

# Influence of Crosslinkers on Properties of New Polyurethane Elastomers

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*A series of poly(ester urethane)s were synthesized, containing, poly( $\epsilon$ -caprolactone) diol of  $M_n = 2000$  as soft segments. Each series used the same diisocyanate in the hard segment, i.e., 1,6 hexamethylene diisocyanate, with the same content. The polyurethane polymers were prepared by a two-step polymerization in the absence of catalyst, at the molar ratio of OH/soft segment /NCO/ OH chain extenders = 1/2/1. The chain extenders were 1,12-dodecan diol, glycerin and castor oil. For all polymers the structures were determined by FTIR, the physico-chemical and thermal properties were determined by thermogravimetric analysis and additionally tensile properties as well as Shore A hardness were analyzed. Poly(ester urethane)s with castor oil exhibited higher tensile strength (up to 27 MPa vs 30 MPa) and elongation at break (up to ~780% vs. 1000%) in comparison with the corresponding glycerin poly(ester urethane)s.*

*Keywords: polyurethane elastomers, chain extenders, crosslinkers, mechanical properties, thermal behaviour*

Poly(ester urethanes) with poly(lactide), poly(glycolide), and poly( $\epsilon$ -caprolactone) blocks and diisocyanate in their structure have good elastomer properties and biocompatibility as well as high physical and mechanical properties.

Typical PU elastomers are multiblock copolymers including alternate "soft" polyether or polyester segments and "hard" polyurethane segments. The thermodynamic incompatibility of these segments often combined with crystallization of either one or both segments, drives their microphase separation into hard and soft domains. This microphase separation is responsible for the excellent elastic properties of polyurethanes [1-3].

PU based on poly(ester)urethanes and poly(carbonate) urethanes have been claimed to be promising biodegradable materials with potential uses in biomedical applications, as long or short term medical implants, mainly in blood contact devices [4-11]. These polyurethanes have received great attention as they possess a broad range of chemical and physical properties, good biocompatibility and can be designed to degrade in biological environments due to the possibility of easily varying their chemical composition.

Commonly used polyurethanes are based on aromatic diisocyanates. These, however, lack biocompatibility due to toxic degradation products originating from the aromatic hard segment [11, 12]. Aliphatic diisocyanates in addition to biocompatibility also provide polyurethanes better light stability and better resistance to hydrolysis and thermal degradation.

Vegetable oils are one of the cheapest and most abundant biological sources available, and their use as starting materials has numerous advantages such as: low toxicity, inherent biodegradability, and high purity [13].

Poly(caprolactone), commonly used as soft segment in polyurethanes [14], is known to be biocompatible, with low hydrolytic and enzymatic degradation tendency. It is already used for several long term applications and is expected to be very suitable as a reconstruction material. Usually, these syntheses are carried out with the aid of a catalyst, but catalysts do not only catalyze chain extensions but also promote several side reactions [15]. Moreover,

the absence of catalysts will also increase biocompatibility [16,17].

We studied crosslinked PUs that were synthesized by reacting polycaprolactone diol with 1,6-hexamethylene diisocyanate and 1,12-dodecandiol, glycerin or castor oil, as chain extenders, at different molar ratios.

The aim of this work is to investigate the structural and thermal properties, as well as the mechanical behaviour of PUs, depending on the structure of the chain extenders and the nature of the crosslinking in the PU at a constant amount of soft segment.

## Experimental part

### Materials

1,6-hexamethylene diisocyanate (HDI) supplied by Fluka was used as received. The polyester diol was poly(caprolactone)(PCL). This polymer was provided by Aldrich. The polydiol average molecular weight is 2000 g/mol. The chain extenders: 1,12 -dodecane diol (DDD), glycerin (Gly), castor oil(CO) provided from Aldrich were used as received. Polyester diol and chain extenders were checked for the content of moisture and, if necessary, dried under a vacuum until the content of water was below 0.03%.

### Polyurethanes synthesis

Typically, synthesis of PU was done by the following procedure and the molar ratios of added reagents for the various PU are shown in table 1.

The polyurethanes were synthesised via the two step polymerization procedure under a constant nitrogen flow to avoid the water presence in the reaction vessel. The average hard-segment (HS) composition was controlled by the molar ratios of polyester-diol / HDI / diol and triol and nature of diol and triol used in the synthesis. The OH diol / OH triol ratio used was of 1/1 in the each of the synthesized polyurethane samples. The synthesis of PUs was performed in a 1-L glass reactor at normal pressure, under a nitrogen blanket and vigorous agitation. The NCO/OH ratio of all formulations was 1.03-1.05. In the case of the prepolymer procedure, polyester diol was reacted with a diisocyanate at 80°C for 2 h, in order to yield a prepolymer

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**Table 1**  
FORMULATIONS AND HARDNESS OF THE POLYURETHANE ELASTOMERS OBTAINED

Nr.	Designation Samples	Molar ratio PCL / HDI / Chain extenders	Chain extenders	Hardness Shore A
1	PU1	1:2:1	1,12 -dodecandiol	96
2	PU2	1:2:1	glycerin + 1,12 -dodecandiol	89
3	PU3	1:2:1	Castor oil + 1,12 -dodecandiol	98
4	PU4	1:2:1	Castor oil	98.4

that was mixed in the second step with chain extenders at 80°C for 10 min. The progress of the reaction was followed by using infrared absorption of the isocyanate stretching band at 2200-2300 cm<sup>-1</sup> and the reaction was considered to be complete when this band disappeared. The resulting material was poured into a mold and left to cure at 80°C for 20 h, post-curing of the PU proceeding at room temperature for 7 days. Under these conditions the addition of catalysts was not necessary. Polyurethane sheets thus prepared were used for the determination of mechanical and physical properties and for the thermal analysis.

#### Measurements

The FTIR spectra were recorded on a Bruker VERTEX 70 equipped with a Golden Gate single reflection ATR accessory. The spectra were recorded in the range 600-4000 cm<sup>-1</sup> with a nominal resolution of 4 cm<sup>-1</sup>.

The thermal stability of polyurethanes was tested in an air atmosphere by thermogravimetric analysis (TGA) using a DERIVATOGRAPH Q-1500 D apparatus (Hungary). The heating rate was 10°C / min. The initial weight of the samples was about 50 mg and the temperature range was 30-700°C.

Stress-strain measurements were performed on dumbbell-shaped samples cut from the obtained polyurethane sheets. The tests were performed at room temperature using a Shymadzu EZTest (Japan), equipped with a 5kN load cell. The used cross-head speed was 50 mm/min. At least five identical dumbbell-shaped specimens for each PU type were tested, and their average mechanical properties are reported. The reported errors are the subsequent standard deviations.

Contact Angle Measurements (CA) were performed using deionized water and ethylene glycol droplets of 5 µL over the different neat polyurethanes surfaces using a Dataphysics Contact Angle System KSV Instruments LTD, Finland. Water contact angle measurements were acquired using the sessile drop method [18]. The contact angle was measured within 45-60 s of the addition of the liquid drop with an accuracy of ±1°. Measurements were repeated six to ten times with different test pieces of the same PU sheet to check the accuracy.

Hardness measurements were done using an INSTRON machine according to Shore A standard.

## Results and discussions

### IR Spectroscopy

The FT-IR spectra of the polymers indicated the absence of any residual isocyanate (no absorption at 2270 cm<sup>-1</sup>) and showed strong absorptions at 1720 and 3300 cm<sup>-1</sup>

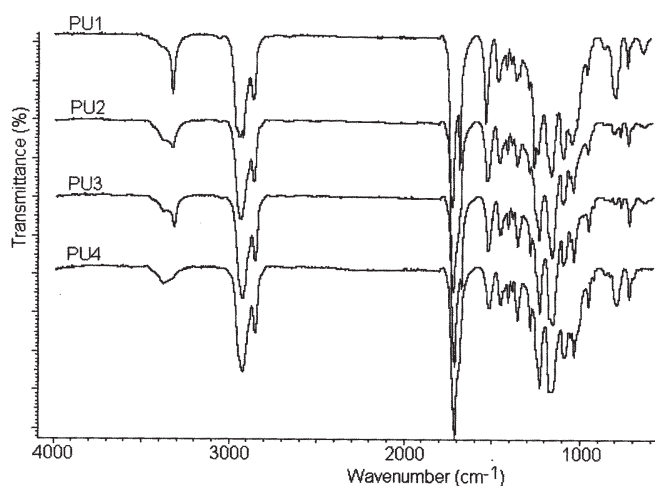


Fig. 1. FTIR spectra of polyurethane elastomers

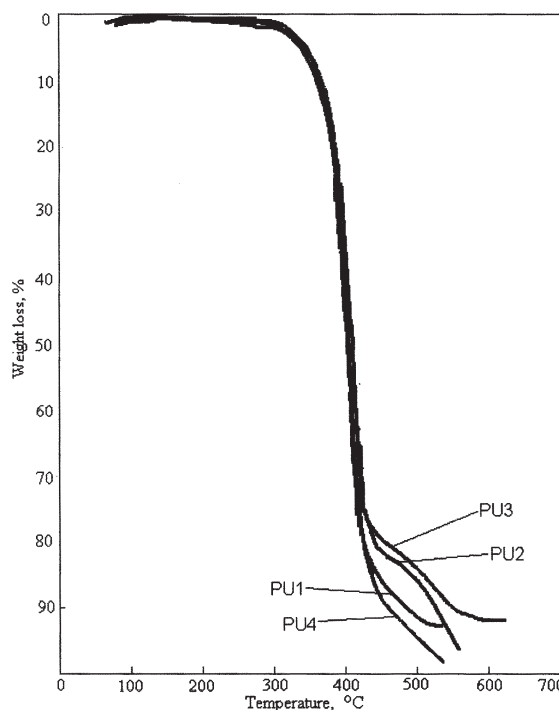


Fig. 2. TG curves of polyurethane elastomers

indicating the formation of the urethane linkage. The FTIR spectra of the series with different hard segment structure are shown in figures 1,2.

The FTIR spectra of the polyurethane exhibited the typical bands for polyurethanes: -NH, (free and bonded) at 3300-3400 cm<sup>-1</sup>, CH<sub>2</sub> at 2850-2970 cm<sup>-1</sup>, C=O in bonded

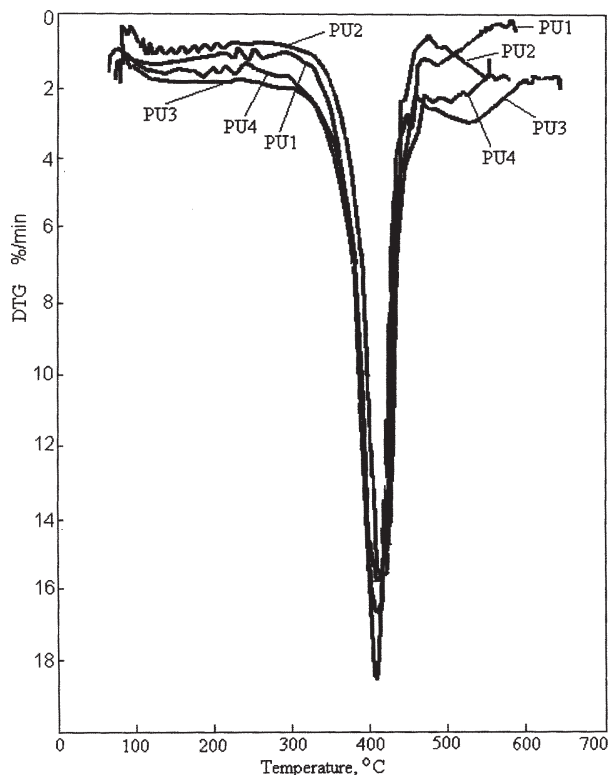


Fig. 3 Differential thermogravimetric curves of polyurethane elastomers

urethane group at  $1680\text{--}1720\text{ cm}^{-1}$  and  $\text{C-O-C}$  in ester group at  $1053\text{ cm}^{-1}$ .

Almost all the infrared studies on polyurethanes were focused on two principal vibration regions: the N-H stretching vibration ( $3200\text{--}3400\text{ cm}^{-1}$ ) and the carbonyl  $\text{C=O}$  stretching vibration in the amide I region ( $1680\text{--}1720\text{ cm}^{-1}$ ). Polyurethanes are capable of forming several kinds of hydrogen bonds due to the presence of a donor N-H group and a  $\text{C=O}$  acceptor group in the urethane linkage. This is why that hard segment-hard segment or hard segment-soft segment hydrogen bonding can exist.

In the case of DDD-polyurethane elastomers, the appearance of a single N-H band at  $3310\text{ cm}^{-1}$  which is growing bigger with the nature of cross-linking of the hard segment suggested that most of its N-H groups were hydrogen bonded.

#### Thermogravimetric analysis

Thermogravimetric analysis (TGA) has been used to examine the thermal stability of the PUs. The results are presented in figures 3,4.

All the polyurethane elastomers are stable at  $300^\circ\text{C}$ . Weight loss was very slow until  $300\text{--}340^\circ\text{C}$ , when a rapid drop followed, which ended at approximately  $400\text{--}450^\circ\text{C}$ . The shapes of the weight loss curves of PU elastomers were similar in the temperature range of  $100\text{--}450^\circ\text{C}$ .

TGA data for PU1, PU2, PU3 and PU4 reveal different degradation processes correlated with the structure of hard segments in the temperature range of  $450\text{--}600^\circ\text{C}$ .

The weight loss increases at lower temperatures when only castor oil is used as chain extender. This is in accordance with the existence of the plasticizing effect of dangling chains of the castor oil. The main degradation process can be observed at temperatures around  $400^\circ\text{C}$ .

The increase of the temperature of degradation indicates a lower rate of diffusion of the degraded products out of the cross-linking matrix [19].

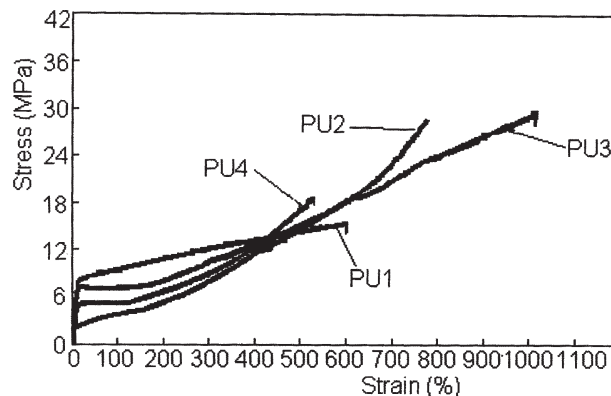


Fig. 4. Stress vs strain curves for the polyurethane obtained

#### Mechanical properties

By varying the chain extender molecular weight, as well by varying the structure of chain extenders, modifications of stress-strain, modulus and elongation occur [20].

Figure 4 presents the stress-strain curves representing the various chain extender polyurethane elastomers, having a common soft segment.

Clearly three different regimes are visible. First, the behaviour at low deformations is explained by the pure elastic deformation belonging to regular elastomers [21]. Second, we encounter an area of plastic flow. This is much the same for all the studied polymers, indicating great possibility of shear - induced crystal fragmentation.

Third, at strains above 200% an upswing in some of the curves can be observed, which can be attributed to strain - induced crystallization of soft segment chains.

In the case of PU sheet with DDD, the tensile strength at break is 14 MPa and maximum elongation is 600 %. The PU sheet with DDD and castor oil had the tensile strength at break of 30 MPa and maximum elongation of 1000 %. PU sheets with DDD and glycerin display strength of 27 MPa and elongation of 780 %. The PU sheet with castor oil only is more rigid having a tensile strength at yield of 19 MPa and elongation at break of 540 %.

It is clear that varying the chain extenders structure and cross-linking affects the tensile properties of the cross-linked polyurethane materials.

#### Surface wettability

Contact angle measurements with water were performed in order to study the relative capacity of the materials to interact with water at the surface of the materials thus giving us an idea of their relative polarity. Surface wettability and reduced friction are considered to play a major role in the wearing comfort of implants. The hard segment fraction was varied in the formulation of the polyurethane films in order to determine its influence on the wettability. Table 2 presents contact angles and the work of adhesion obtained for the different materials depending on the hard segment composition used.

It is remarkable that glycerin-based polyurethanes had higher contact angles than castor oil-based polyurethanes, this meaning lower polarity. This difference could arise from two different reasons, (a) the different degree in which the hard segments interact among themselves and (b) the notable difference in phase segregation behaviour. Hydrophobic surfaces are known to inhibit the proliferation and increase of the rate of apoptosis of anchorage-dependent osteoblastic cells compared to cells grown on hydrophilic surfaces [22].

**Table 2**  
CONTACT ANGLE ( $\theta$ ) AND WORK OF ADHESION ( $W_a$ ) VALUES  
OF THE POLYURETHANE FILM SURFACES

sample	water		ethylene glycol	
	$\theta$ ( $^\circ$ )	$W_a$ (mN/m)	$\theta$ ( $^\circ$ )	$W_a$ (mN/m)
PU1	82.63	82.13	62.53	70.141
PU2	88.72	79.34	78.82	75.342
PU3	85.43	78.59	75.45	60.058
PU4	82.54	82.25	71.34	63.357

**Table 3**  
INTERFACIAL TENSION FOR A SOLID-LIQUID SYSTEM ( $\Gamma_{sl}$ )  
POLYURETHANE ELASTOMERS OBTAINED

sample	$\lambda_{sv}^p$ (mN/m)	$\lambda_{sv}^d$ (mN/m)	$\gamma_{sl}$ (mN/m)	
			water	ethylene glycol
PU1	10.05	15.57	16.28	3.48
PU2	13.56	20.60	17.62	10.82
PU3	15.55	5.68	15.44	9.18
PU4	16.50	6.72	13.78	7.87

p-polar, d- disperse

The work of adhesion,  $W_a$ , was calculated using the following equation:

$$W_a = \gamma_{lv} (1 + \cos \theta)$$

where  $\gamma_{lv}$  is the surface tension of the liquid used for the contact angle measurement.

There was a difference between the work of adhesion of PU with diol chain extenders and that of the cross-linked PU.

The interfacial tension for a solid-liquid system ( $\gamma_{sl}$ ) was calculated using the following equation [23]

$$\gamma_{sl} = \left( \sqrt{\gamma_{lv}^p} - \sqrt{\gamma_{sv}^p} \right)^2 + \left( \sqrt{\gamma_{lv}^d} - \sqrt{\gamma_{sv}^d} \right)^2$$

The resulting interfacial tensions are listed in table 3.

The drop of liquid forming an angle may be considered as resting in equilibrium enabled through balancing the three forces: the interfacial tensions between solid and liquid SL, those between solid and vapor SV and those between liquid and vapor LV.

From table 3, we can see that the values of the interfacial tension to liquid of polymer containing glycerin are higher compared to those of the other compositions, due to the differences in matrix. The variation of the hard segment structure in the polymer matrix may also have affected the surface properties. The smaller  $\gamma_{sl}$  variable is, the more biocompatible the material is.

### Hardness

The influence of the different polyurethane microstructures on their macroscopic behaviour was reflected in their hardness. Table 1 shows Shore A hardness of polyurethane elastomers with different compositions of hard segment. There is no great difference between the hardness of different samples. It seems that the similarity of the structures and the small difference in cross-linking density of the different samples are the main reasons for this behaviour.

### Conclusions

High molecular weight polyurethanes were synthesized without the use of solvents or catalysts, by reacting polyols with terminal primary functional groups with aliphatic diisocyanate. The prepolymers were chain-extended with bifunctional precursor chains and/or with castor oil or glycerin as a trifunctional crosslinker at stoichiometric ratios.

Depending on the parameters of the formulation, the resulting PU exhibited hardness of about 90-98 Shore A.

These polyurethanes displayed a typical behaviour of a hard rubber at room temperature with a tensile strength of 14-30 MPa and elongation at break of 540 - 1000%. Three well-defined steps of degradation of the PU were observed by using TGA measurements.

The variation of the hard segment structure in the polymer matrix may also have affected the surface properties. The properties of the PU sheets were mainly governed by the stoichiometric balance of the components used in the reaction and the nature of cross-linking.

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