

Synthesis and properties of cross-linked poly(ester urethanes) from poly(lactide) triols and poly(caprolactone) diols

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Abstract. Segmented polyurethanes, whose soft segments were formed by poly(caprolactone) diols with the average molecular weight (M_n) ranging from 400 to 2700 and hard segments by poly(lactide) triols with a M_n of 600–3000, and 1,6-hexamethylenediisocyanate and 4,4'-methylene bis(cyclohexyl) diisocyanate were studied. For poly(lactide) triol and poly(caprolactone) diol synthesis, glycerol and 1,4-butane diol, respectively, were used as D,L-lactide and ε-caprolactone polymerization initiators. The effect of a change in the soft segment content on the properties of polyurethanes at a constant value of molecular weight between cross-links was investigated. The obtained polyurethanes have an amorphous or semicrystalline structure with a minor phase separation degree. Varying the M_n of poly(lactide) and poly(caprolactone) blocks as well as their ratio in the structure, polyurethanes with different tensile, thermal, and biodegradation properties were obtained.

Key words: segmented poly(ester urethanes), poly(caprolactone) diols, poly(lactide) triols, glycerol, tensile properties, thermal properties.

INTRODUCTION

Poly(ester urethanes) with poly(lactide) (PLA), poly(glycolide), and poly(ε-caprolactone) (PCL) blocks and diisocyanate in their structure have good elastomer properties and biocompatibility as well as high physical and mechanical properties. Linear and star-shaped poly(lactides), which are necessary for synthesis of poly(urethanes) (PUs), were prepared by using alcohols with

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different hydroxyl numbers as initiators. The reaction of L-lactide with sorbitol in the presence of stannous octoate (Sn oct) gave a series of novel polyesters [1, 2]. Prepolymers were synthesized by ring opening copolymerization of L-lactide or glycolide with ε-caprolactone initiated by hexahydroxycyclohexane [3].

Peptide-based PUs were synthesized from glycerol and ethyl 2,6-diisocyanatohexanoate (L-lysine diisocyanate). This polymer was degraded in vivo to non-toxic components, such as lysine, glycerol, and ethanol [4].

Biodegradable PUs were obtained from copolymers of γ-valerolactone and ε-caprolactone, cross-linked with 1,6-hexamethylenediisocyanate (HDI) [5]. Bio-absorbable poly(ester urethane) networks were synthesized from a series of polyester triols of D,L-lactide and ε-caprolactone and copolyester triols with L-lysine diisocyanate [6]. In this study, mainly the effect of biodegradation on PU properties was investigated. Initial results indicate that these materials display good network properties, which justifies their further investigation as potentially absorbable biomaterials.

The aim of this work was to investigate the structural and thermal properties, as well as the mechanical behaviour and degradation change of PUs, depending on the soft segment content in the PU at a constant cross-links density. We studied segmented PUs whose soft segments were formed by PCL diols, but hard segments from PLA triols and HDI or 4,4'-methylene bis(cyclohexyl) diisocyanate (H₁₂MDI). For poly(lactide) triol and PCL diol synthesis, glycerol and 1,4-butane diol were used as D,L-lactide and ε-caprolactone polymerization initiators.

EXPERIMENTAL

PLA triols were synthesized from D,L-lactide in bulk at 135°C during 36 h, using glycerol as a polymerization initiator and Sn oct (0.05%) as a catalyst. Depending on the necessary molecular weight (M_n) of PLA, the glycerol amount in the synthesis varied from 3.1% to 15%. PLA triols were synthesized with the average M_n of 580–2940. The OH groups of PLA triols were determined by the acetylation method. The ¹H NMR analysis of low molecular weight polymers showed that the amount of the hydroxyl group was close to theoretical [7]. The value of M_n was calculated from the content of OH groups, taking into account the polymer functionality of three.

PCL diols with M_n ranging from 400 to 2760 were synthesized from ε-caprolactone in bulk at 135°C during 36 h, using 1,4-butanediol as a polymerization initiator and Sn oct (0.05%) as a catalyst. Depending on the necessary poly(lactone) M_n , the 1,4-butanediol amount in the synthesis varied from 3.3% to 22.5%.

PU was synthesized in a toluene solution at a temperature of 70°C. The functional group ratio was NCO:OH = 1.1:1, and the solution concentration was 60–70%. When the conversion of NCO groups reached 60–70%, the solution was

poured on a fluoroplastic support and left at a temperature of 85 °C for 2–3 h. The obtained films had a thickness of 200–250 µm.

The mechanical characteristics of PU samples were determined by tensile testing using a dumbbell-shaped sample on a Zwick Roell materials testing device [8]. The strain diagrams in the stress-relative displacement coordinates were taken at the rate of clamp movement 120 mm/min, and the initial distance between the clamps was 25 mm, with the sample thickness of 200–300 µm. The number of samples tested for each experimental point was 8–10. The variation coefficient of the determined characteristics did not exceed 5–6%.

Calorimetric measurements were made on a differential scanning calorimeter Mettler DSC-30. The first heating of the samples was carried out at 20–150 °C at a rate of 10 degrees/min, and the repeated heating in the range from –60 to 150 °C. All characteristics were determined using the original program METTLER Graph Ware TA 72 PS.5.

The degradation of PU films was conducted at 37 °C in a 0.1 N solution of phosphate buffer (pH 7.4) using 20 × 20 mm films, with a thickness of about 150 µm. After a definite time, the samples were taken from the solution, washed with distilled water, vacuum dried at 40 °C, and weighed.

RESULTS AND DISCUSSION

For synthesis of cross-linked PUs with a constant cross-links density but a variable content of soft segments, PLA triols with M_n ranging from 580 to 2940, PCL diols with M_n 400–2760, and HDI (Table 1) or H₁₂MDI (Table 2) were used.

The thermal properties of PUs were studied using differential scanning calorimetry (DSC). As follows from Table 1, the glass transition temperature (T_g) of the PUs with soft segments and hard segments formed by PCL blocks and PLA blocks, respectively, is higher than that of PCL (–62 °C) [8] and lower than that of PLA (49 °C) [9].

Table 1. Characteristics of the structure and thermal properties of PU networks from PLA triols, PCL diols, and HDI*

PU	M_n of PLA blocks	M_n of PCL blocks	Content of soft segments, %	Gel fraction, %	Weight loss, % after 14 days	T_g , °C	T_m , °C	ΔH_m , J/g
PU-1	2940	400	10.6	88.0	6.83	35.6	43.0	6.5
PU-2	2700	600	16.0	91.6	5.56	30.6	nd	0
PU-3	2340	1000	26.5	–	–	18.7	nd	0
PU-4	1840	1500	40.0	91.1	8.0	–22.3	nd	0
PU-5	1340	2000	52.9	94.6	5.96	–33.7	nd	0
PU-6	580	2760	73.0	93.1	7.91	nd	46.3	42.1

* Calculated average molecular weight between cross-links M_c 3800.

nd – Not detected.

– No data.

Table 2. Characteristics of the structure and thermal properties of PU networks from PLA triols, PCL diols, and H₁₂MDI

PU	<i>M_n</i> of PLA blocks	<i>M_n</i> of PCL blocks	Content of soft segments, %	Gel fraction, %	Weight loss, % after 14 days	<i>T_g</i> , °C	<i>T_m</i> , °C	ΔH_m , J/g
PU-7	2940	400	9.9	74.9	4.0	53.9	52.2	10.8
PU-8	2700	600	14.9	—	1.2	nd	nd	0
PU-9	2340	1000	24.8	88.0	2.1	31.4	nd	0
PU-10	1840	1500	37.5	90.1	2.4	17.0 —3.8	nd	0
PU-11	1340	2000	52.8	91.4	2.2	nd	nd	0
PU-12	580	2760	72.6	93.2	2.3	nd	48.5	42.1

nd – Not detected.

— No data.

According to [7], the crystallization of the PCL blocks of PUs proceeds at the *M_n* of the soft segment ≥ 1200 , *T_g* tends to decrease for PU-4 and PU-5 from 35.6 to -33.7°C , which testifies the growth in the degree of phase separation between the hard and soft segments with an increase in the length of PCL segments. At the equivalent *M_n* values of the PLA and PCL blocks, in the case of H₁₂ MDI (PU-10) (Table 2) two values of *T_g* are observed. However, the obtained polymers have a small phase separation degree, since the cross-linking between the macromolecules of the elastomers disturbed this process. The structure of the obtained elastomers varies from amorphous to semi-crystalline. PUs with the PLA block *M_n* 2700 and lower have an amorphous structure, while with an increase in the *M_n* of the PLA block above 2700, the melting temperatures (*T_m*) observed for PU-1 and PU-7 equal to 43.0 and 52.2°C , respectively, are assigned to the PLA blocks. Poly(D,L-lactide) has an amorphous structure [9], although in this case the hard segment is formed by a poly(lactide) block together with diisocyanate and at a low *M_n* of the PCL blocks, its partial crystallization apparently occurs, while the *T_m* of PU-6 equal to 46.3°C is assigned to the PCL blocks as the *M_n* of the PLA blocks decreases from 2940 to 580.

The tensile strength (σ_t) of the films is affected by factors such as the content of soft and hard segments in the PU structure, their cohesion energy, packing degree of macromolecules, phase separation, cross-linking degree of PUs, etc. [8]. In the curves shown in Fig. 1, the dependence of tensile strength on the content of soft segments has a V-type character. A break in the curves is observed at the soft segment content of about 40 wt %, which corresponds to the soft segment *M_n* of 1500 (Tables 1 and 2). A similar dependence of tensile strength on the soft segment *M_n* is observed also for PU with segments of linear structure, whose soft segments are formed by PCL diols with *M_n* 400–5000. In this case, a bend is observed on the curves also at *M_n* 1500. This is explained by the fact that with the increasing of the PCL block's *M_n* > 1500 the ordering degree of these blocks increases, and they are capable of forming crystalline structures, which promotes the growth of their tensile strength and Young's modulus [8].

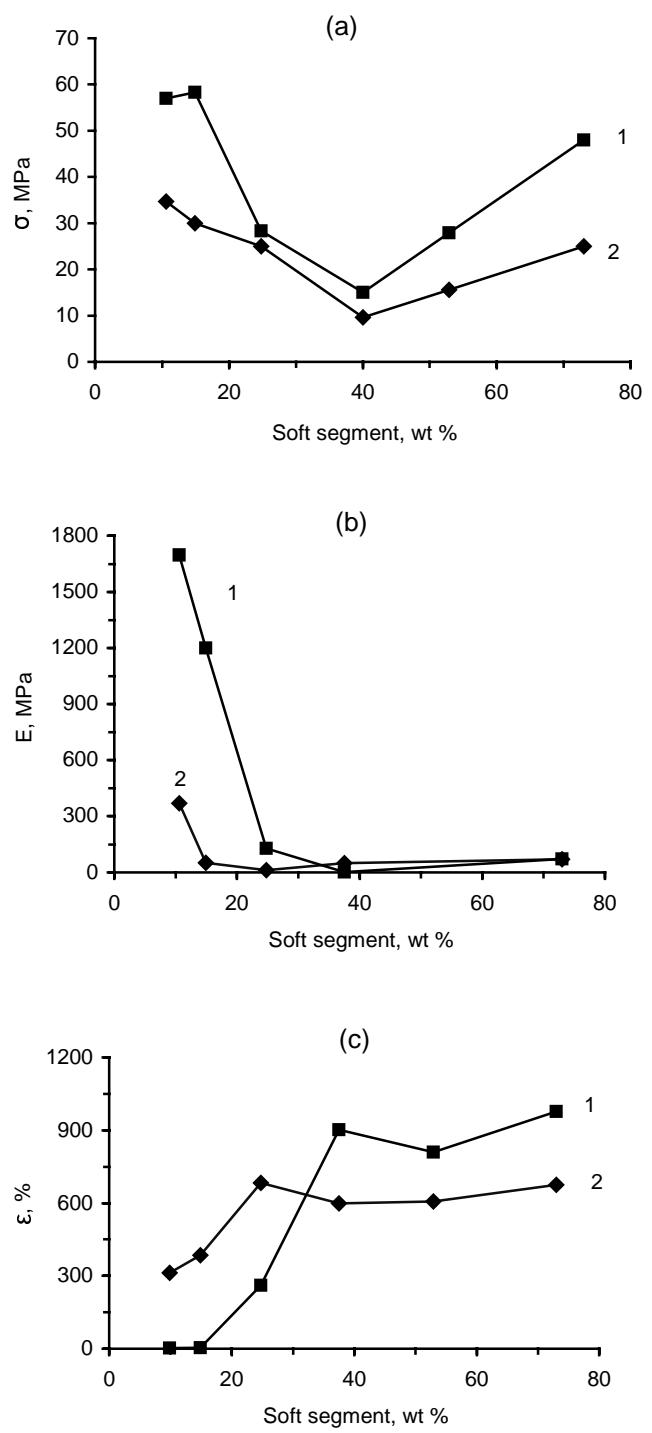


Fig. 1. Plots of tensile strength (a), Young's modulus (b), and relative elongation at break (c) versus the content of soft segments in PU networks containing: 1 – $H_{12}MDI$; 2 – HDI.

As can be seen from Fig. 1a, the PUs with the hard segment content of 85–90 wt % are characterized by high tensile strength values. This can be explained by the high cohesion energy of the lactide units present in the polymer structure, which follows from the high values of its solubility parameter ($\delta = 22.75 \text{ J}^{1/2}/\text{cm}^{3/2}$) [8]. The higher tensile strength indices are in the PU network whose hard segments were formed from diisocyanate or $H_{12}\text{MDI}$: $\sigma = 55\text{--}58 \text{ MPa}$ and 30 MPa , respectively. It can be seen from the curves in Fig. 1a that with the increasing of the soft segment content from 10 to 40 wt %, the PU network tensile strength decreases. This agrees with the existing notion that the properties of PUs with segments of amorphous structure depend on the soft segments content in them. In turn, with the increasing of the soft segments content over 40 wt %, the M_n of these segments also grows, and they have already a higher ordering degree of segments. As follows from Fig. 1b, the PU network samples, especially those in whose hard segments the formation of $H_{12}\text{MDI}$ takes place, have very high Young's modulus indices. From Fig. 1c and Tables 1 and 2 follows that at the soft segment content ≥ 40 wt %, the PU network has properties typical of elastomers, namely, their T_g values are lower by 20°C , and elongation at the break for PU4–PU6 and PU10–PU12 is within the range from 600% to 676% and from 810% to 980%, respectively. The density of the synthesized PUs varies from 1.184 to 1.188 g/cm³.

It can be concluded from Figs 1a, 1b, and 1c as well as Tables 1 and 2 that both rigid and elastomer type materials with high mechanical properties can be obtained from PCL diols and D,L-lactide triols using HDI or $H_{12}\text{MDI}$ for the formation of PU network hard segments and that the mechanical properties of PUs mainly depend on the ratios of the hard and soft segments in the structure.

Poly(D,L-lactide urethane) does not swell in water and degrades within approximately 60 days of immersion in saline solution [6]. The water absorption for PUs with a PLA and PCL block structure reaches 0.65–1.2%. The biodegradation of PU films was investigated in phosphate buffered saline solution (pH 7.4) at a temperature of 37°C . The obtained results for samples with M_c 3800 after 14 days in the solution are presented in Tables 1 and 2. Figure 2 shows the present change in mass versus immersion time in phosphate buffer solution of PUs with M_c 6500 (curves 1 and 2) and M_c 10 500 (curves 3 and 4). PU samples with the soft segment content of 70% (curves 2 and 4) and 16% (curves 1 and 3) were degraded. The structure of polyurethanes with the soft segment content of 70% has PCL blocks with M_n 4600 and 7400, and PLA blocks with M_n 1500 and 2700. PUs with the soft segment content of 16% have PCL blocks with M_n 4800 and 8400, and PLA blocks with M_n 4800 and 8400. It can be seen that the mass losses in the first 30 days do not exceed 2–5%, and degradation occurs mainly in the film's surface, while as the degradation time increases, the mass losses accelerate and when 15–20% is reached, the films' break-up occurs.

With the increasing of M_c from 6500 to 10 500, the polymer cross-linking density decreases. As a result, the crystallization ability of PCL blocks increases. With the increasing degree of crystallinity of PCL blocks (curves 2 and 4), the

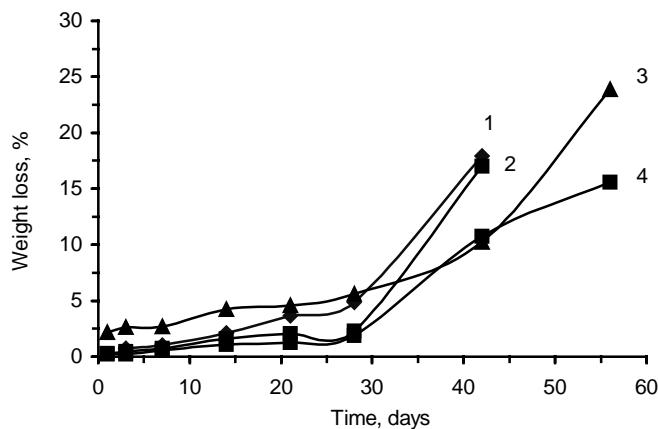


Fig. 2. Weight loss of PUs versus time of degradation samples in 0.1 N solution of phosphate buffer (pH 7.4) at 37°C. Soft segment content: 1 and 3 – 16%, 2 and 4 – 70%; 1 and 2 – M_n 6500, 3 and 4 – M_n 10 500.

degradation rate tends to decrease, while the amorphous PU structure regions are more susceptible to degradation. With increasing M_n of PLA blocks (curves 1 and 3), the PU hydrophily decreases and the mass losses of the films decrease.

CONCLUSIONS

Degradable polyurethane networks were synthesized by cross-linking poly(D,L-lactide) triols and poly(caprolactone) diols with 1,6-hexamethylenedi-isocyanate or 4,4'-methylene bis(cyclohexyl) diisocyanate. Varying the content of soft segments in the PU structure, both rigid and elastomer type materials with high mechanical properties are obtained. With increasing the amount of soft segments in PUs, the ordering degree of the blocks grows, and crystalline structures are formed therein. The degradation rate of PUs is affected simultaneously by factors such as the M_n of PLA and PCL blocks, phase separation, and degree of crystallinity.

The obtained cross-linked PUs can be interesting for the creation of biodegradable biomaterials with enhanced deformation strength characteristics.

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Polü(laktiid)trioolidest ja polü(kaprolaktoon)dioolidest ristseotud polü(esterureetaanide) süntees ja omadused

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On sünteesitud polüureetaanid, mille pehmed plokid on moodustunud polü(kaprolaktoon)dioolide ja kõvad polü(laktiid)trioolide reaktsioonil erinevate diisotsüanaatide ja initsiaatoritega. On määratud pehmete ja kõvade plokkide arvkeskmise molaarmassi mõju polüureetaanide erinevatele omadustele.