

# Characterization of some soft polyesterurethane films

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Soft polyurethane films are ideal for use in medical products as a backing film for scaffold devices. Two series of polyesterurethanes (PEUs), synthesized from polyethylene adipate diol (PEA) and polycaprolactone diol (PCL), both with  $M_n$  of 2000 g/mole, diphenylmethane diisocyanate (MDI), and ethylenediol (ED) or diethylenediol (DED) in combination with glycerine (Gly) as chain extenders, were analysed in this study. The effect of the hard and soft segments concentrations, polyols nature and chain extender structures on the polymers has been discussed with respect to thermal, mechanical and wetting properties. By rigorous selection of the polyurethane matrix, it is possible to obtain polymers with great potential of advanced materials.

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## 1. Introduction

Polyurethanes are an important and versatile class of polymer materials, which are used in a broad range of applications like: elastomers, foams, coatings, fibres, adhesives, leather-like materials and biomedical devices [1-3]. The group of polyurethanes comprises all polymers that contain urethane, urea or other isocyanate derived groups [4-6]. Polyurethanes are formed by linear polymeric chains of segmented structure. They are prepared by the addition reaction of difunctional isocyanates, long chain polyols and chain extenders. Most of conventional polyurethanes are based either on polyester or polyether as polyol components, diisocyanates and glycols as a chain extender [7, 8]. This broad class of segmented polyurethanes has gained considerable position as useful biomaterials for implants or biomedical devices [9-11]. The biocompatibility of these materials represents the most important factor. Soft polyurethane films are ideal for use in medical products as a backing film for proteins or polysaccharides such as collagen, elastin and hyaluronic acid for construction of many medical devices [13]. By mixing of polyurethanes and natural polymers were prepared some scaffolds, which offer improved quality especially biocompatibility [13].

Development of soft grades of polyurethane elastomers (having hardness about 60-70 °ShA) has been reported among the latest trends that are taking place in the polyurethane market. The main interest of researchers is focused on the influence of the polyol components saturated [14] and unsaturated [15-17] chain extender components diols and triols [18] and aromatic or aliphatic diisocyanates [19].

The aim of this study is to determine how the hard and soft segments content, type of hydroxyl groups of the chain extenders (primary or secondary) and its molecular weight, polyester nature (PEA or PCL) influenced the

thermal, mechanical and wetting properties of these polymers.

## 2. Experimental

### 2.1. Materials

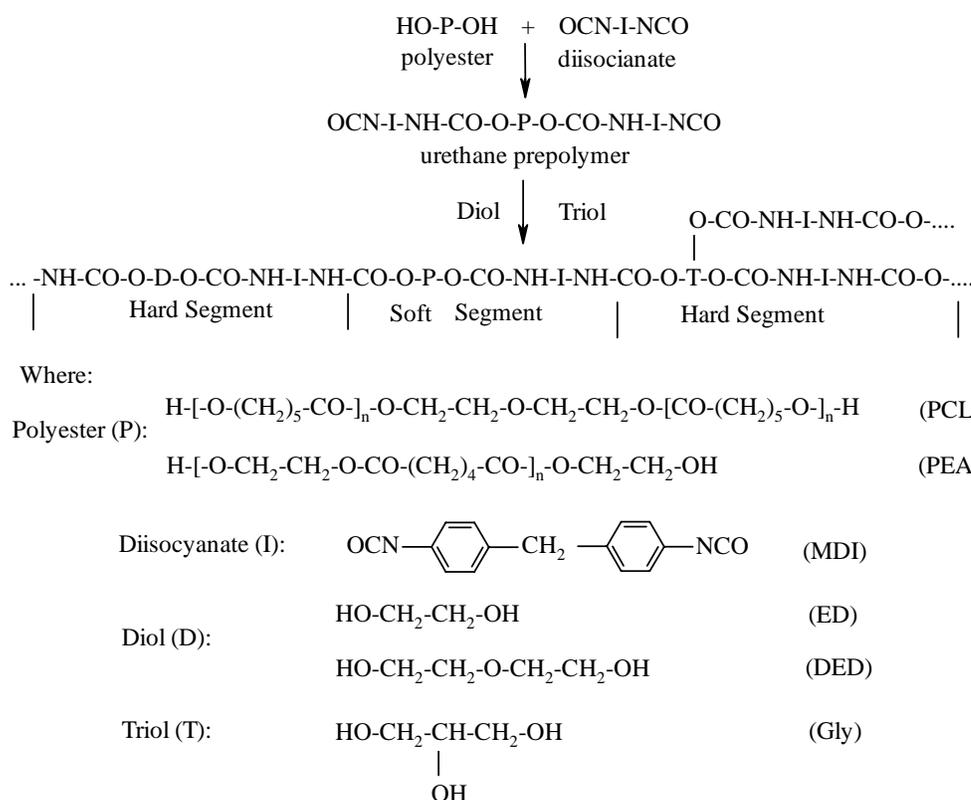
The basic materials used in this study were polycaprolactone diol (PCL) -Aldrich,  $M_w$  2000, hydroxyl number 56 mgKOH/g; polyethylene adipate diol (PEA) – synthesized in our laboratory from adipic acid and ethylene glycol,  $M_w$  2000, hydroxyl number 56 mgKOH/g; 4,4'-diphenylmethane diisocyanate (MDI-Aldrich), freshly distilled,  $M_w$  250.14; ethylenediol (ED-Fluka),  $M_w$  62.07,  $d$  1.113 g/cm<sup>3</sup>; diethylenediol (DED) - Fluka,  $M_w$  106.12,  $d$  1.118 g/cm<sup>3</sup>; glycerine (Gly),  $M_w$  92.09,  $d$  1.231 g/cm<sup>3</sup>. The polyesters and the chain extenders were tested for the moisture content and, if was necessary, dried under vacuum until content of water of less than 0.03% was reached.

### 2.2. Preparation of PEUs

The polymers were synthesized by bulk polymerization using the prepolymer method (Scheme 1). The syntheses of the polymers were performed in a glass vessel at normal pressure, under nitrogen blanket and vigorous stirring. The molar ratio of polymers was 1:3:2 of polyester: diisocyanate: chain extender. As chain extenders were used mixture of ED with Gly or DED with Gly, the molar ratio of OH-diols: OH-triols was 1:1. In the case of the prepolymer procedure, polyester diol was reacted with the diisocyanate at 80 °C for 1 hour to give up a prepolymer that was mixed, in the second step, with chain extender at same temperature for 2 minutes. The reactor was connected to a vacuum line for 1 minute, when the reaction mass are degassed. The resulting material was poured into mould and cured at 100 °C for 24 hrs, post-

curing of this polymers proceeded at room temperature for one week. Under these conditions the addition of catalyst was not necessary. The polyurethane sheets, thus prepared,

were used for determination of the thermal, mechanical and wetting properties.



Scheme 1. Synthetic route for preparation of the PEUs samples

### 2.3. Measurements

Fourier transform infrared (FTIR) spectra were measured on a Bruker Vertex 70 FT-IR instrument, equipped with a Golden Gate single reflection ATR accessory, spectrum range  $600\text{--}4000\text{ cm}^{-1}$ , at ambient temperature.

Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo TGA/SDTA851e thermogravimetric analyzer under a flow of nitrogen (20 mL/min) with a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$  from room temperature to  $700\text{ }^\circ\text{C}$  and 3-5 mg of sample mass. The operational parameters were kept constant to all probes for obtainment of comparable data.

A Perkin-Elmer DSC-7 was used for thermal analysis and was operated under a nitrogen atmosphere with a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$  and the temperature range was  $-60$  to  $+60\text{ }^\circ\text{C}$ .

Dynamic-mechanical thermal analysis (DMTA) experiments were made using a Diamond Perkin Elmer instrument that applies a sinusoidal stress to the sample and measures the resulting strain. The force amplitude used was well within the linear viscoelastic range for all investigated samples. The thermo-mechanical properties were evaluated for a heating rate of  $2\text{ }^\circ\text{C}/\text{min}$  and a

frequency of 1 Hz, under nitrogen atmosphere. Temperature investigated range  $-100\text{ }^\circ\text{C}$  to  $250\text{ }^\circ\text{C}$ . The variations of the storage modulus  $E'$ , loss modulus  $E''$  and tension loss tangent,  $\tan\delta$  as a function of temperature were obtained.

Stress-strain measurements were performed on dumbbell-shaped cut from thin films on a TIRA test 2161 apparatus, Maschinenbau GmbH Ravenstein, Germany, equipped with a 100 N load cell. The samples were tested at an extension rate of 30 mm/min, at room temperature. All samples were measured three times and the averages were retained.

Compression tests were performed on rod shaped specimens of about 15.5 mm diameter and 10 mm width, cut from the plates. The experiments were performed at ambient temperature with a 5 KN load cell and a strain/compression rate of 5 mm/min using a Shimadzu EZTest universal testing machines. The compression modulus was determined at 40% compression.

Abrasion resistance was determined using a rotating cylindrical drum device, make by Bareiss Prufgeratebau GmbH. According STAS 7405-88 the specimen ( $\text{O}=\text{16}\pm\text{0.2 mm}$ ,  $h=\text{12...16 mm}$ ) must be led across the abrasion sheet by a constant pressure of  $10\pm\text{0.2 N}$ , and the distance abrasion has got a length of 40 m at peripheral

speed of roller with abrasion sheet of 0.32 m/s at room temperature.

Izod impact strength (unnotched) was measured on a Resil Impactor from CEAST (Italy), according to SR EN ISO 180/2000 standard method. The dimensions of the specimens were 80 mm in length, 10 mm in width and 4 mm in thickness. Pendulum instrument is dedicated to the determination of energy and resilience help up a hammer of 50 J and starting angles at 150 deg. At least five specimens were used for each test.

Dynamic contact angles were performed by the Wilhelmy plate technique, using a Sigma 700 precision tensiometer produced by KSV Instruments. The sample plate dimensions were 50x8 mm and rate of immersion-emersion was 5 mm/min in water. Immersion depth was 5 mm in standard conditions. All measurements were the average of 3 contact angle measurements of samples.

### 3. Results and discussion

#### 3.1. Hard and soft segment content

In an attempt to obtain even softer PEUs, two sets of samples with low hard segment content (HSC) have been made. The syntheses were performed using PEA 2000 for samples denoted PEU3 and PEU4, and respectively PCL 2000 for samples denoted PEU5 and PEU6. The rate of polyester: diisocyanate: chain extender was 1:3:2. The hardness, formulations and distribution of hard (HSC) and soft segments contents (SSC) of PEUs are presented in Table 1. Theoretical calculations of the hard and soft segments were based on the reaction from scheme 1, respectively on rate of polyol: isocyanate: chain extender. HSC is composed of crystalline hard segment portion, from diisocyanate part, and respectively amorphous hard segment portion, from chain extender. Hard and soft segments content, type of hydroxyl groups of the chain extenders (primary or secondary) and its molecular weight were tested in order to find out the structure-property relationship of the polyurethane samples. All polyurethanes based on PEA or PCL, MDI and chain extenders lead to polymers with hardness up to 65 °ShA that may be classified as soft grade polyurethanes. In general, the contributions of both the soft and hard segments in the polyurethanes can be correlated with the properties observed. The soft segments principally affect

resiliency, wear, tear, compression set and low temperature properties, while the hard segments affects hardness, modulus and tensile properties. Examining the soft and hard segments and their relation to hardness, it is observed that the amorphous hard segment behaves like the polyester soft segment. It is evident that as the crystalline hard segment content of PEUs is decreased, the polymer hardness also decreases. By decreasing the hard segment content was synthesized polyurethane with hardness as low as 60 °ShA. The influence of chain extenders, molecular weight and type of OH groups can, also, be seen from the Table 1. All these PEUs have comparable properties; however, the use of EG done a small increase of hardness. The formulations with DEG yielded a very soft polyurethane product with hardness about of 60 °ShA, good elongation and relatively high softening temperature. Mechanical properties of PEUs are comparable with those of good quality rubber materials. The polymers like these have great potential to reducing of level of vibration and noise.

#### 3.2. FTIR Spectroscopy

FTIR spectra of the polymers were used to confirm the structure of polyurethanes (Fig. 1). The characteristic bands are found as mentioned in the literature. Formation of the PEU is confirmed by the disappearance of NCO stretch at 2260  $\text{cm}^{-1}$ . The absorption at 3337 and 3333  $\text{cm}^{-1}$  (PEU3, PEU4) respectively 3331 and 3326  $\text{cm}^{-1}$  (PEU5, PEU6) is assigned to hydrogen-bonded of -NH groups. The absorption bands at 2960  $\text{cm}^{-1}$  is associated with -CH<sub>2</sub> groups. The strong band at 1728 and 1725  $\text{cm}^{-1}$  corresponds to the free and hydrogen-bonded of -C=O groups. The absorption of amide II appears at 1532 and 1530  $\text{cm}^{-1}$ . The peak for CH stretch, from benzene ring, appears to 1598  $\text{cm}^{-1}$ . The bands between 1456 and 1365  $\text{cm}^{-1}$  manifest diverse modes of -CH<sub>2</sub> vibrations. The band at 1310 and 1258  $\text{cm}^{-1}$  corresponds to aliphatic -R-NH-COO- groups. The bands at 1216 and 1065  $\text{cm}^{-1}$  are assigned to the stretching vibration of the ester group -CO-O-C-, and the band at 817-779  $\text{cm}^{-1}$  is assigned to the out-of-plane bending of the ester group.

Table 1. Polyurethanes composition, hardness and distribution of hard and soft segments.

Sample code	Polyol/MDI/ Extender	Polyester type	OH <sub>diol</sub> :OH <sub>triol</sub> 1:1	HSC %		SSC %	Hardness °ShA
				Crystalline	Amorphous		
PEU3	1:3:2	PEA	ED+Gly	25.93	4.93	69.14	68±1.15
PEU4	1:3:2	PEA	DED+Gly	25.42	6.80	67.78	63±1.15
PEU5	1:3:2	PCL	ED+Gly	25.93	4.93	69.14	65±1.01
PEU6	1:3:2	PCL	DED+Gly	25.42	6.80	67.78	60±0.87

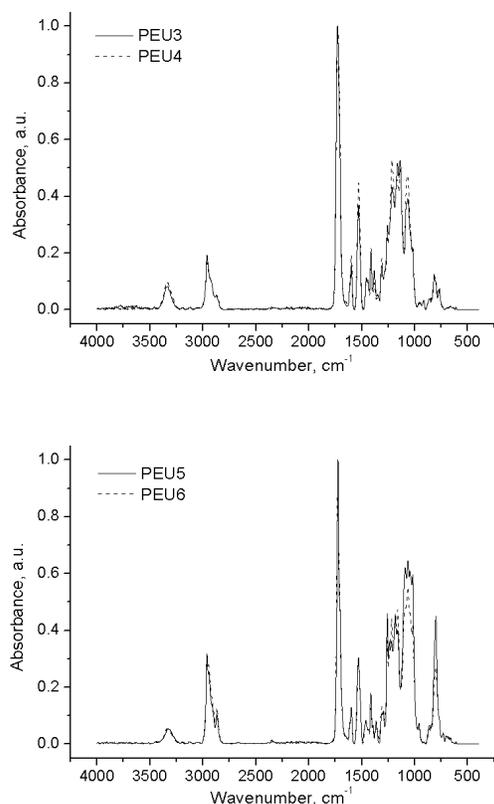


Fig.1. FTIR spectra of PEU based on PEA (PEU3, PEU4) and PCL (PEU5, PEU6).

### 3.3. Thermogravimetric analysis

The details of degradation temperatures have been presented in Table 2. The TGA was used to study of some

linear polyesterurethanes attempting to outline the increase in the thermal stability brought by components from their structure. To achieve this, the same testing conditions were used for all the copolymer samples being analyzed. The onset ( $T_i$ ) degradation temperature was defined as the initial temperature of degradation, corresponding to the intersection of the tangent drawn at the inflection point of the decomposition step with the horizontal zero-line of the TG curve [20,21].

The MDI based system can also have more complete microphase separation. The physical crosslinks are important to providing dimensional stability and to stop cold flow in the uncured materials. The effect of restricting segmental motion in a three dimensional network by chemical crosslink sites is similar to that of microdomain physical crosslinks except that the former is irreversible. The crystalline polyester domain acts as an additional physical crosslink site below there melting temperature.

Generally, polyurethanes analyzed decomposed in two steps and the temperature which the weight losses were maximum is 290-430 °C (Fig. 1). The glycerine contribution, by ramified structures generated, and increase of flexible chain, lead to relative stability, because is high the possibility of order the main molecular chain. The first stage was associated with the hard segment degradation and the second one, with the soft segment. The reaction orders, calculated through Reich-Levi method [22] are below to 1/2, this suggests that some diffusion processes accompany decomposition in various conditions.

The increase of the temperature maximum indicates a lower rate of diffusion of the degraded products out of the matrix as indicated by the lower peak degradation rates exhibited at these temperatures. Thus, it is evident that the crosslinking bonds restrict the diffusion of the degradation products from the matrix.

Table 2. Thermogravimetric data for the polyurethane samples.

Sample code	Reaction order*		Weight losses (%) and decomposition temperature ranges			Energy Activation*	
	Step I	Step II	Step I	Step II	Residue %	Step I	Step II
	PEU3	0.3	0.3	54.8(300-358)	34.6(358-475)	10.6	118.3
PEU4	0.3	0.4	78.3(290-385)	17.5 (385-460)	4.2	76.4	7.0
PEU5	0.2	0.2	75.2(300-415)	21.4(415-485)	3.4	63.2	6.2
PEU6	0.2	0.2	73.7(330-410)	20.8(410-485)	5.5	76.7	5.4

\* Calculated through Reich-Levi method.

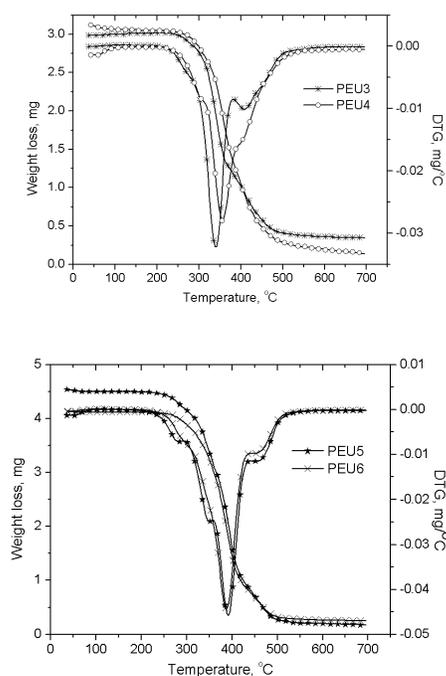


Fig. 2. TG and DTG curves of PEU based on PEA (PEU3, PEU4) and PCL (PEU5, PEU6).

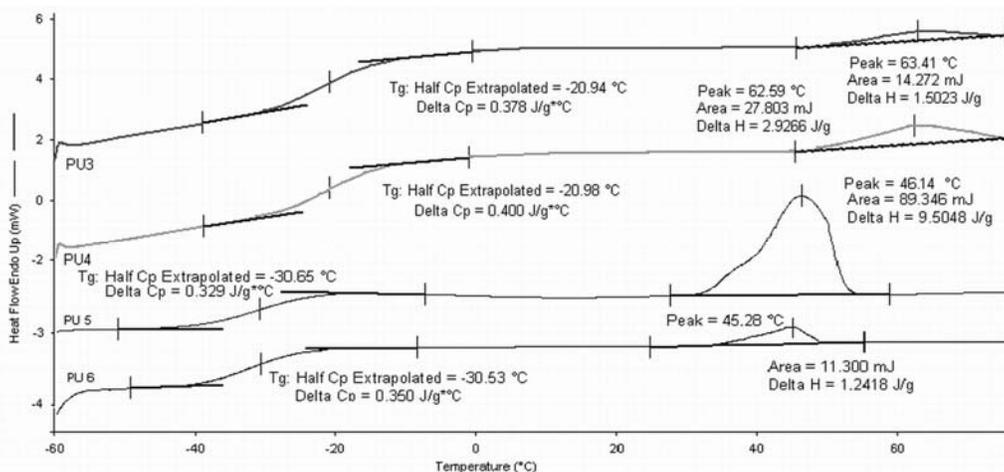


Fig. 3. DSC traces of PEU based on PEA (PEU3, PEU4) and PCL (PEU5, PEU6).

### 3.5. Dynamic mechanical thermal analysis (DMTA)

Polyurethanes are characterized by their high and heterogeneous morphology and by important intermolecular forces that determine their mechanical behaviour, in such way, the forces applied to polymers and the deformations produced by those are not thoroughly local. Consequently the response of the polymer to the foreign solicitations is extended in a wide time interval (relaxation time), originating its peculiar viscoelastic

### 3.4. DSC analysis

The thermal properties of the samples were studied too, by means of Differential Scanning Calorimetry (Figs. 3). DSC is a thermal analytical technique which measures the amount of energy absorbed or released by a material as it is heated, cooled or held at constant temperature. This method was appropriate for the evaluation of the glass transition temperature. The polyurethanes PEU3, PEU4 based on PEA/MDI exhibit  $T_g$  around to  $-20$  °C, while the polyurethanes PEU5, PEU6 based on PCL/MDI exhibit  $T_g$  around to  $-30$  °C. These samples exhibit  $T_{melt}$  at  $+63.41$  °C (PEU3),  $+62.59$  °C (PU4),  $+46.14$  °C (PEU5) and  $+45.28$  °C (PEU6). The glass transition ( $T_g$ ) is influence by macrodiol nature. The polyurethane based on PCL present a  $T_g$  down up to  $10$  °C in opposition with polyurethane based on PEA. Same situation for  $T_{melt}$ , case in which, the difference was of approximately  $20$  °C.

behaviour. While energy supplied to a perfectly elastic material is stored and a purely liquid dissipates it, polymeric materials dissipate a part of energy that excites to them. DMA is a sensitive technique used to study and characterize macroscopic responses of the materials as well local internal motions. By monitoring property changes with respect to the temperature and/or frequency of oscillation, the mechanical dynamic response of the material is referred to two distinct parts: an elastic part ( $E'$ , storage modulus) and a viscous component ( $E''$ , loss modulus). The elastic process describes the energy stored

in the system, while the viscous component describes the energy dissipated during the process. Samples can be either solids or melts. The sample deforms under the load. From this the stiffness of the sample can be determined, and the sample modulus can be calculated. By measuring the time lag in the displacement compared to the applied force it is possible to determine the damping properties of the material. The time lag is reported as a phase lag, which is an angle. The damping is called tan delta, loss factor or loss tangent,  $\tan \delta = E''/E'$  as it is reported as the tangent of the phase lag. With increasing temperature different physical states are revealed: glass, leathery, rubbery and elastic of rubbery flow, viscous flow. Identification of the glass transition and how various system modifications affect  $T_g$  is a major application of DMTA. The glass transition is easily identified from dynamical mechanical data because of the sharp drop in storage modulus, peaks of loss dispersion modulus or  $\tan \delta$ .  $\tan \delta$  peak may occur at higher temperatures than those given by  $E'$  drop or  $E''$  peak, because it responds to the volume fraction of the relaxing phase, its shape and height depends on the amorphous phase, being a good measure of the 'leather like' midpoint between glassy and rubbery state, [23]. The glass transition temperature ( $T_g$ ) is often measured by DSC (Differential Scanning Calorimetry), but the DMA technique is more sensitive and yields more easily interpreted data. DMA can also be used to investigate the frequency (and therefore time) dependent nature of the transition. This is usual as the degree of dependence is specific to the transition type.  $T_g$  has a strong dependence on frequency but melting is frequency independent. DMA can also resolve sub- $T_g$  transitions, like beta, gamma, and delta transitions, in many materials that the DSC technique is not sensitive enough to pick up. In addition, DMA gives modulus values. The magnitude of the low temperature relaxations is much smaller than that of  $\alpha$ -relaxation considered as the glass transition. These relaxations are due to local mode (main chain) relaxations of polymer chains and rotations of terminal groups or side chains, or crankshaft motion of a few segments of the main chain.

The glass transition of the soft segment (SS) was determined from DMTA curves as follows: from the intersection of tangents to the  $E'$  ( $\log E'$ ) curves from the glassy region and the transition "leathery" region, from  $E''$  ( $\log E''$ ) peaks and  $\tan \delta$  peaks.  $T_g$  of the soft segment from DSC was evaluated from the second heating scan. It can be noticed that  $T_g$  from DSC are close to those from DMTA. For both series of polyesterurethanes based on PEA or PCL it was evidenced by DMTA (Fig. 4) two series of  $T_g$ , first for samples with PEA ( $T_g$ :  $-20.1^\circ\text{C}$  - PEU3 and  $-17.5^\circ\text{C}$  - PEU4), and second for samples with PCL ( $T_g$ :  $-27.1^\circ\text{C}$  - PEU5 and  $-29.8^\circ\text{C}$  - PEU6), values appropriate of results done by DSC (Figure 3), which reveals glass transitions of approximately ( $-20^\circ\text{C}$  for PEA, respectively  $-30^\circ\text{C}$  for PCL) and  $T_m$  for soft segments ( $62.5^\circ\text{C}$  for PEA and  $45.6^\circ\text{C}$  for PCL). By DMTA was revealed that amorphous hard segment portion affects the glassy state modulus, which affects the storage modulus and shape and position of  $\tan \delta$  by changing the degree of

order and motion of molecules through concentration of molecular structural units.

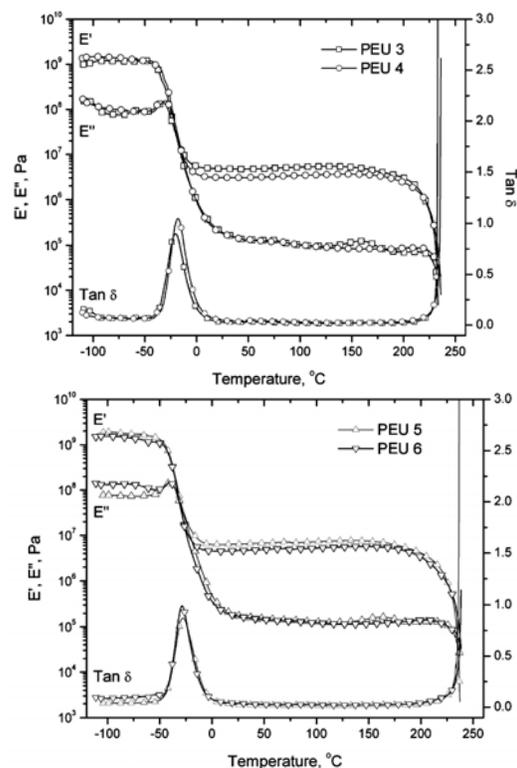


Fig. 4. DMTA traces of PEU based on PEA (PEU3, PEU4) and PCL (PEU5, PEU6).

### 3.6. Mechanical properties

The stress strain curves and compression measurements of the polyesterurethane samples are shown in Fig. 5 and 6. Characteristic values derived from these curves are presented in Table 3. The tensile strength of the polyurethane samples can be affected by factors such as the content of soft and hard segments in the polyurethane structure, their cohesion energy, packing degree of macromolecules, phase separation, cross-linking degree of PEUs, etc. [24].

Physico-mechanical analysis evidence the extent of the super molecular modifications of polyurethanes obtained as a function of their structural modifications (Fig. 5). Stress-strain, modulus and elongation are important for polymer characterization, depending on their structure by varying the polyol and/or diisocyanate molecular weight, as well as variation of chain extenders structure, leading to modifications of stress-strain, modulus and elongation [25, 26].

If the amount of hard segments is greater, then the stress, modulus and Izod impact are higher. Reverse effects occur with more numerous and longer soft segments. The shorter soft segment implies that a higher hardness of polyurethane would be obtained. This result may be due to an increase in polar groups and cohesive

energy density. In this situation is expected a higher hardness because these polar groups, which have a high cohesive force, participate in intermolecular hydrogen bonding and restrict the rotation of polymer segments. At lower hardness levels, practically all polyurethane

materials can be used under impact. When have a higher degree of hardness, they tend to lose elasticity and crack under impact. However, even at their highest hardness levels, they have significantly better impact resistance than most plastics.

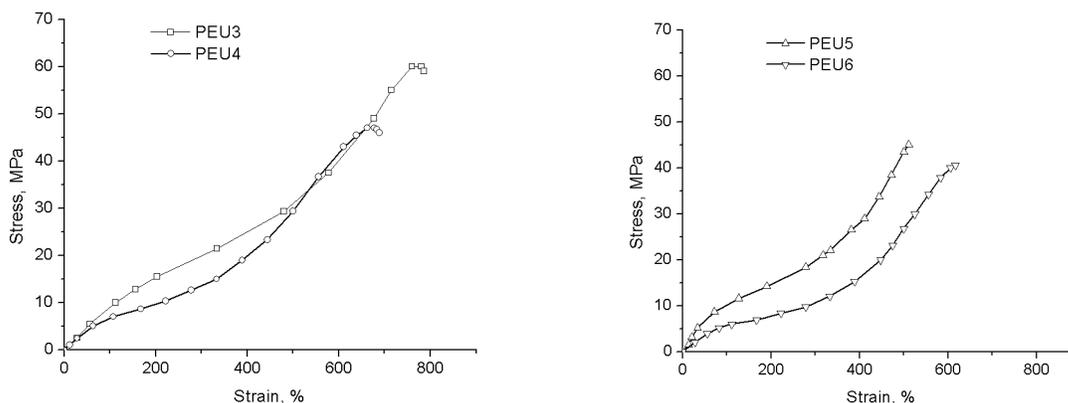


Fig. 5. Stress-strain measurements of polyurethane sample: PEU 3, 4 based on PEA; PEU 5, 6 based on PCL.

Table 3. Tensile properties of polyurethane samples.

Sample code	Tensile strength MPa	Elongation at break %	E, Young's modulus MPa	Izod Impact Test, KJ/m <sup>2</sup>	Abrasion mm <sup>3</sup> /cm <sup>2</sup>	Compression Modulus MPa
PEU3	61.50±0.87	760±6.06	7.93±0.10	9.40±0.06	97.72±0.56	5.7±0.06
PEU4	47.00±1.15	670±6.06	6.27±0.09	8.18±0.02	78.05±0.49	2.02±0.03
PEU5	46.00±0.58	510±5.77	14.78±0.11	13.33±0.11	117.36±0.49	5.38±0.12
PEU6	41.58±0.84	610±6.12	9.27±0.14	9.08±0.01	109.52±0.46	4.09±0.06

The results of physical and mechanical measurements are presented in Table 3, evidencing that an increase of the methylene group number of the chain extenders employed leads to a lower tensile strength, which may be explained by decreasing concentration of the ester groups on the macromolecular chain.

Young's Modulus,  $E$ , is a constant that describes the ratio of stress to strain for polyurethane experiencing.

$$E = \text{Stress/Strain} \quad \text{or} \quad F/A = E \Delta L/L \quad (1)$$

where:  $F$  is the force applied and  $A$  is the cross-sectional area of the material, [N/m<sup>2</sup>];  $L$  is the original length of the material, and  $\Delta L$  is the change in length that results after the stress is applied.

Table 3 illustrate that the Young's moduli present different values for polyurethanes with similar composition. For example, in the case of PCL-based polyurethanes, the Young's modulus values are greater than similar PEA-based polyurethanes. This fact, can be explained by the formation of hydrogen bonds

(NH...O=C<) with a much higher frequency in the case of PCL, which may be explained by the trans-planar structure formed [27]. In addition, with an increase of the applied stress, result an increase of the forces impeding deformation, by the rearrangement of the macromolecules [28].

Because the crystalline regions play a similar role to crosslinks in improving mechanical properties, the tensile properties of crystallisable material are superior in opposition with non-crystallisable material. The influence of molecular weight on the ultimate tensile properties of the hard segment is larger than that of the previously studied factors, especially at low molecular weight. It is clear that, an increase in the hard segment content produces an increase of the crosslinking density. Varying the chain extenders molecular weight affects the tensile properties of the polyurethanes and the crosslinked materials.

In segment polyurethanes, the mechanical properties were generally accredited to the result of a pseudo-crosslinking effect resulting from the hard-segment

aggregation. The hard-segment domain generally exhibits a different degree of order or semicrystalline structure, which was considered to be able to reinforce the hard segment domain and, in the case of these polyurethanes, added a crosslinking effect of the glycerine.

Izod impact test is an early destructive test designed to determine the resistance of a plastic to the impact of a rapidly applied force. It is a measure of impact strength determined by the difference in energy of a swinging pendulum before and after it breaks a notched / unnotched specimen held vertically as a cantilever beam.

Compared to plastics, urethane elastomers offer superior impact resistance, offering excellent shape and elastic memory. The impact resistance of polyurethane samples depend, in principal, on the composition of polymer and temperature. Environmental factors other than temperature also play a role in impact resistance (ex. moisture of sample). In this study it is observed that a great content of hard segments (samples PU3...PU6) give a high impact test.

The products based on polyurethane materials utilized in passive isolation railways, bridges, buildings

construction and other domains are subjected to compression forces during the process of reducing of vibration and noise [28]. Therefore it is necessary to be able to take care of these forces as good as possible. This makes the compression properties of the products a key property of the polyurethane material. The major variables that influence, in this case, the compression modulus are the polyester nature and the hard segments content.

Fig. 6 show the compression modulus of the polyurethane samples based on PEA and PCL polyester. The modulus value was determined at 40% compression. For all of the samples tested resilience was >95 %. Resilience is the property of a material to absorb energy when it is deformed elastically and then, upon unloading to have this energy recovered. From presented values it is evidence that many formulations are possible in a wide range of resiliencies. For shock-absorbing uses, urethane can be made with recover values of 20-25%. When is necessary quick recovery, or where high-frequency vibrations are an important factor, the polyurethane can be made with recover values >40%.

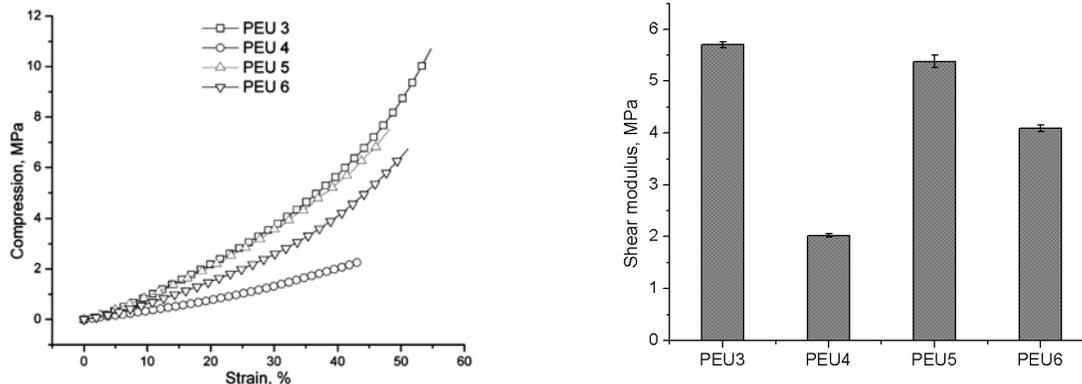


Fig. 6. Compression and shear modulus (40%) of PEU samples.

Shear modulus,  $G$ , (or rigidity modulus),  $G$ , is defined as the ratio of shear stress to engineering shear strain on the loading plane.

### 3.8. Wetting properties

#### 3.8.1. Dynamic contact angle measurements

Advancing and receding contact angle measurements of the polyurethane samples based on PEA-PCL/MDI/Chain extenders could provide more information on the hydrophilicity of films and hence the wettability. The samples were immersed and withdrawn into and out from a liquid simultaneously measuring the force acting on the samples. The advancing and receding contact angles were determined from the obtained force curve. The difference between the maximum (advancing) and minimum (receding) contact angle values was called

the contact angle hysteresis. The measured force  $F_t$  was related to the dynamic contact angle through the general equation:

$$F_t = \text{weight probe} + \text{wetting force} - F(\text{buoyancy}) \quad (2)$$

Sigma 700 tensiometer tared the weight of the probe and was removed the effects of the buoyancy force by extrapolating the graph back to zero depth of immersion. The remaining component force was the wetting force ( $F_w$ ) which was defined as:

$$F_w = \gamma_{lv} P \cos \theta \quad (3)$$

Where  $\gamma_{lv}$  represented the surface tension of the fluid,  $P$  the perimeter of the plate and  $\theta$  is the contact angle. Both advancing and receding contact angles could obtain from Eq. (3).

Table 4. Water contact angle of polyurethanes samples.

Sample	Ratio Polyol/MDI/Extender	Chain extenders	HSC, %	$\theta_{adv}$ (deg)	$\theta_{rec}$ (deg)	Hysteresis (deg)
PEU3	1:3:2	ED+Gly	31.86	79.26 ±0.66	31.59 ±1.00	47.67±0.34
PEU4	1:3:2	DED+Gly	32.22	83.29 ±0.34	38.10 ±0.49	45.19±0.81
PEU5	1:3:2	ED+Gly	31.86	85.62 ±0.16	42.53 ±0.20	43.09±0.35
PEU6	1:3:2	DED+Gly	32.22	89.66 ±0.28	48.27 ±0.41	41.38±0.18

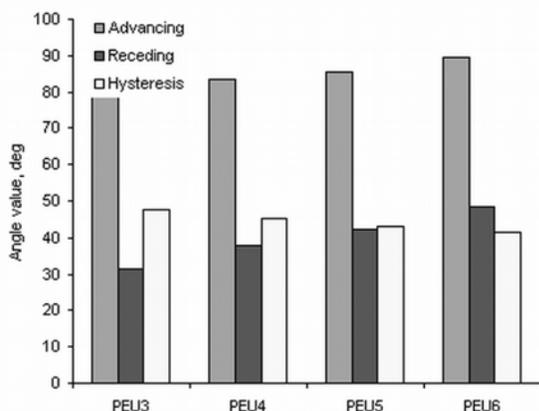


Fig. 7. Dynamic contact angle (advancing, receding contact angle and hysteresis) of PEUs.

In Fig. 7 and Table 4 are showed the results of the dynamic contact angle study. The obtained results of contact angle measurements revealed that the wettability increased with decrease of the hard segment contents of PEUs. The chain extenders nature increased wettability in the order: ED > DED. Additionally, the polyurethane films were found to have the hysteresis values between 41.38 and 47.67 degree. This meant that the polymer film surface shows a significant chemical or physical heterogeneity.

#### 4. Conclusions

This present study provides possibilities to improve the mechanical property of some soft polyurethane materials. Polyethylenadipate diol and polycaprolactone diol were used for the preparation of polyurethane elastomers employing prepolymer procedure. Ethylenediol, diethylenediol, and glycerine were found to be suitable chain extenders for based polyurethanes. The thermal stability is a function of the components present in the formulation. Polyurethanes show a two-step thermal degradation. The first stage was associated with the hard segment degradation and the second one, with the soft segments. Higher length of the soft segment and the presence of glycerine linkages increased the polyurethane thermal stability. Longer chain lengths between crosslinks produce higher elongations at break and lower mechanical moduli. The crosslinking process increases the urethane domain rigidity and decreases the soft segment crystallinity. These factors enhance the tensile strength,

modulus and Izod impact of the materials. Depending on the parameters of the formulation, the resulting polymers exhibited hardness about 55-65 °ShA or lower, making them prospective materials falling into the category of the soft grade polyurethanes, which may be used as backing films for biomedical applications.

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