

Biodegradable crosslinked polymers based on triethoxysilane terminated polylactide oligomers

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Abstract

Lactic acid based polymers and their copolymers are widely used in biomedical applications. Different properties are introduced by modifying the composition. In this study, crosslinked polymers were produced from DL-lactide oligomers, which were functionalised with (3-isocyanatopropyl)triethoxysilane (IPTS) and crosslinked by acid catalysis in the presence of water without the use of solvent. The polymers were characterised by fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC), and their crosslinking density and compressive properties were measured. Functionalised linear and star-shaped oligomers were characterised by FTIR and DSC and also by ^1H NMR and size exclusion chromatography (SEC). According to ^1H NMR, 79–95% of the hydroxyl groups were functionalised by IPTS during the early part of the synthesis. The formation of a strong polymer network was found to require a curing temperature of at least 90°C. The best mechanical properties were achieved with the oligomer initiated with 5% pentaerythritol. The properties of the polymer were then compressive yield strength 81 MPa, modulus 2260 MPa and 4.4% strain at yield point. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Silane; Lactide; Crosslinking

1. Introduction

Crosslinked polymers offer a different set of properties from thermoplastics and are important in many applications. Often they are relatively hard and rigid [1], and their production does not necessarily require high temperatures, so that they can be cured where they are used. This in situ polymerisation is common in the formation of bone cements by the reaction of polymethyl methacrylates with methyl methacrylate monomer [2]. Crosslinked materials are normally very stable because networks are practically invulnerable to the breakage of a single bond. Only severe breakage will cause visible damage to crosslinked materials. Lactic acid polymers, on the other hand, degrade hydrolytically [3,4], so that combining crosslinking with the degradability of poly(lactic acids) should give us a polymer that is both degradable and possesses the good mechanical properties available with crosslinking.

Biodegradable crosslinked matrices have been prepared, for example, by functionalising poly(ϵ -caprolactone) or DL-lactide and glycolic acid oligomer with maleic anhydride or fumaric acid. The oligomers have then been crosslinked in the presence of radical initiator [5,6]. Double bonds have

also been used in the production of bioresorbable bone cement composites from fumarate based polyesters as described by Kharas et al. [7] and Gresser et al. [8]. However, the pure polymer matrices produced in these studies were not mechanically strong and a composite structure was required in order to achieve mechanical strength.

Alkoxysilane functionalisation has been used in the compatibilisation of glass fibre reinforced composites [9,10] and in the production of inorganic–organic hybrid materials, because alkoxysilanes can provide covalent bonding between inorganic and organic components [11–13]. Alkoxysilanes also have been used in the production of biodegradable crosslinked materials. Jerome and co-workers [14–16] produced ϵ -caprolactone based crosslinked polymers and hybrid materials from tetraethoxysilane (TEOS) and ϵ -caprolactone oligomers with THF as solvent. The reactions of alkoxysilanes have been studied widely by Schapman et al. [17–20]. After functionalising telechelic butadiene oligomers either via urethane linkage or addition of thiol to double bond they crosslinked the oligomers with moisture and with and without catalyst.

The objective of our study was to prepare mechanically strong biodegradable crosslinked polymers. To do this we started with telechelic polylactide oligomers of different structure and functionalised them with alkoxysilanes by

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Table 1
Properties of DL-lactide based oligomers, functionalised oligomers and crosslinked samples

Sample	PDLA								
	BD			PERYT		PGL-06			
Initiator									
Initiator (%)	3	5	10	5	8	1	3	5	
<i>Oligomer</i>									
\bar{M}_n (theoretical; g/mol)	4890	2970	1530	3020	1940	14,860	5260	3340	
\bar{M}_n (SEC; g/mol)	8220	5130	2580	3990	2790	15,700	5440	3530	
\bar{M}_w (SEC; g/mol)	10,550	6260	3160	5440	3320	19,780	6550	4320	
MWD (SEC)	1.3	1.2	1.2	1.2	1.2	1.3	1.2	1.2	
Number of arms ($^1\text{H NMR}$)	2.0	1.9	2.0	3.4	3.9	6.2	5.9	4.0	
T_g (DSC; °C)	38	30	17	34	27	42	30	23	
<i>Functionalised oligomer</i>									
\bar{M}_n (theoretical; g/mol)	5390	3470	2025	4010	2930	16,840	7240	5320	
\bar{M}_n (SEC; g/mol)	9450	6470	3690	8900	4080	19,770	7750	5920	
\bar{M}_w (SEC; g/mol)	12,820	9100	4740	20,900	5000	39,800	10,250	8440	
MWD (SEC)	1.4	1.4	1.3	2.4	1.2	2.0	1.3	1.4	
Free OH ($^1\text{H NMR}$; %)	21.2	13.0	8.5	21.2	20.8	19.4	4.9	5.1	
T_g (DSC; °C)	36	22	7	22	13	42	17	6	
<i>Crosslinked polymer</i>									
Crosslinking temperature (°C)	120	90	60	90	60	120	90	60	
Gel content (%)	100	82	94	100	100	97	98	100	
T_g (DSC; °C)	44	43	39	52	59	57	66	64	

urethane linkage. The alkoxy silane functionalised oligomers were then crosslinked with acid catalyst and water. Oligomers were linear or star-shaped depending on the initiator used in their preparation. The molecular weights of the oligomers were controlled by the amount of initiator added in the ring-opening polymerisation of lactide. Lactide based oligomers were used because linear high molecular weight polylactides are known to be biodegradable and to possess appropriate mechanical strength and they are widely used in biomedical applications [3]. The simplicity of the process was also a key consideration. Traditionally alkoxy silane functionalisations and crosslinking have been done in the presence of solvent, but we performed both steps without solvent to keep the process simple and avoid the removal of solvent from the products. This is also a prerequisite for in situ crosslinking since solvent removal is unacceptable in real applications.

2. Experimental

2.1. Materials

The DL-lactide oligomers were polymerised from DL-lactide (Purac) with 1,4-butanediol (BD; Fluka Chemica), pentaerythritol (PERYT; Acros Organics), or polyglycerine-06 (PGL-06; Daicec Chemical Industries) as initiator. Sn(II)octoate (Sigma) was used as catalyst in the ring-opening polymerisation.

(3-Isocyanatopropyl)triethoxysilane (IPTS) from ABCR GmbH was used in the functionalisation step. The cross-

linking was performed with nitric acid (65%) from Merck and distilled water.

2.2. Preparation of linear and star-shaped polylactide oligomers

The polylactide oligomers were polymerised from DL-lactide in a batch reactor at 160°C for 3 h. The monomer was fed to the reactor with an appropriate amount of initiator and 0.02 mol% of a catalyst, Sn(II)octoate. The synthesis and properties of the oligomers are described in detail in our parallel manuscript [21]. The properties are summarised in the first part of Table 1. All the oligomers were amorphous, and the molecular structure of the oligomers was varied by changing the initiator and its quantity. An increase in the amount of initiator caused the molecular weight to decrease. This lowered the glass transition temperatures (T_g) of the oligomers. Linear oligomers were obtained with BD, star-shaped four-armed oligomers with PERYT, and even more branched structure, sometimes with over six arms, with PGL-06 (see Table 1).

2.3. Preparation of triethoxysilane terminated polylactide oligomers

Telechelic DL-lactide based oligomers were terminated with IPTS in a reaction carried out in a glass vessel with mechanical stirring. Oligomers were first melted in the reactor at 160°C in nitrogen atmosphere and a stoichiometric amount of IPTS was fed to the reactor. The reaction time was 10 min. The amount of IPTS was calculated from the

theoretical molecular weight of the synthesised oligomer and the functionality of the initiator.

2.4. Crosslinking of triethoxysilane terminated polylactide oligomers

For crosslinking, the functionalised oligomers were heated to an appropriate reaction temperature (60, 90, 120°C). Aqueous solution of nitric acid (1 wt%) was added to the functionalised oligomer in the ratio 1/20 of aqueous solution to oligomer. The mixture was stirred with a spatula until homogeneity was achieved and was then applied to a bone cement mould (ASTM F 451-86) producing cylindrical specimens 12 mm in height and 6 mm in diameter. The samples were cured first for 4 h in a Fontijne table press practically without compression. After the initial curing, test specimens were removed from the mould and cured for an additional 72 h in the oven at 90°C.

2.5. Characterisations

Molecular weights (\bar{M}_n and \bar{M}_w) and molecular weight distributions (MWD) were determined relative to polystyrene standards by size exclusion chromatography (SEC). The Waters Associates system was equipped with a Waters 700 Satellite wisp injector, a Waters 510 HPLC solvent pump, four linear PL gel columns (10^4 , 10^5 , 10^3 , and 100 \AA) connected in series, and a Waters 410 differential refractometer. All samples were analysed at room temperature. Chloroform (Riedel-de Haen Ag, stabilised with 1% ethanol) was used as the eluent and was delivered at a flow rate of 1.0 ml/min. The samples were dissolved in chloroform at a concentration of 1.0% (w/v). The injection volume was 200 μl .

For ^1H NMR measurements, the samples were dissolved in chloroform- d_1 (Fluka Chemica, deuteration degree not less than 99.8%) in 5 mm NMR tubes at room temperature. The sample concentration was about 1.0% by weight. NMR spectra were recorded on a Varian XL-300 NMR spectrometer working at 300.032 MHz for proton.

IR spectra were measured on a Nicolet Magna Spectrometer 750 with 2 cm^{-1} resolution by using thin films for crosslinked samples and KBr discs for uncrosslinked samples. The sample concentration in the discs was 1 wt%.

Differential scanning calorimetric (DSC) measurements were made on a Mettler Toledo Star^e DSC 821^e. The measurements were run from -40 to 180°C , at a heating rate of $10^\circ\text{C}/\text{min}$ and a cooling rate of $10^\circ\text{C}/\text{min}$. The T_g values were measured during the second heating period.

The degree of crosslinking (i.e. gel content) of the polymers was measured by extracting the soluble phase in acetone with a Soxhlet apparatus for 20 h (ASTM D 2765). The gel content was determined as the weight of non-extractable material divided by the total weight of the original sample and is expressed as the percentage.

Compressive properties of the samples were measured on an Instron 4204 tensile testing machine adopting the stan-

dard ISO 604-1973(E). The compressive yield strength, strain and modulus for the polymers were measured for five parallel air-conditioned specimens, which had been left for 72 h at 23°C and 50% relative humidity.

Hydrolysis study was performed with five parallel weighed test specimens for each time point. Cylindrical specimens produced with bone cement mould were immersed in 10 ml of phosphate buffer solution at $\text{pH } 7.00 \pm 0.01$ at 37°C in test tubes. The buffer solution was changed once a month. The test specimens were recovered from the test tubes at different intervals and weighed and their compressive properties were tested. Specimens were then vacuum dried for two weeks and stored for further analysis.

3. Results and discussion

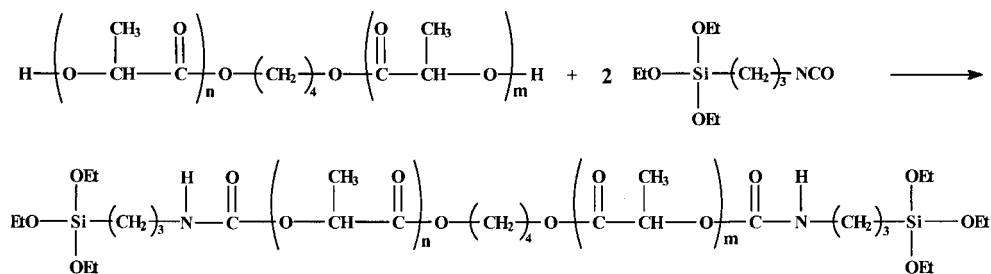
The process that we used in proceeding from lactide monomer to crosslinked matrix consisted of three steps. In the first part of the synthesis, lactide was polymerised to low molecular weight telechelic oligomers. Initiators were used for hydroxyl termination and to control the molecular weight of the prepolymer as well as to initiate the ring-opening polymerisation of lactide. In the second step, telechelic oligomers were functionalised with IPTS to intermediate product, and in a third step the functionalised oligomers were crosslinked with water and acid catalyst, as shown in Scheme 1, reaction scheme of ethoxysilane functionalisation and crosslinking.

The effect of the oligomer structure on the crosslinking temperature and the properties of the crosslinked samples was demonstrated. Eight oligomers were tested, differing in either the initiator or the amount used in the ring-opening polymerisation. Both linear and branched oligomers were used to demonstrate the effects of branching in the oligomers, and molecular weights of the oligomers were varied by using different amounts of initiator. The effect of these two factors was studied on the synthesis of amorphous crosslinked DL-lactide based polymers and their properties. Finally, the hydrolytic degradation of the crosslinked polymer was studied.

3.1. Preparation of triethoxysilane terminated polylactide oligomers

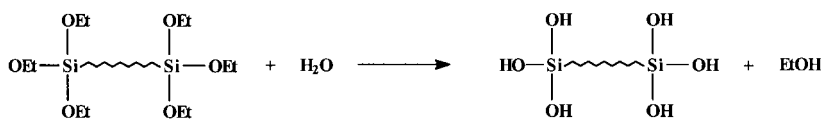
Telechelic polylactide oligomers were terminated with triethoxysilane groups through reaction between isocyanates and hydroxyl groups at a high temperature, without catalyst or solvent. In an earlier work by our group [22] on the chain extending reactions of isocyanates with hydroxyl groups, the high temperature was introduced as a means of avoiding the solvents and catalysts typically used in the functionalisation of hydroxyl groups with isocyanates. If high temperatures are allowed a more straightforward route to the desired products is achieved without the use of these additional components.

Functionalisation of butanediol initiated lactide oligomer with IPTS:

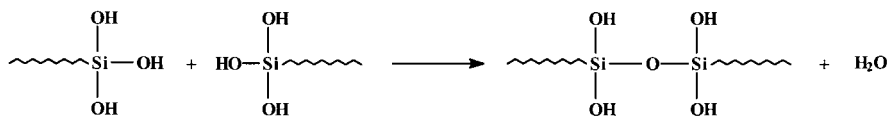


Crosslinking reactions of functionalised oligomers:

1. Hydrolysis



2. Condensation



Scheme 1.

The extent of the functionalisation reaction was studied mainly by ^1H NMR. The spectra of the oligomer PDLA (5% PERYT) before and after the functionalisation are shown in Fig. 1 together with the analysed peaks. The spectra of the intermediate triethoxysilane functionalised oligomers showed that peaks from hydroxyl terminated lactide chains decreased considerably and even disappeared in some cases. The ratio of the methine protons next to the hydroxyl groups (4.32 ppm) to the methine protons in the polylactide chains (5.13 ppm) was compared before and after the functionalisation. The conversion calculated in this way was from 79 to 95% with a trend such that increasing molecular weight of the oligomers decreased the conversion, and the best conversions were obtained with smallest oligomers. The results are presented in Table 1 as the percentage of the free hydroxyl groups (free OH) in the functionalised oligomers.

Similarly, and as expected, the peaks (2.69 ppm) of the hydroxyl end groups in polylactide chains nearly disappeared. The spectra of the functionalised oligomers showed the characteristic peaks of ethoxysilane groups, confirming the successful functionalisation. Ethoxy groups created a triplet at 1.19 ppm and a quartet at 3.78 ppm. Methylene protons from propylene chain could be seen at 3.15 ppm (quintet) and 0.60 ppm (triplet). The third multiplet from the propylene group was probably overlapped by the strong

methyl peak from lactide chain (1.5 ppm). Overlapping probably also explains why the resonance from urethane proton was uncharacterised.

Molecular weights were determined by SEC. Theoretically, functionalisation connects IPTS molecules with every hydroxyl group in the oligomer and increases the number average molecular weight by one to several thousand. The SEC results presented in Table 1 demonstrate this trend. Functionalisation increased the number average molecular weights in every case. The difference in the molecular weights before and after the functionalisation increased with the increase in the functionality, from two in BD initiated oligomers to eight in PGL-06 initiated oligomers. Functionalisation also appeared to broaden the molecular weight distribution. In most cases there was only a slight change, but for some oligomers, such as PDLA (5% PERYT), the MWD was almost doubled during the triethoxysilane termination. A possible explanation for this could be that the ethoxysilanes react in part and connect a few oligomer molecules together during functionalisation.

The structure and properties of the functionalised oligomers were also studied by fourier transform infrared spectroscopy (FTIR) and DSC. Because these methods do not require the samples to be soluble, they are valuable in the characterisation of crosslinked samples too. The FTIR spectra of the samples used in this study were dominated by the

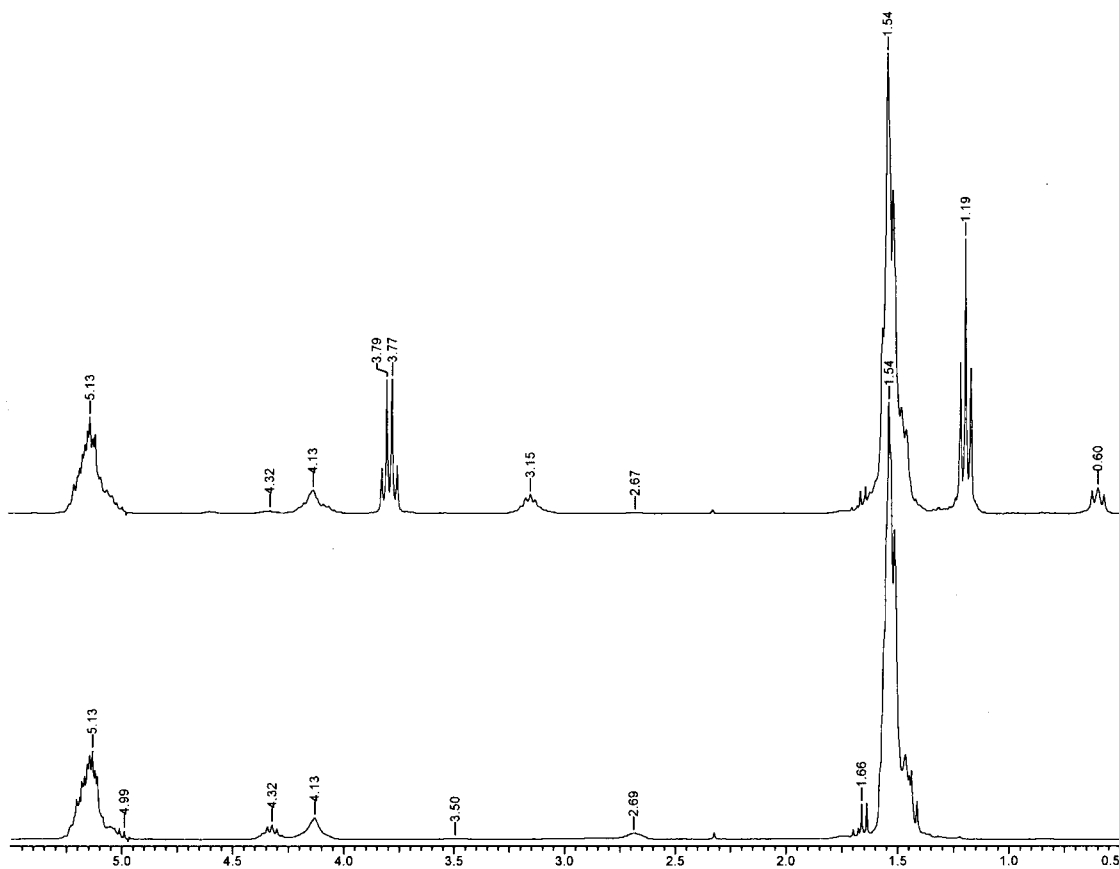


Fig. 1. ^1H NMR spectra of PDLA (5% PERYT) oligomer before (lower) and after functionalisation (upper).

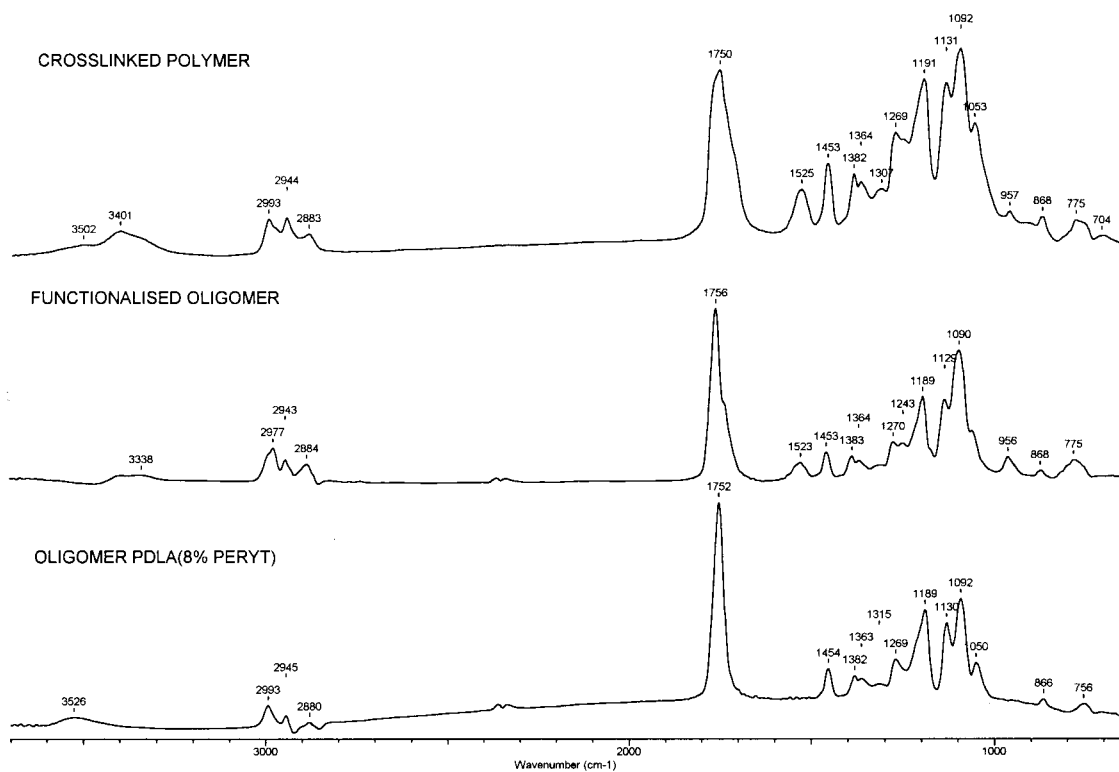


Fig. 2. Effect of functionalisation and crosslinking as seen in FTIR spectra.

ester carbonyl absorbance of lactide units at 1752 cm^{-1} , as can be seen in Fig. 2. The functionalisation created absorbances at 1523 and 956 cm^{-1} and, as expected, the broad hydroxyl absorbance at 3526 cm^{-1} disappeared as the urethane ($-\text{NH}$) absorption at 3338 cm^{-1} appeared. The urethane bonds should absorb at 1738 – 1732 cm^{-1} [23] and at 1550 – 1510 cm^{-1} [24]. The former was found as a shoulder on a carbonyl absorbance and the latter was visible in all spectra. Importantly no free isocyanate (2275 – 2250 cm^{-1}) was detected in the functionalised samples. Triethoxysilane termination is expected to absorb at 1175 – 1165 , 1100 – 1075 , and 965 – 940 cm^{-1} [23]. Although the $\text{Si}-\text{O}-\text{Et}$ absorbance should produce at least one strong band, the bands are mostly overlapped by other absorbances from oligomer units. In our case, the intensity of the absorbances at 1100 – 1000 cm^{-1} was increased and the absorbance at 956 cm^{-1} was clearly visible in the spectra of the functionalised oligomers.

Thermal properties were also affected by the functionalisation. The T_g values of the amorphous samples were lowered by 10°C on average. IPTS termination served as internal plasticiser and made the oligomers softer. This was an important effect, since it lowered the viscosity enough to make the oligomers processable at lower temperatures.

3.2. Crosslinking of triethoxysilane terminated polylactide oligomers

The main purpose of our study was to determine the effect of the molecular structure of the oligomer on crosslinking and the properties of the crosslinked product. For this reason, linear oligomers were used in addition to branched ones, and the molecular weights of the oligomers were varied. The different triethoxysilane terminated polylactide oligomers were crosslinked with water and acid catalyst as presented in Scheme 1.

Nitric acid was chosen as the catalyst because of its known performance in sol–gel technology [25]. Acid catalysed crosslinking proceeded with all the samples to the extent where the gel content was at least 80%. As presented in Table 1 in most cases the gel content was higher and very close to 100%. Because solvents were not used, the initial curing temperature had to be varied with the oligomer, but for all samples the final curing was performed at 90°C . The viscosity of the functionalised oligomers determined the initial curing temperature, i.e. the temperature was chosen so that the viscosity was sufficient to enable mixing of the oligomer with water and catalyst. The oligomers with smallest molecular weights were initially crosslinked at 60°C and the intermediates at 90°C , while the oligomers with highest molecular weights required a reaction temperature of 120°C as shown in Table 1.

The crosslinking reaction consists of hydrolysis of ethoxysilanes to silanols and a condensation of silanol groups. Both reactions produce side products — ethanol in the

hydrolysis and water in the condensation. These side products and the water added to the reaction mixture may become trapped inside the polymer and cause porosity in the crosslinked matrix when the viscosity of the crosslinking material increases. Slow reaction with low catalyst concentration was used to decrease the porosity and good specimens were obtained with initial curing in the mould at temperatures of 60 and 90°C . This initial curing gave the specimen the desired dimensions, but final curing was required for the samples to obtain optimal mechanical strength. The samples with highest molecular weights also had the highest viscosities and the reaction temperature had to be raised to 120°C . At this temperature the viscosity was adequate for mixing, but vaporising water and ethanol caused the samples to be too porous for mechanical testing. Because of the use of water, the crosslinking reaction should be preferably performed at temperatures under 100°C .

Differences between the crosslinked products were mainly in their thermal and compressive properties. The samples produced from BD initiated oligomers were almost rubbery. As presented in Fig. 3, they had a compressive yield strength of 18 to 21 MPa with relatively low modulus. Also their T_g values were lower than those of other samples. Evidently the networks formed from linear BD initiated oligomers were looser than those formed from star-shaped oligomers. This lower network density together with flexible BD centre unit prevents the polymer from obtaining high mechanical strength.

The highest compressive strength was observed with PDLA (5% PERYT). The compressive yield strength was 81 MPa with modulus of 2260 MPa . Increasing the initiator content to 8% lowered the strength to 55 MPa . Symmetrical star-shaped oligomers initiated with PERYT were found to efficiently crosslink to dense networks with high mechanical strength. The T_g of these samples was close to the T_g of polylactide, which is 55°C . By way of comparison, compressive strengths of 120 – 130 MPa and modulus of 5.1 GPa have been reported for linear poly(L-lactides) depending on their molecular weights [26]. The highly branched structure of the oligomers initiated with PGL-06 gave good compressive strengths to the crosslinked samples and raised their T_g values close to or above 60°C .

The T_g values of the crosslinked polymers were affected by the type and amount of initiator. With the branched initiators, T_g was higher with increased initiator content. This can be related to the higher crosslinking density as chains become more tightly connected to each other. As the distance, i.e. the average molecular weight, between crosslinks decreased, the T_g increased as also reported by Schapman et al. [20]. However, this does not explain the difference in T_g values depending on the initiator itself. The T_g value appeared to increase with the number of branches in the initiator. This could be related to crosslinking density as the crosslinking points are increased and the networks become tighter.

The mechanical properties were highly dependent on the

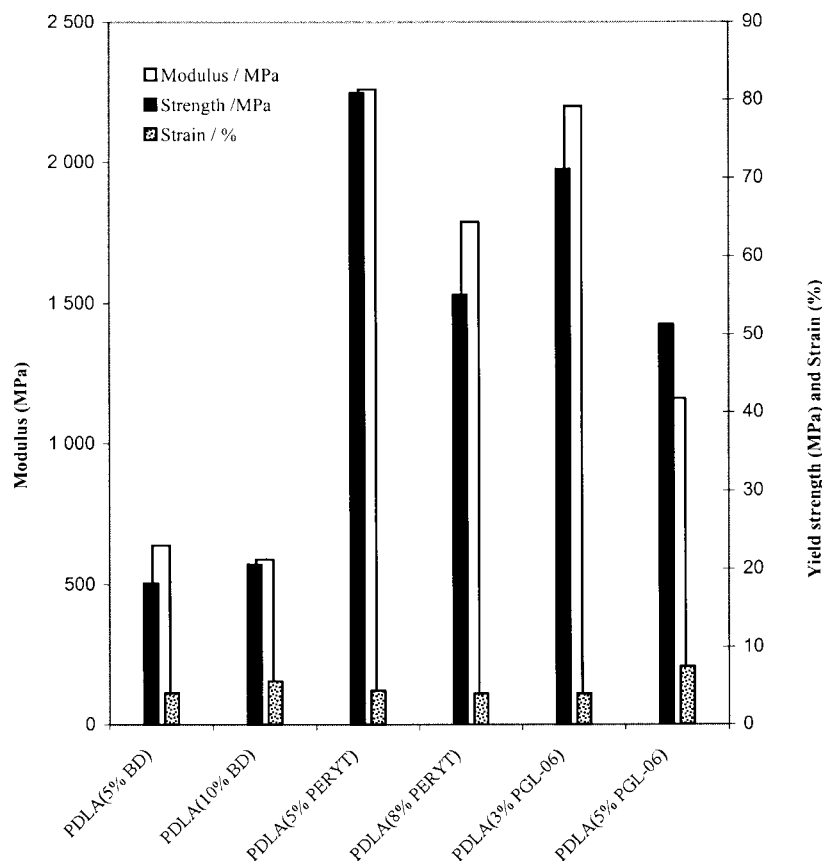


Fig. 3. Compressive properties of the crosslinked samples.

curing. Early vitrification made the samples practically insoluble and increased the T_g values, but the mechanical strength remained low. Thus the gel content and thermal analysis seem to be inadequate indicators of the curing process. An example of this was the sample PDLA (8% PERYT), which had reasonably good mechanical strength after curing for 72 h at 90°C, but after a final curing at 60°C it was still rubbery with no yield stress, and the modulus was less than 20 MPa. The gel content appeared to be close to 100% and the T_g obtained a similar value to those of well-cured samples. Possibly a loose network structure with portions of cured material and still unreacted silanol and ethoxysilane groups was formed, requiring a final curing for the crosslinking to proceed to mechanically tough material. This loose network was sufficiently crosslinked to be insoluble in solvents, i.e. the gel content was close to 100%, and the measured T_g was the T_g of the portions of cured material. It is necessary for the reactive end groups to meet in order for them to react and the curing to proceed, and the motion of molecules becomes more restricted as the curing proceeds. This restriction of motion suggests that low curing temperatures are not suitable for applications where good mechanical strength is required.

In the FTIR spectra the crosslinking can be detected mainly in the region from 3700 to 3200 cm^{-1} , where the

silanol groups formed in the hydrolysis absorb together with hydroxyl and urethane groups. Siloxanes should have at least one strong band at 1100–1000 cm^{-1} [24], but this was overlapped by the absorbances of lactide chains. However, the strong intensity of the peak at 1092 cm^{-1} relative to the carbonyl absorption at 1750 cm^{-1} was significantly further enhanced by the crosslinking, as can be seen in Fig. 2. There were two absorbances, at 3500 and 3400 cm^{-1} , in the spectra of crosslinked samples. These appeared either as two separate bands or as a single band with a clear shoulder. The absorbance at 3500 cm^{-1} is attributable to the silanol groups (Si–OH) formed in the hydrolysis and the absorbance at 3400 cm^{-1} to the urethane bond (N–H). The peaks characteristic of the functionalisation were still present in the spectra of the crosslinked samples.

The hydrolytic behaviour of one of the crosslinked polymers, PDLA (5% PERYT), was studied in order to demonstrate the hydrolytic lability of these new polymers. It is widely known that poly lactides degrade hydrolytically [3], but the effect of crosslinking on the degradation has not been clear. Our study shows that mass erosion of the crosslinked samples started after seven weeks immersion in vitro (Fig. 4) and simultaneously a change occurred in water absorption and T_g . At seven weeks, water absorption was

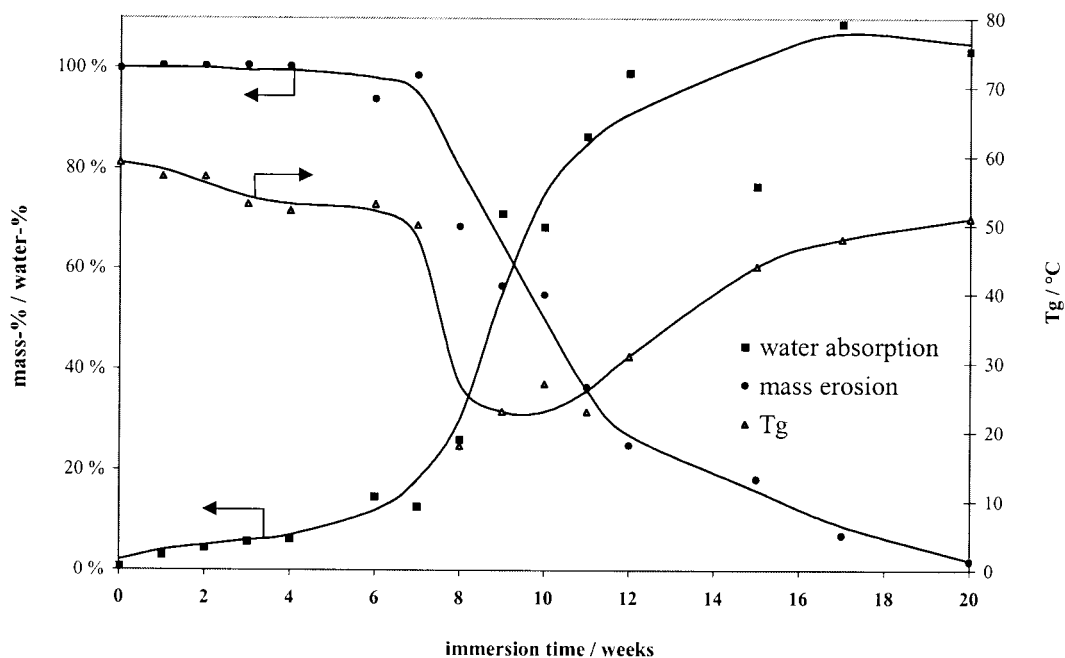


Fig. 4. Mass erosion, water absorption and T_g for crosslinked polymer, PDLA (5% PERYT), as a function of hydrolysis time.

significantly increased from a few to 50% and over. A marked drop in T_g was also discovered as the polymer networks began to degrade. After 12 weeks only 25% of the original mass of the samples remained and after 20 weeks less than 2% remained, showing almost complete degradation. Bimodal degradation behaviour was observed as the specimens were hollow after 12 weeks of immersion. This type of heterogeneous degradation is typical for poly(DL-lactide), in which the degradation proceeds more rapidly in the centre than at the surface [27,28]. In addition to the hollowness of the samples we tested, this was seen in the T_g values, which started to rise again after the core of the sample had mainly degraded. Samples for thermal analysis were taken from the bulk material and after considerable bimodal degradation, probably the oligomeric degradation products from the core with low T_g have diffused out of the sample and the T_g measured is the T_g of the shell material with a slower degradation rate.

The compressive strength of the samples was also monitored during hydrolysis. One week of immersion lowered the compressive yield strength from over 80 to just 4 MPa, where it remained for six weeks. After this the samples were too deformed and soft for mechanical testing.

In general, these crosslinked polymers have many characteristic features of their main component, polylactide. As compared with linear polylactides these crosslinked polymers have a degradation behaviour similar to PDLA and a compressive strength almost of PLLA. Although the process is more complicated than ring-opening polymerisation of lactide, lower processing or curing temperatures is a benefit of these crosslinked polymers. Biocompatibility and degradation products of these modi-

fied polymers remain to be an open issue. However, Tian et al. [29] have studied the biocompatibility of crosslinked poly(ϵ -caprolactones) prepared similarly as we did and in their study these crosslinked polymers did not show any negative indications in preliminary in vitro cell cultures and biodegradation tests.

4. Conclusions

We have demonstrated that alkoxy silane functionalisation and crosslinking can be performed without the use of additional components, which then have to be removed from the product. The obtained polymers possess a unique combination of properties — plasticity before crosslinking and a mechanically strong biodegradable product after crosslinking. Functionalisation of telechelic lactide based oligomers succeeded, with conversions from 79 to 95%. This plasticised the oligomers and their T_g values were lowered by 10°C on average. Crosslinking, on the other hand, raised the T_g to 39–66°C with high crosslinking densities. Compressive properties of the crosslinked lactide based polymers were measured and evaluation showed that the best mechanical properties, with compressive yield strength of 81 MPa at maximum, were achieved with oligomer initiated with 5% of star-shaped PERYT. Highly branched oligomers initiated by PGL-06 also had good mechanical properties after the crosslinking, but the linear oligomers initiated with BD did not obtain the same level of compressive strength. With branched oligomers, final curing at 90°C produced mechanically strong polymers with proven biodegradability.

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