter 5** describes the synthesis of high molecular weight copolymers of L-lactide and glycolide. Copolymerization with the much more hydrophilic glycolide will decrease the initial crystallinity of the copolymers and simultaneously increase the rate of hydrolytic degradation. The influence of the glycolide content on the thermal- and mechanical properties was studied. Excellent mechanical properties and a large melting point depression were observed. The dyad splitting of the carbonyl carbon atom in the  $^{13}\text{C}$  NMR spectrum was used to determine average lengths of monomer sequences. The synthesized copolymers did not reveal a truly random monomer distribution. Hydrolytic degradation experiments *in vitro* showed that large amounts of highly crystalline material were still present after 140 days. True random copolymers, with shorter L-lactide sequences should not display this large increase in crystallinity and slow mass loss upon hydrolysis.

The synthesis of a bicyclic bis-carbonate and its use in the formation of poly(L-lactide) networks is described in **Chapter 6**. Spiro-bis-dimethylene-carbonate proved to be an effective cross-linker for cyclic carbonates as well as for lactones. In the copolymerization with L-lactide, the high gelpercentages of upto 100 % and the very low gelpoint of 0.06 mole % cross-linker are indicative of the ease with which this cross-linker copolymerizes with L-lactide. The molecular weights between cross-links determined from swelling experiments were in accordance with those expected from the charged amounts of monomer, indicating homogeneous cross-linking to have taken place (at concentrations below 2 mole % spiro-bis-DMC). A large melting point depression and a significant reduction of the heat of fusion are attained. The values of tensile- and impact strength are higher than those of unmodified as-polymerized poly(L-lactide).

**Chapter 7** is concerned with the copolymerization of L-lactide with several cyclic esters and cyclic carbonates. The thermal properties of the as-polymerized, nascent copolymers and networks were evaluated with respect to the nature of the comonomer. Comonomers with a reactivity equal to L-lactide are most effective in decreasing the melting temperature and crystallinity. During long term hydrolysis and accelerated degradation experiments at 100 °C, it was shown that the presence of crystallizable L-lactide sequences in the copolymers resulted in long degradation times before complete loss of mass takes place.

In **Chapter 8** the influence of copolymerization of L-lactide with cyclic esters and cyclic carbonates on the mechanical properties is investigated. The extent of crystallization of poly(L-lactide) homo- and copolymers has a large effect on their tensile- and impact properties. While amorphous poly(lactide) is brittle in impact tests, crystalline poly(lactide) materials are much tougher. Sharp maxima in the impact strength versus the comonomer composition and the heat of fusion were obtained, reflecting the important role of the presence of a crystalline fraction in the material. The toughest materials are obtained at conditions where the entanglement density is high and the interconnectivity of the physical network due to the presence of crystallites is maximal.

**Chapter 9** describes the effect of the (melt) entanglement density on the impact strength and the drawability of amorphous and semi-crystalline L-lactide homo- and stereocopolymers. The molecular weight between entanglements in amorphous poly(L-lactide) is found to be close to  $10 \times 10^3$ , corresponding to a characteristic ratio  $C_{\infty}=12$ . This value is much higher than previous determinations by Flory and coworkers, they found  $C_{\infty}=2$  for poly(L-lactide).

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The observed brittle fracture behaviour of amorphous poly(lactide) can be explained by such a high value of the characteristic ratio.

Poly(lactide) networks, prepared by copolymerization of L-lactide with spiro-bis-DMC, could be conveniently hot-drawn at temperatures above the melting temperature, or the glass-transition temperature in the case of amorphous networks, to give very strong, oriented rods with strengths varying from 400 to over 800 MPa depending on the draw-ratio. The maximum obtainable draw-ratio is determined by the entanglement density and the cross-linker concentration. Semi-crystalline, as-polymerized networks of poly(L-lactide) are very low entangled and could be hot-drawn much further than the more entangled amorphous L- and D-lactide copolymer networks.

**Chapter 10** describes the block copolymerization of star-shaped degradable rubbers with poly(lactide). Normally amorphous poly(85/15 L/D-lactide) polymers are brittle in tensile- and impact test, but block copolymerization with star-shaped trimethylene-carbonate/ $\epsilon$ -caprolactone rubbers and other degradable rubbers leads to very tough, impact resistant degradable materials. The relatively low softening temperatures of these amorphous materials allows convenient processing by compression moulding.

The block copolymerization and blending of amorphous poly(lactide) with several degradable rubbers is described in **Chapter 11**. Rubber toughening of brittle amorphous poly(lactide) matrices with poly(trimethylene-carbonate) and trimethylene-carbonate/ $\epsilon$ -caprolactone rubbers leads to very effective toughening. The presence of a discrete rubber phase in the glassy matrix could be demonstrated by dynamic mechanical analysis and transmission electron microscopy. Optimal toughening is achieved at rubber(block) molecular weights higher than  $40 \times 10^3$ . The Izod notched impact strength and the tensile yield strength of poly(lactide) materials modified with 20 weight % trimethylene-carbonate/ $\epsilon$ -caprolactone rubber is even higher than that of HIPS and ABS.

The **Appendices** describe preliminary experiments concerning the hydrolytic- and thermal degradation of rubber modified amorphous poly(lactide), as well as the synthesis and copolymerization of lactones with a bicyclic bis-ether.

Incorporation of carbonate groups in the block copolymer chain results in thermally less stable polymers. Therefore the thermogravimetric analysis of these (rubber)modified lactide polymers, described in **Appendix A**, yields important information concerning the processability of these materials at elevated temperatures.

The hydrolytic degradation of poly(lactide) block copolymers with rubbers and poly(lactide) stereo-copolymers of various molecular weights is described in **Appendix B**. **Appendix C** describes the synthesis of 2,6-dioxa-[3,3]-heptane. This bicyclic bis-oxetane was copolymerized with several lactones and cyclic ethers. The cationic copolymerization of  $\epsilon$ -caprolactone with this cross-linker resulted in networks which could be hot-drawn in a very straightforward manner, leading to strong materials. The initial cross-linking reactions of lactones with this cross-linker, show that cationic copolymerization with a bicyclic bis-oxetane is a promising alternative method to prepare poly(lactone) networks.