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Synthesis and properties of new polyurethane elastomers: influence of hard segment structure

Summary — Two series of poly(ester urethane) (PUR) elastomers, containing poly(ε-caprolactone) diol of M_n = 2000 as soft segments were synthesized. In each series the same diisocyanate in hard segment, *i.e.*, 1,6-hexamethylenediisocyanate was used in the same content. The PUR polymers were prepared in two-step polymerization in the absence of a catalyst; the molar ratio of OH_{polyol} / NCO / $OH_{chain\ extender}$ was 1/2/1. The chain extenders were 1,4-cyclohexane diol, 1,4-bis(hydroxymethyl)cyclohexane diol, glycerin or castor oil. The structures of all polymers were determined by FTIR, the physico-chemical and thermal properties were determined by differential scanning calorimetry and by thermogravimetry and additionally tensile properties were analyzed. Poly(ester urethane)s with 1,4-cyclohexane diol exhibited higher tensile strength (up to 16 MPa *vs* 13 MPa) and elongation at break (up to ~780 % *vs*. 600 %) in comparison with the corresponding poly(ester urethane)s based on 1,4-bis(hydroxymethyl)cyclohexane diol. A decrease in the chain length between crosslinking points was accompanied by an increase in thermal stability. Tensile strength can be attributed to a relatively dense crosslinking network and strong intermolecular hydrogen bonding.

Key words: poly(ester urethane)s, elastomers, chain extenders, crosslinking, mechanical properties, thermal properties, wettability.

SYNTEZA I WŁAŚCIWOŚCI NOWYCH ELASTOMERÓW POLIURETANOWYCH: WPŁYW SEGMENTÓW SZTYWNYCH

Streszczenie — Badania dotyczą poliestrouretanów (PUR) na podstawie poli(ε-kaprolaktanu) diolu (PCL) o Mn = 2000 tworzącego segmenty elastyczne oraz 1,6-diizocyjanianu heksametylenu (HDI). Syntezę prowadzono dwuetapowo, bez udziału katalizatora, a w charakterze przedłużaczy łańcucha otrzymanego na pierwszym etapie prepolimeru zastosowano związki dwufunkcyjne, mianowicie 1,4-cykloheksanodiol (CHD) lub 1,4-bis(hydroksymetylo)cyklometyloheksan (HMCD), indywidualnie bądź w mieszaninie z poliolami — gliceryną albo olejem rycynowym. Syntezę PUR prowadzono w warunkach stałego stosunku molowego grup: OH z wyjściowego poliolu: NCO:CH z przedłużacza łańcucha wynoszącego 1:2:1. Otrzymano dwie serie PUR (na podstawie CHD bądź HMCD), z których każda obejmowała 3 etapy produktów różniące się rodzajem przedłużacza łańcucha (por. tabela 1, próbki PUR1—3 i PUR4—6). Budowę chemiczną elastomerów scharakteryzowano metodą IR (rys. 1 i 2), określono ich właściwości cieplne (TGA — rys. 3 i 4, DSC — rys. 5 i 6) oraz dynamiczne i statyczne właściwości mechaniczne (rys. 7—10). Produkty te scharakteryzowano także metodą pomiaru kąta zwilżenia (θ) określając na tej podstawie wartości pracy adhezji (W_a) i napięcie międzyfazowe (γ_{sl}, tabele 2 i 3). Wyniki zinterpretowano z uwzględnieniem wpływu wywieranego przez wyjściowy stosunek stechiometryczny składników oraz stopień usieciowana PUR i rodzaj wiązań sieciujących.

Słowa kluczowe: poli(estrouretany), elastomery, przedłużacze łańcucha, usieciowanie, właściwości mechaniczne, właściwości cieplne, zwilżalność.

Polyurethane (PUR) elastomers are multiblock copolymers comprised of alternating "soft" polyether or polyester segments and "hard" polyurethane segments. The thermodynamic incompatibility of these segments often combined with crystallization of either one or both of them, drives to phase separation into hard and soft domains. This phase separation is responsible for the excellent properties of PUR elastomers [1—3].

Poly(ester urethanes) with poly(ε-caprolactone) blocks and diisocyanate fragments in their structures have good biocompatibility as well as good physical and mechanical properties. So, they have been claimed to be promising biodegradable materials with potential use in biomedical applications, especially as long or short term medical implants, mainly in blood contact devices [4—11]. These types of PUR have attracted great attention as they show not only biodegradability but also good chemical and physical properties and can degrade in biological environments. In addition to biocompatibility, aliphatic diisocyanates also provide these products with better light stability and better resistance to hydrolysis and thermal degradation.

The versatile properties of these PUR are attributed to the micro-phase separated structures that these materials present. The hard domains generally formed of diisocyanate — chain extender units act as thermally breakable physical crosslinking sites, as well as reinforcement for the soft segment phase. Soft segment domains provide elastomeric character to the polyurethane. [6, 9, 10, 12]. Poly(ε-caprolactone) is commonly used as soft segments in polyurethanes [13]. This polymer is known to be biocompatible, show low hydrolytic and enzymatic degradability tendency, and is already used for several long term applications [14] so is expected to be very suitable as a reconstruction material.

Usually, the syntheses of PUR described are carried out with the aid of a catalyst, but catalysts do not only catalyze chain extensions but also promote several side reactions [15]. The absence of catalysts should also increase biocompatibility [15—17].

The aim of this work was to investigate dependence of the structural and thermal properties, as well as the mechanical behavior of PUR, on the chain extenders' structures and nature of the crosslinking in PUR at a constant amount of soft segment. In this work we studied segmented PUR in which the soft segments were formed of polycaprolactone diols in each case, while hard segments were from 1,6-hexamethylene diisocyanate and various polyols used as chain extenders, namely glycerin or castor oil triols, 1,4-cyclohexane diol, or 1,4-bis(hydroxymethyl)cyclohexane diol.

EXPERIMENTAL

Materials

1,6-Hexamethylene diisocyanate (HDI) obtained from Fluka was used as received. The polyesterdiol — poly(ε-caprolactone) (PCL) with average molecular weight 2000 g/mol was provided by Aldrich. The chain extenders — 1,4-cyclohexane diol (CHD) and 1,4-bis(hydroxymethyl)cyclohexane diol (HMCD) from Fluka, glycerin and castor oil from Aldrich — were used as received. Polyester diol and chain extenders were checked for the content of moisture and dried under a vacuum until the content of water was below 0.03 %.

Polyurethanes syntheses

Table 1 presents the compositions of poly(ester urethane)s obtained at the same initial molar ratio of substrates PCL:HDI: chain extender equal to 1:2:1, differing in chain extender type. Typically, synthesis of PUR was done according to the following procedure:

The products were synthesised *via* the two-step polymerization at a constant nitrogen current flow to avoid the presence of water in the reaction vessel. The average hard-segments composition was controlled by the molar ratios of the components and nature of diol and triol used in the synthesis. The OH_{diol} / OH_{triol} ratio used was 1:1 in the each of the synthesized polyurethane samples. The synthesis of PUR was performed in a 1 L glass reactor at normal pressure, under a nitrogen blanket and vigorous agitation. The NCO/OH ratio in all formulations was 1.03—1.05. In the first step PCL was reacted with HDI at 80 °C for 2 h in order to yield a prepolymer, that was mixed in the second step with chain extenders at 80 °C for 10 min. The end of the reaction was monitored by IR absorption of the isocyanate stretching band at 2200—2300 cm^{-1} 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. 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 resistance study.

Table 1. Types of chain extenders in poly(ester urethane)s prepared from the systems with constant initial molar ratio of PCL:HDI: chain extender = 1:2:1

Designation of samples	Chain extenders
PUR1	1,4-cyclohexane diol
PUR2	glycerin + 1,4-cyclohexane diol
PUR3	Castor oil + 1,4-cyclohexane diol
PUR4	1,4-bis(hydroxy-methyl)cyclohexane
PUR5	Glycerin + 1,4-bis-(hydroxymethyl)cyclohexane
PUR6	Castor oil + 1,4-bis-(hydroxymethyl)cyclohexane

Methods of testing

The FTIR spectra were recorded using a Bruker-VERTEX 7 Instruments equipped with a Golden Gate single reflection ATR accessory. The spectra were recorded in the range 600—4000 cm^{-1} with a nominal resolution of 4 cm^{-1}.

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

A differential scanning calorimeter (DSC) type DSC-7 Perkin-Elmer was used for thermal analysis and was operated at a heating rate of 10 °C/min. The thermal transition behavior was studied using measurements involving a temperature range of -100 °C to 100 °C. Tests were conducted for samples of about 10 mg exposed to a gradual heating procedure in order to observe the glassy transition temperature (T_g).

Dynamic mechanical analysis (DMA) was performed using a Perkin Elmer Diamond DMA to determine the storage modulus (*E′*) and the loss tangent (tan δ). All samples were scanned from a temperature of -100 to 200 °C at a constant heating rate of 2 °C per min. The resulting plots for *E′* and tan δ are displayed as functions of frequency at 1 Hz .

Stress-strain measurements were performed using the dumbbell-shaped samples cut from the polyurethane sheets obtained. The tests were performed at room temperature using a Shimadzu EZTest (Japan) apparatus equipped with a 5 kN load cell. The used cross-head speed was 50 mm/min. Five identical dumbbell-shaped specimens for each PUR type were tested, and their average mechanical properties have been reported.

Contact angle (θ) measurements 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 θ value was measured within 45—60 s of the addition of the liquid drop with an accuracy of ±1°. The measurements were repeated six to ten times for different test pieces of the same PUR sheet to check the accuracy.

RESULTS AND DISCUSSION

Chemical structures

The FTIR spectra of the two PUR elastomers with different hard segment structures are shown in Figures 1 and 2. These spectra indicated the absence of any residual isocyanate (no absorption at 2270 cm^{-1}) and showed strong absorptions at 1730 and 3320 cm^{-1} indicating the formation of the urethane linkages.

The spectra exhibited also the bands typical for polyurethanes: -NH, (free and bonded) at 3300—3400 cm^{-1}, CH_2 at 2850—2970 cm^{-1}, C=O in bonded urethane group at 1720—1740 cm^{-1}, aromatic group at 1500 cm^{-1} and -C-O-C- in ester group at 1053 cm^{-1}.

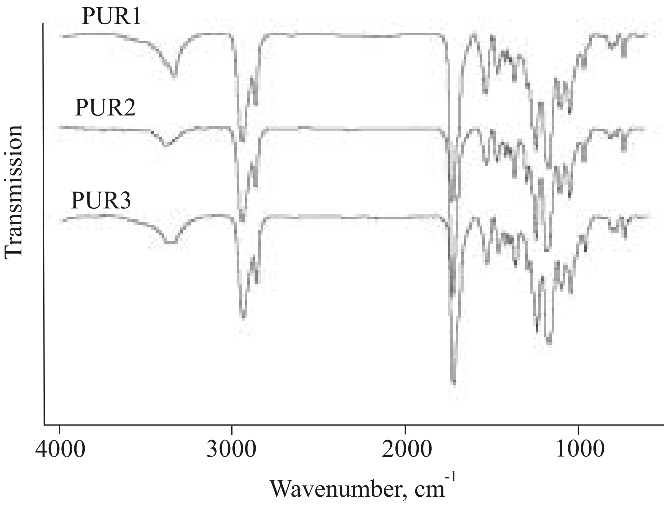

Fig. 1. FTIR spectra of polyurethane elastomers synthesized with CHD as chain extender

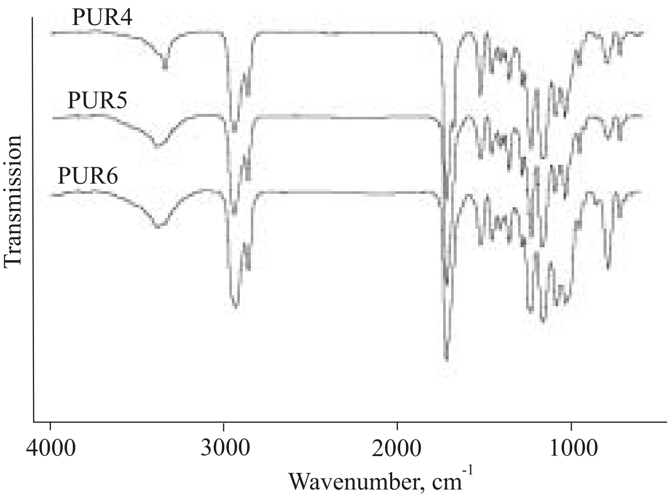

Fig. 2. FTIR spectra of polyurethane elastomers synthesized with HMCD as chain extender

Almost all the infrared research studies on polyurethanes have been focused on two principal vibration regions: the N-H stretching vibration (3200—3400 cm^{-1}) and the carbonyl C=O stretching vibration in the amide I region (1690—1730 cm^{-1}). Polyurethanes are able to form several kinds of hydrogen bonds due to the presence of a donor N-H group and C=O acceptor group in the urethane linkage. It is because the hard segment-hard segment or hard segment-soft segment hydrogen bonding can exist.

These bands have been widely used to characterize the hydrogen bonding state of the polymer, and to correlate this with the phase separation in the system [19—21]. It is well known that in hydrogen-bonded urethanes N-H and C=O bands appear at lower wavenumbers than the bands that appear in urethanes free from hydrogen bonding [21]. In the case of HMCD-polyurethane elastomers (Fig. 2), the appearance of a single N–H band at 3310 cm^{-1} which is growing bigger with crosslinking of the hard segment suggested that most of its N–H groups were hydrogen bonded. In the case of CHD based polyurethane (Fig. 1), N–H absorption band at 3320 cm^{-1} was found, indicating the existence of non-hydrogen-bonded N–H groups. This is due to a steric hindrance effect appearing in CHD, which blocks the formation of hydrogen bonds.

Thermal properties

Thermogravimetric analysis (TGA) has been used to examine the thermal stability of the PUR. CHD based PUR (Fig. 3) is stable at 300 °C, while HMCD based PUR (Fig. 4) is stable at 340 °C. In both cases weight loss was very slow until 300—340 °C, when a rapid drop followed, which ended at approximately 450—500 °C. The

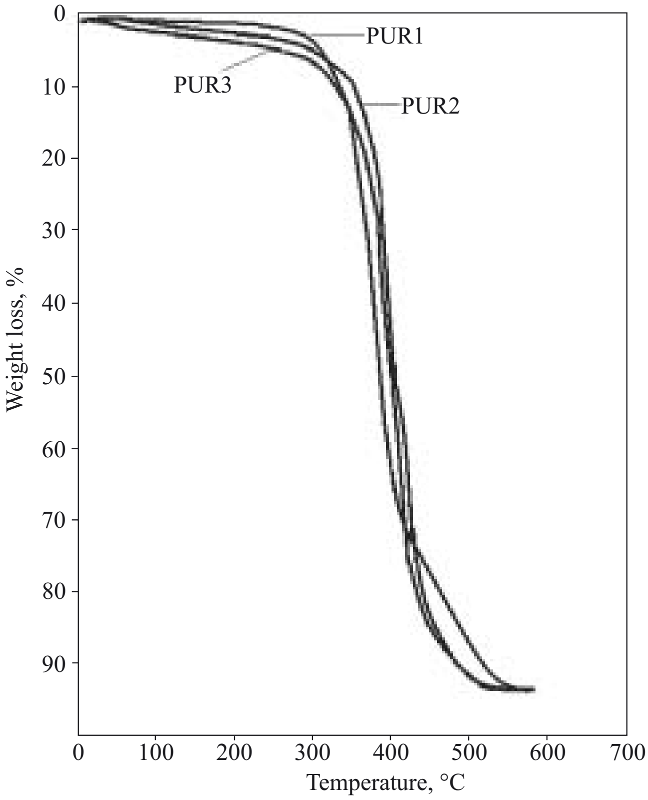

Fig. 3. TGA curves of CHD-based polyurethane elastomers

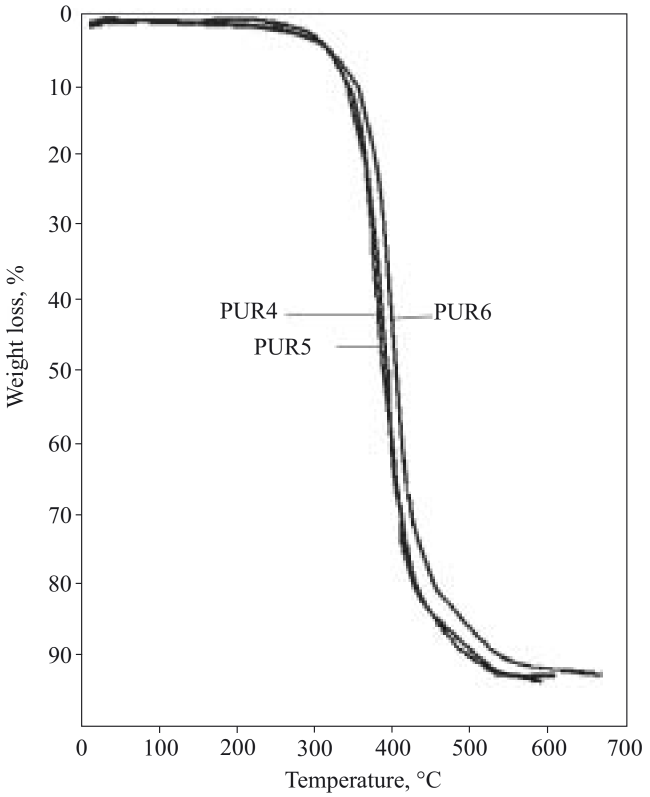

Fig. 4. TGA curves of HMCD-based polyurethane elastomers

weight loss curves of PUR elastomers were similar in the temperature range of 300—500 °C independently on the type of the chain extender used.

TGA data for PUR1, PUR2 and PUR3 reveal different degradation processes correlated with the structures of hard segments. PUR3 based on castor oil had its fastest rate of loss at 300 °C, while PUR2 based on glycerin had its fastest rate of loss at 350 °C. So, this weight loss occurs and increases for sample subjected to lower temperature when castor oil is used, what is in accordance with the existence of the plasticizing effect of dangling chains of the castor oil.

The increase in the temperature maximum for PUR2 and PUR3 in comparison with PUR1 indicates a lower rate of diffusion of the degraded products out of the matrix [22]. Thus, it is evident that the crosslinking bonds restrict the diffusion.

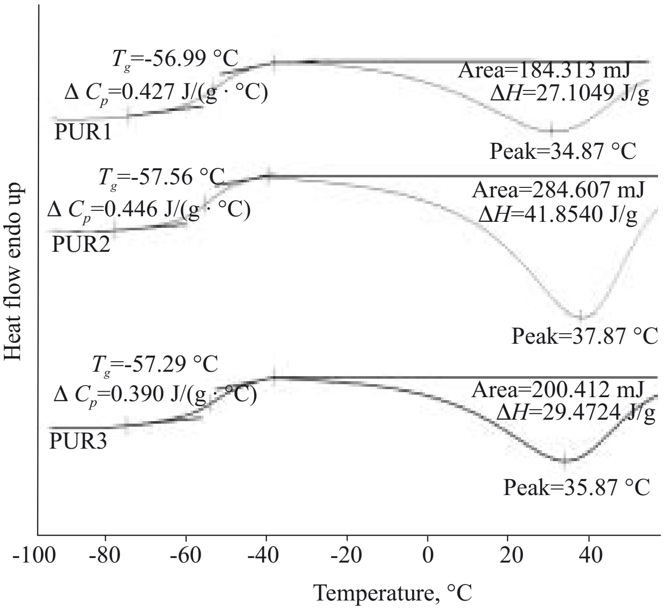

Fig. 5. DSC plots of CHD-polyurethane samples

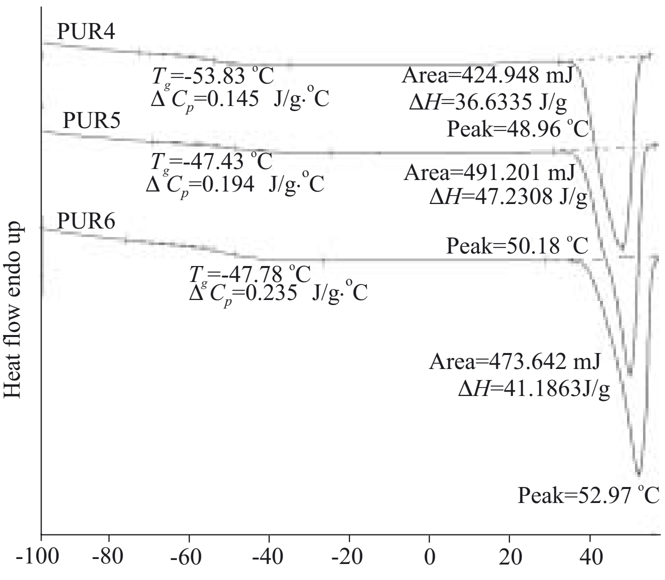

Fig. 6. DSC scan plots of HMCD-polyurethane samples

Figures 5 and 6 present the DSC thermograms obtained for the different polyurethanes in temperature range between -100 and 100 °C. It was evident that the hard segment structure influenced the glass transition temperature of the crosslinked polyurethanes.

The hard segment of HMCD-PUR was expected to have a more ordered structure because hard segments are mainly connected by the long and flexible chains. On the other hand, the alignment of the hard segments of CHD is hindered or restricted due to the small length and low flexibility of these segments. For HMCD-based polyurethanes (Fig. 6) glass transition temperature values indicate the influence of the hard segment composition on the polyurethanes soft microdomains composition, thus again indicating a high tendency of phase separation.

In this case the difference might also be due to the various chain extenders employed. The increase in T_g is attributed to a certain degree of phase mixing of hard and soft segments. This suggests that in this case the physical crosslinking has a larger influence on the soft segment T_g than phase mixing.

The value of T_g is about 10 °C higher for HMCD-PUR than that of CHD-PUR, indicating the presence of some hard segments in the soft segment phase. The higher T_g, as well as the absence of a high melting temperature are indicators of phase mixing.

Dynamic and static mechanical properties

The dynamic mechanical behavior of the polymers is shown in Figures 7 and 8.

All the polymers exhibit loss modulus transitions at approximately -45 to -50 °C, corresponding to the soft segment glass transition. The CHD based PUR (Fig. 7) shows another loss peak at 55—60 °C which is attributed to the melting of the crystalline phase of poly(ε-caprolactone). For HMCD based PUR (Fig. 8) this transition is observed as a shoulder at 50 °C.

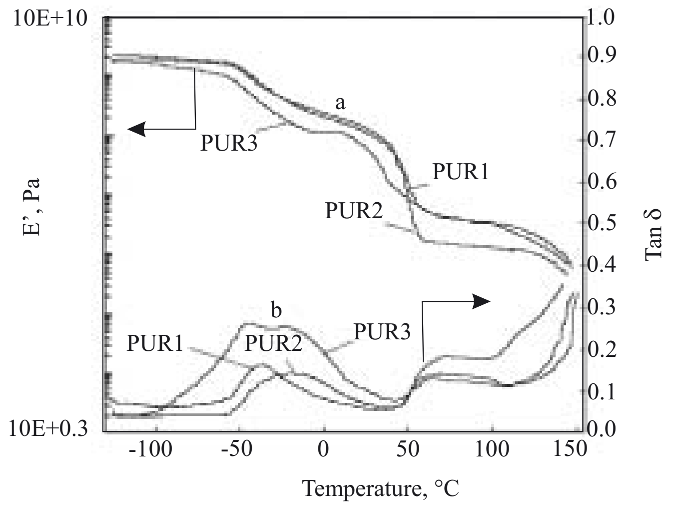

Fig. 7. Typical DMA spectra of the polyurethane samples with CHD: a) storage modulus — E′, b) damping — tan δ

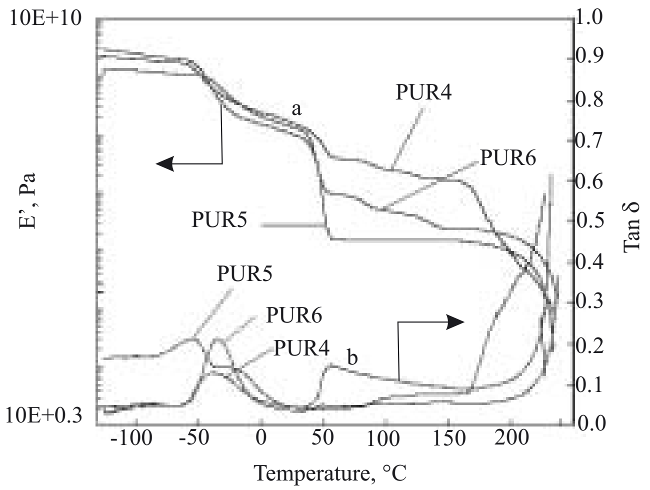

Fig. 8. Typical DMA spectra of the polyurethane samples with HMCD: a) storage modulus — E′, b) damping — tan δ

The CHD based PUR shows a small rubber plateau from 50 °C to 100 °C, while the HMCD based PUR shows a rubber plateau in the broader temperature range of 50 °C to 150—200 °C. The plateau is more extensive for polyurethanes formed by glycerin crosslinking (PUR2 and PUR5). The changes of chain extender diol structure and of the nature of crosslinking agent considerably affect the thermal properties of the polymer. This might have caused some branching, which is likely to contribute to the variations in thermal and mechanical behaviors of the polymers.

Stress-strain, modulus and elongation are important for polymer characterization and depend on its structure. By varying the diisocyanate and/or chain extender molecular weight, as well by varying the chain extender structure, the stress-strain characteristics, modulus and elongation can be modified [23].

Figures 9 and 10 present the stress-strain curves representing polyurethane elastomers, having common soft segments but various chain extenders. Clearly three

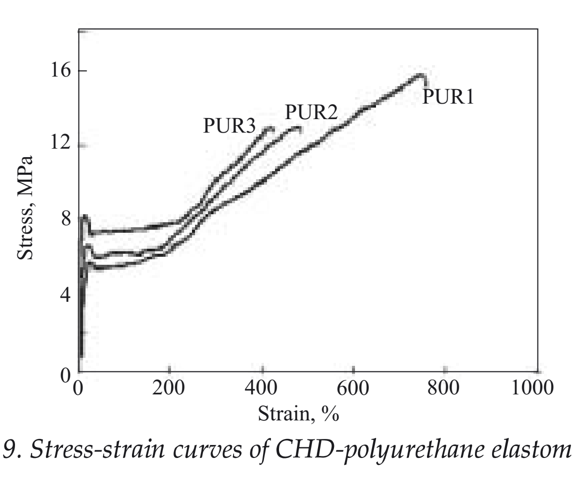

Fig. 9. Stress-strain curves of CHD-polyurethane elastomers

different regimes are visible. First, the behavior at low deformations is explained by the pure elastic deformation belonging to regular elastomers [15, 24]. Next, there is an area of plastic flow. This is much the same for all the polymers studied, indicating a great possibility of shear induced crystal fragmentation. And then, at strains above 200 %, an increase in some of the curves can be observed, which can be attributed to strain induced crystallization of soft segment chains [15].

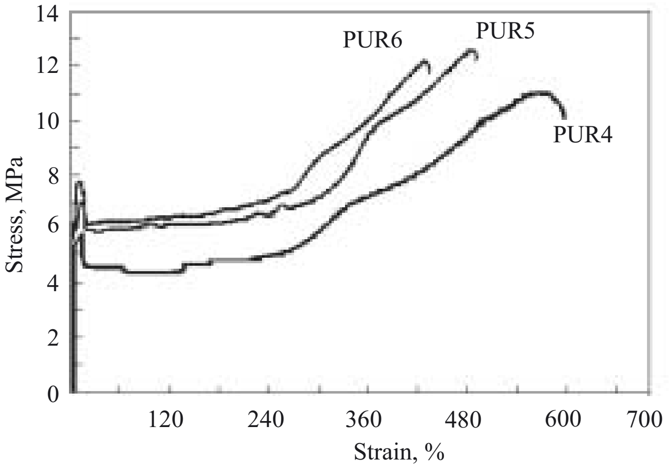

Fig. 10. Stress — strain curves of HMCD-polyurethane elastomers

In the case of PUR sheet with CHD (Fig. 9), the tensile strength at break is 16 MPa and maximum elongation is 780 % (PUR1). The PUR sheet with HMCD (Fig. 10) had the tensile strength at break of 13 MPa and maximum elongation of 600 % (PUR 4). PUR sheets with CHD and glycerin display strength of 13 MPa and elongation of 250 %. The PUR sheets with castor oil (samples 3 and 6) more rigid having tensile strength at yield of 12.5 MPa and elongation at break of 450 %.

These results indicate that the increase of length in the chain extenders leads to a lower tensile strength. With increasing relative chains of the difunctional curing agent and, consequently, decreasing the crosslinking density, there was a general decrease in strength. So, it is clear that the changes in chain extenders structures and crosslinking densities affect the tensile properties of crosslinked polyurethane materials.

Contact angle measurements

Contact angle measurements with water were performed in order to study the relative capacity of the materials to interact with water alongside the materials' surface thus giving us an idea of their relative polarity. The contact angle (CA) is a quantitative measure of the wetting of a solid by a liquid. Surface wettability and reduced friction are considered to play major roles in the wearing comfort of implants. Wettability of polyurethane elastomers was examined by CA measurements using two probe liquids—water and ethylene glycol. Table 2 presents contact angles (θ) and the work of adhesion (W_a) obtained for the different materials, dependently on the hard segment composition used.

Table 2. Contact angle (θ) and work of adhesion (W_a) values of the polyurethane film surfaces

Sample	Water		Ethylene glycol	
	θ, °	W_a, mN/m	θ, °	W_a, mN/m
PUR1	88	75	41	84
PUR2	97	63	78	57
PUR3	94	67	44	82
PUR4	92	70	78	58
PUR5	98	74	80	56
PUR6	96	75	76	59

It is remarkable that CHD-based polyurethanes had higher contact angles than HMCD-based polyurethanes, this meaning lower polarity. This difference could arise from two different reasons: the different degree in which the hard segments interact by themselves and the notable differences in phase segregation behaviors. Hydrophobic surfaces are known to inhibit the proliferation and increase the rate of apoptosis of anchorage-dependent osteoblastic cells compared to cells grown on hydrophilic surfaces [25].

The work of adhesion was calculated using the following equation:

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

where: γ_{lv} *— surface tension of the liquid used in the contact angle measurement.*

There was a difference between the work of adhesion of PUR with diol chain extenders only and that of the additionally crosslinked PUR.

The interfacial tension of a solid-liquid system (γ_{sl}) was calculated using the following equation [26]

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

where: upper indexes mean polar (p) and disperse (d) interactions respectively.

The resulting interfacial tensions are listed in Table 3.

From Table 3 we can see that the values of the interfacial tension of polymer containing CHD are higher compared to those of the other compositions, due to the differences in matrix. For the glycerin systems the interfacial tension is slightly lower compared to those of other compositions, which accounts for the decrease in the total solid surface free energy. The variation of the hard segment structure in the polymer matrix may also affect the surface properties. The smaller is γ_{sl} variable, the more biocompatible is the material [6].

Table 3. Interfacial tension of solid-liquid system (γ_{sl}) of polyurethane elastomers obtained[*)]

Sample	λ_{sv}^{p} mN/m	λ_{sv}^{d} mN/m	γ_{sl}, mN/m	
			water	ethylene glycol
PUR1	0.1	57	55	21
PUR2	4	13	27	8
PUR3	3	34	29	5
PUR4	8	9	21	7
PUR5	14	4.5	13	11
PUR6	13	7	17	8

[*)] See equation (2).

CONCLUSIONS

High molecular weight polyurethanes were synthesized without the use of solvents or catalysts, in reactions of polyols with terminal primary functional groups (PCL) with aliphatic diisocyanate (HDI). The prepolymers were chain-extended with bifunctional precursor chains and/or with castor oil or glycerin as a trifunctional crosslinking agent at constant stoichiometric ratios.

The T_g value of the elastomer sheet depends on the crosslinking agent used. These polyurethanes displayed relatively low glass transition temperature of about -50 °C and typical behavior of polyurethane elastomer at room temperature with a tensile strength of 13—16 MPa and elongation at break of 600—780 %. Three well-defined steps of degradation of PUR were observed in TGA measurements. The mechanical properties of PUR sheets were mainly governed by the stoichiometric balance of the components used in the reaction and the nature of crosslinking.

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