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Evaluation of some polyetherurethane elastomers for chemicals, oils and solvents resistance

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In this study were synthesized and evaluated some polyetherurethanes (PEUs) for chemicals, oils and solvents resistance. Two series of PEUs were synthesized by two step polymerization. In first stage, the polytetramethyleneetherglycol prepolymer (PTMEG - Mw 1400 g/mol) was terminated with two different diisocyanate: 4,4'-diphenylmethane diisocyanate (MDI) and 1,6-hexanediisocyanate (HDI). In second step the prepolymers were extended with a mixture of ethylene glycol (EG) and glycerine (Gly). Like most polyether-based elastomers, PTMEG polyol-based elastomers will swell in solvents due to its less polar nature. The PEUs have been characterized by FTIR and thermogravimetric analysis (TGA, DSC) and swelling measurements in diverse types of oils, solvents and different aggressive solution. The mechanical behaviour and hardness of the polymers, before and after swelling was the way to determine the resistance to these different mediums.

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Keywords: Oil resistance, Polyetherurethane, Solvent resistance, Swelling

1. Introduction

The polyurethanes has been extensively used due to its superior physical properties (e.g. high tensile strength, abrasion and tear resistance, oil and solvent resistance, low temperature flexibility etc) and high versatility in chemical structure [1,2]. Polyurethanes are primarily used for solvent or oil resistance as well as high abrasion resistance and toughness [3]. The resistance of polyurethane elastomers to strong alkaline solutions is less than that of most other elastomers and known to vary with type and formulation. Polyether-based urethanes are more resistant to hydrolysis effects than polyester-based urethanes, and thermoplastic polyurethanes differ slightly from conventional thermosetting polyurethane rubber [4,5]. In some cases, resistance of polyurethanes to dilute solutions is lower than that to more concentrated solutions due to hydrolysis effects. Most references indicate marginal acceptability of polyurethanes in strong alkaline solutions [6]. The radiation resistance of polyurethanes is known to be generically high compared to most other elastomers [7]. However, in absence of vendor information on the specific type used, polyurethanes may be acceptable but cannot be strongly recommended. A number of diisocyanates and polyols are available for formulating special products [8-11]. Polyurethanes are noted for outstanding resistance to abrasion and tear. They provide the highest available tensile strength among all elastomers while providing good elongation characteristics. Sunlight, oxidation, weather, oil and incidental gasoline exposure are environments suited for urethane applications [12]. Polyetherurethanes are not recommended for alkalis, acids and oxygenated solvents, but are typically recommended for hot water, steam and high humidity applications [13].

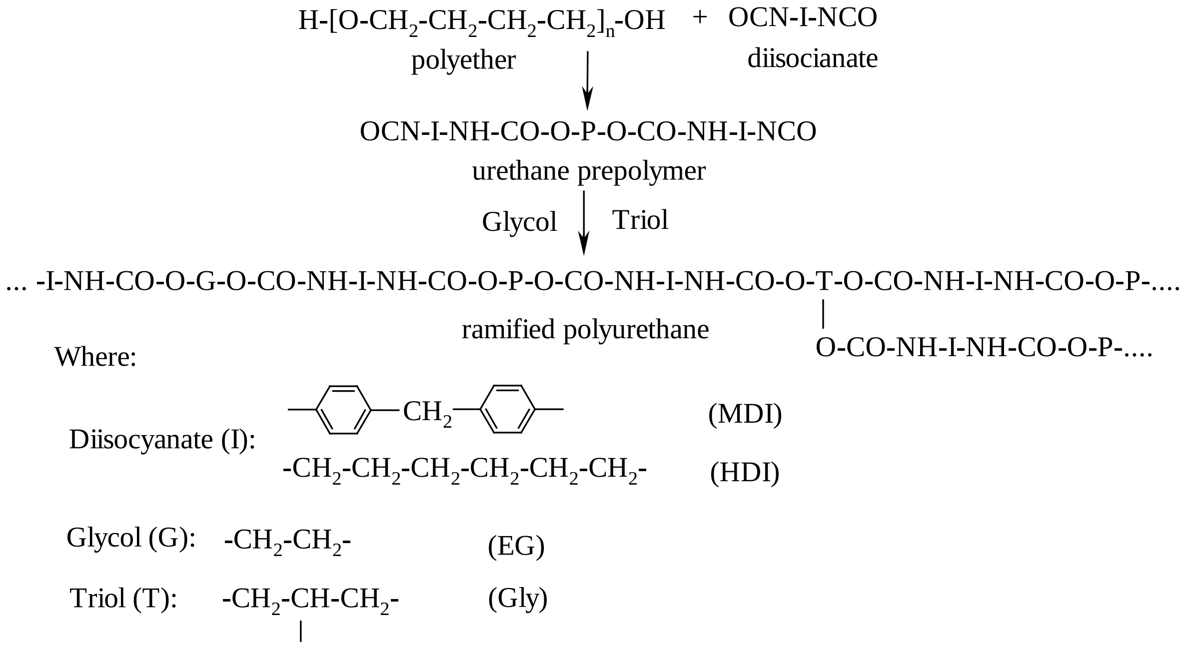
2. Experimental

2.1. Materials

The materials used in this research were Terathane 1400 (polytetramethyleneetherglycol - PTMEG - generous gift from INVISTA BV, Nederland), Mw 1374 g/mol, mp 35-40 ^{o}C, water 115 ppm, hydroxyl number 81.7 mgKOH/g; 4,4'-diphenylmethane diisocyanate (MDI-Fluka), Mw 250.14, mp 42-44 ^{o}C, bp 152-156 ^{o}C/0.2-0.3 mmHg,; 1,6 – hexamethylene diisocyanate (HDI –Fluka), Mw 168.2, bp 255 ^{o}C, d20 1.040, n_D^{20} 1.4520; ethylene glycol (EG –Fluka), Mw 62.07, mp -13 ^{o}C, bp 196-198 ^{o}C, d^{20} 1.113 g/cm^3, n_D^{20} 1.4310; glycerine (Gly- Fluka), Mw 92.9, bp 182 ^{o}C, d^{20} 1.261, n_D^{20} 1.4740. PTMEG and chain extenders were tested for the moisture content and, in some cases, dried under vacuum until a content of water of less than 0.03% was reached. All the chemicals were used as received, without further purification, except MDI, which was distilled prior to use.

2.2. Preparation of polyetherurethanes

Cast polyurethane elastomers are simply made by mixing and pouring a degassed reactive liquid mixture into a mould. These materials have good resistance to attack by oil, petrol and many common non-polar solvents combined with excellent abrasion resistance. Polymerizations were carried out without adding catalyst. The polymers were prepared in a two-step polymerization process under nitrogen atmosphere. The synthesis of PEUs was performed in a 250 cm^3 glass reactor at normal pressure, under nitrogen blanket and vigorous agitation. The molar ratio of all formulations was 1:2:1 or 1:3:2 of Polyol: Diisocyanate: Chain extender (Scheme1). In the case of prepolymer method, the polyether diol was reacted with a diisocyanate at 80 ^{o}C for 2 hours to yield a prepolymer that was mixed in the second step with a chain extender to same temperature. The extent of reaction was determined by measuring the percent isocyanate content (%NCO) of the prepolymer. Heating was continued until the prepolymer was slightly below the theoretical value of %NCO. The resulting material was poured into a mould and left to cure at 90 ^{o}C for 20 hours, post-curing of the polyurethanes proceeded at room temperature for 7 days. Under these conditions the addition of catalyst was not necessary. The polyurethane sheets, therefore prepared, were used to determination the mechanical properties and resistance study.



Scheme 1. Synthetic route preparation of polyetherurethane samples.

2.3 Measurements

The infrared spectra were measured on a Bruker Vertex 70 FT-IR instrument, equipped with a Golden Gate single reflection ATR accessory, spectrum range 600-4000 cm^{-1}, at ambient temperature.

Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo TGA/SDTA851e thermogravimetric analyzer under a flow of nitrogen (20mL/min) with a heating rate of 10 °C/min from room temperature to 700 °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 ^{o}C/min and the temperature range was -100…+40 ^{o}C.

Stress-strain measurements were performed at room temperature on dumbbell-shaped samples cut from thin films on a TIRA TEST-2161 tensile testing machine, Maschinenbau GmbH Ravenstein Germany, equipped with a 100 N load cell. The used cross-head speed was 30 mm/min at room temperature. All samples were measured three times and the averages were obtained.

Abrasion resistance was determined using a rotating cylindrical drum device, make by Bareiss Prufgeratebau GmbH. According STAS 7405-88 the specimen (Ø=16±0.2 mm, h=12…16 mm) must be led across the abrasion sheet by a constant pressure of 10 ±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.

Shore hardness was measured with calibrated Shore A Instron Durometer instruments, on a stack of compression moulded sheet at least 10mm thick on a flat surface and taking the average of three measurements. Ambient temperature was 22ºC.

3. Results and discussion

3.1 Water resistance

A principal advantage of PTMEG is the hydrolysis resistance contributed by the ether backbone. This is demonstrated for MDI and HDI systems by Figure 1, showing the retention of tensile strength after immersion in hot water. The roughly 10% drop with PTMEG is due to the plasticizing effect of water; the original tensile strength is regained on drying, whereas the losses incurred by the polyesters are due to hydrolysis and are not regained. The advantage of PTMEG is even more pronounced after exposure to humid air, as shown in Fig. 2; these samples were dried before testing and show no plasticization with water.

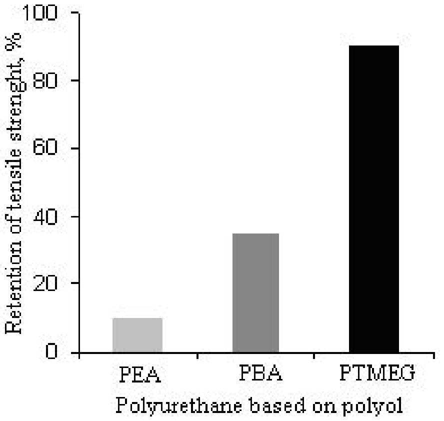


Fig. 1. Effect of water immersion Polyol/MDI(HDI)/EG(DEG)+Gly, three weeks at 70 ^{0}C.

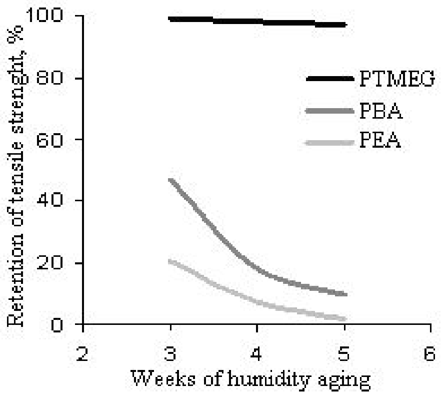


Fig. 2. Effect of humidity Polyol/MDI(HDI)/EG+Gly, 95% relative humidity at 80 ^{0}C.

3.2 Chemicals, solvents and oils resistance

The chemicals, solvents and oils resistance of PEUs synthesized in this study were determined by swelling in oils, fuel and in different dilute solutions such as: acid and alkaline solutions. Equilibrium swelling ratio was determined by conventional gravimetric method as follows:

$$Swell\% = \frac{W_s - W_d}{W_d} \times 100$$

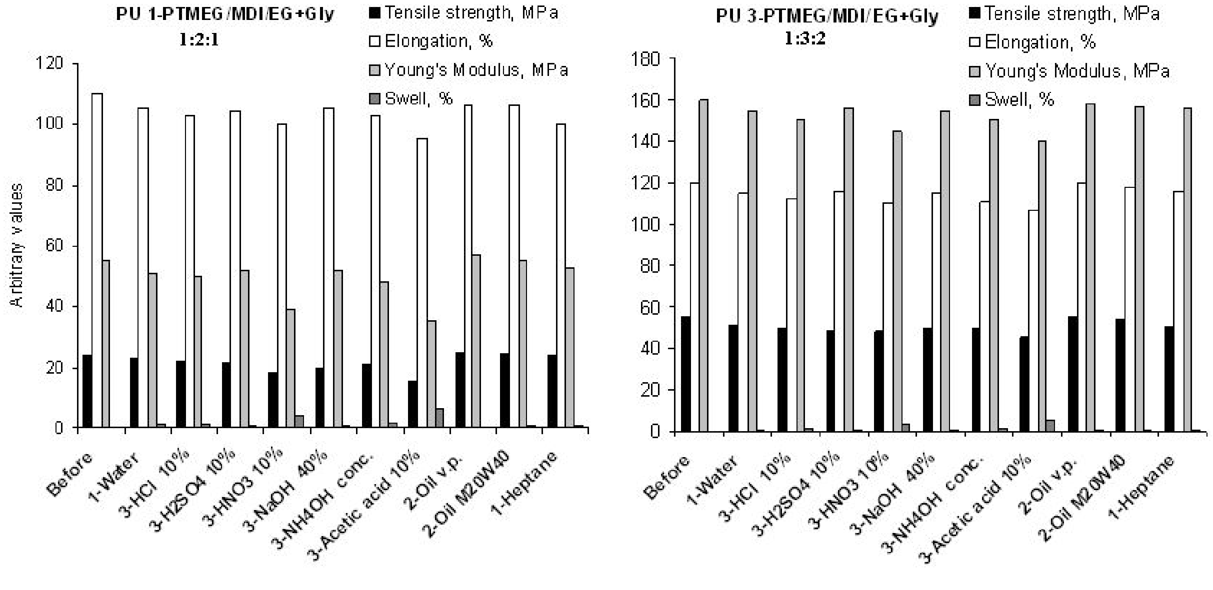
where:

W_s – is the weight of swelled sample;

W_d – is the weight of dry sample.

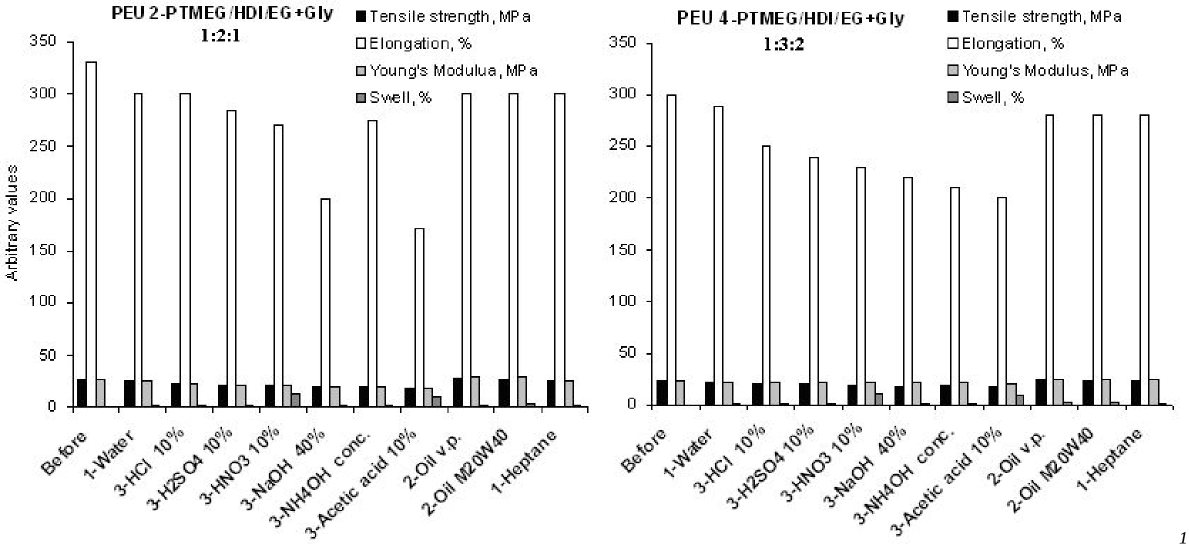
Figs. 3 and 4 show that PTMEG polyol-based polyurethane elastomers have excellent resistance to acids and bases.

In first case, three weeks at 70 ^{o}C in water or heptane, the properties of the polyurethane samples were minor affected, between 0 and 9 % of initial values. In case two, three days at 100 ^{o}C in oil vacuum pump or engine oil, the properties of the polyetherurethane samples were not affected. In last case, three days at 25 ^{o}C in aggressive solution, acids or bases, were important affected between 17 % and 36 % of initial values.



[1] 3 weeks at 70 ^{o}C; [2] 3 days at 100 ^{o}C; [3] 3 days at 25 ^{o}C

Fig. 3. PTMEG polyol-based polyurethane elastomers – MDI (PEU 1 and PEU 3).



[1] 3 weeks at 70 °C; [2] 3 days at 100 °C; [3] 3 days at 25 °C

Fig. 4. PTMEG polyol-based polyurethane elastomers – HDI (PEU 2 and PEU 4).

3.3 FT-IR analysis

The IR spectra of polyurethane based on MDI/PTMEG (PEU 1 or PEU 3) are characterized by amide I bands (C=O stretch) at ~1705 cm^{-1} due to non-hydrogen bonded and hydrogen bonded amide groups respectively, an amide II band (out of phase combination of OCN and NH vibrations) at ~1531 cm^{-1}, C-O stretches at ~1258 - ~1216 cm^{-1} and ~1064 - ~1017cm^{-1}, a C=C stretch (MDI aromatic ring) at 1600 cm^{-1}, and N-H stretch at ~3317 cm^{-1}. The absorption frequency of the N-H stretch is sensitive to hydrogen bonded. A non-hydrogen bonded N-H stretch has a frequency of ~3500 cm^{-1} and for hydrogen bonded N-H stretch the frequency has reduced to ~3200 cm^{-1}. In case of polyurethane based on HDI/PTMEG (PEU 2 or 4) the IR spectra are characterized by amide I bands (~1719 -~1704 cm^{-1}), amide II (~1534 cm^{-1}), C-O stretches (~1242 cm^{-1}) and N-H stretch at ~3333 cm^{-1}. An important remark is absence of the characteristic band between 2276-2240 cm^{-1} of isocyanate groups (NCO), Figs. 5 and 6.

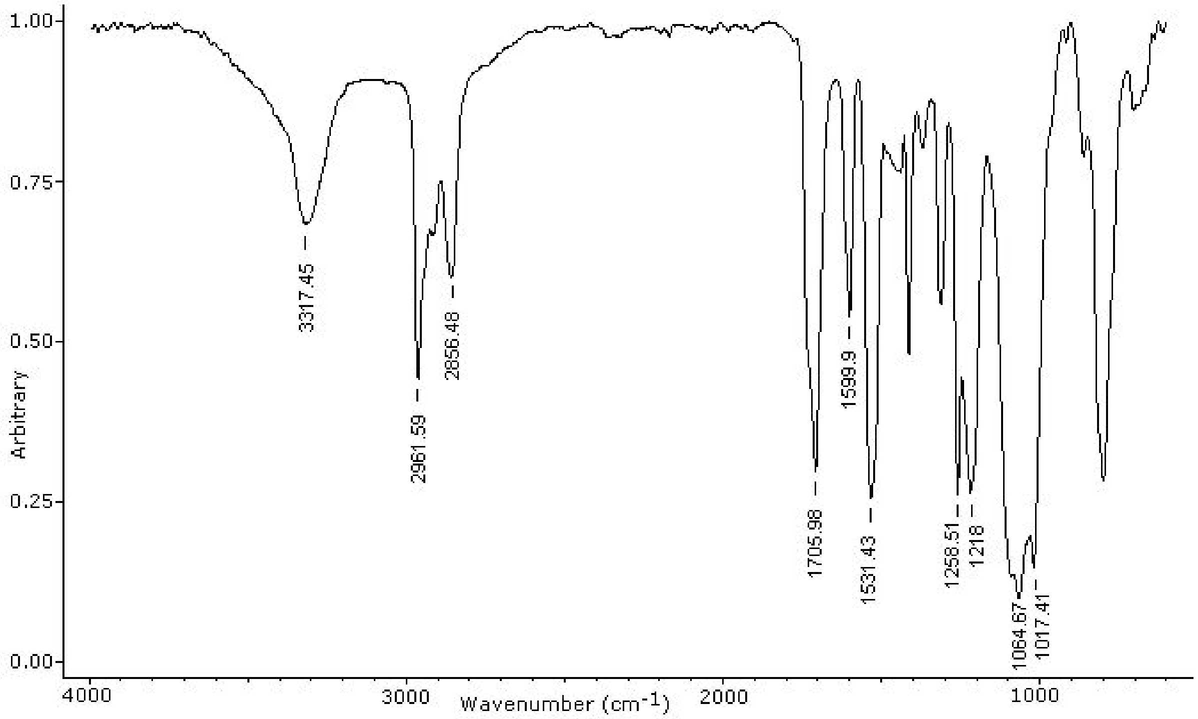


Fig. 5. FT-IR Spectrum of polyurethane based on PTMEG/MDI/EG+Gly (PU 1).

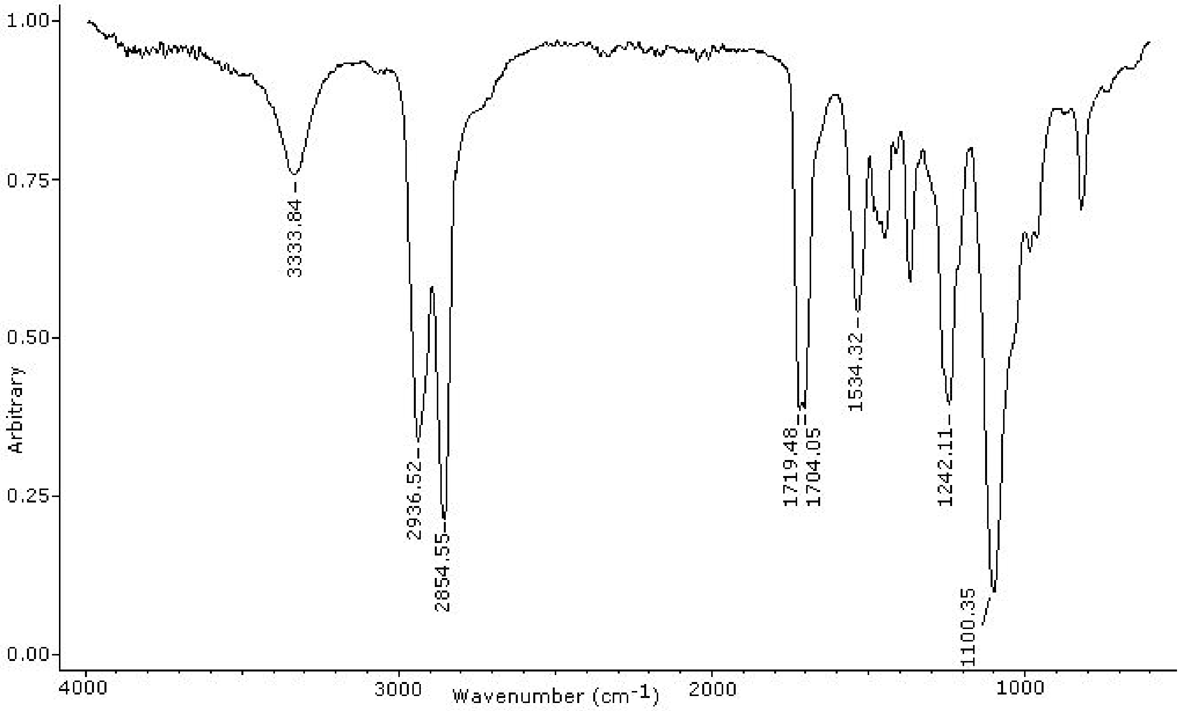


Fig. 6. FT-IR Spectrum of polyurethane based on PTMEG/HDI/EG+Gly (PU 2).

The crystalline structure of polyurethanes is controlled by the formation of hydrogen bonds between NH and C=O groups of the urethane linkages [14]. From the FTIR analysis, the hydrogen bonded C=O present in the crystalline domain can be identified by the peak absorbance at 1704-1719 cm^{-1}.

3.4 Thermal properties

Thermogravimetric analysis has been detailed in Table 1.

This method was used to study of some polyetherurethanes attempting to outline the increase in the thermal stability brought by components from their structure. To achieve this, the operational parameters were kept constant to all probes for obtainment of comparable data. 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 [15].

Table 1. Thermogravimetric data for the polyurethanes based on PTMEG/MDI(HDI)/EG+Gly.

Sample	Reaction order*			Weight losses (%) and decomposition temperature ranges (^{o}C)				Energy Activation* KJ/mol		
	Step			Step			Residue, %	Step		
	I	II	III	I 215-300	II 300-380	III 380-500		I	II	III
PEU 1	0	0	1.3	7.88	16.94	68.71	6.47	15.68	38.34	141.39
PEU 2	0	0	1.1	6.04	16.99	73.61	3.36	29.55	32.97	163.84
PEU 3	0	0	1.0	11.37	13.20	67.32	8.11	30.36	22.92	101.45
PEU 4	0	0	1.0	11.09	18.68	67.59	2.64	68.02	40.58	138.83

** Calculated through Reich-Levi method.*

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 domain acts as an additional physical crosslink site below there melting temperature.

Generally, polyurethanes analyzed decomposed in three steps and the temperature which the weight losses were maximum is 380-500 ^{o}C (Fig. 7). The glycerine contribution, by ramified structures generated, and increase of flexible chain, lead to relative stability, because the possibility of order the main molecular chain is high. 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 [16], are between 0 and 1; 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.

Since the mechanical properties are largely influenced by the morphology, the thermal properties of the polymers were investigated.

Thermogravimetric analysis (TGA) has been used to examine the thermal stability of the polyetherurethane samples. The results are presented in Fig. 7a, where PEU with molar ratio 1:2:1 are stabile up to 410 ^{o}C, and Figure 7b, where PEU with molar ratio 1:3:2 are stabile up to 440 ^{o}C.

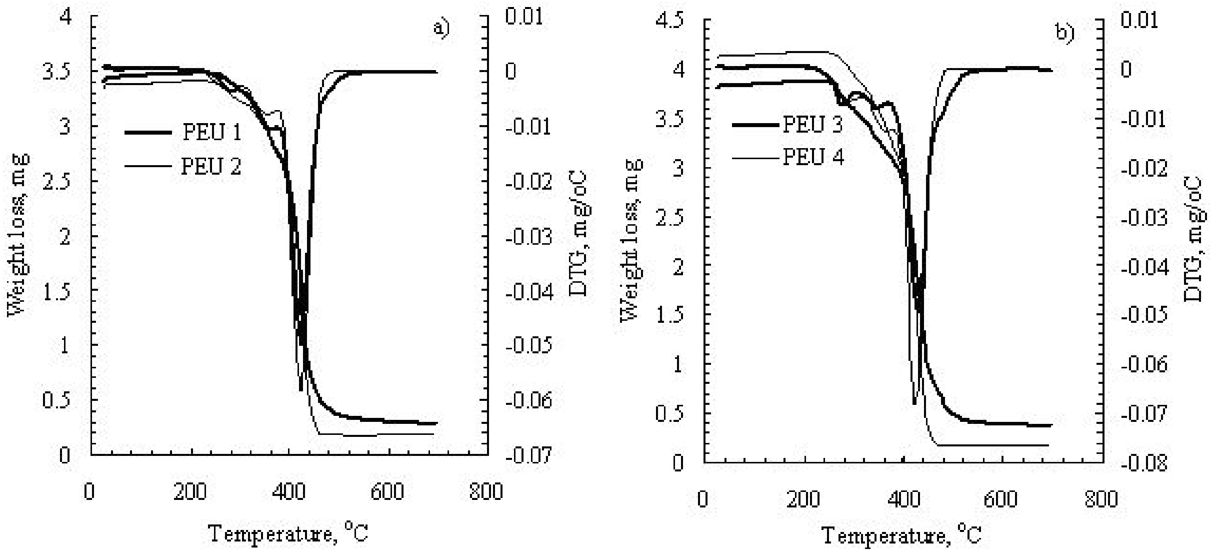


Fig. 7. TG and DTG curves of polyetherurethanes: a) PEU 1 and PEU 2 (molar ratio 1:2:1); b) PEU 3 and PEU 4 (molar ratio 1:3:2).

The dependence of the activation energy (Reich-Levi method) versus conversion degree is presented in Fig. 8. The energy to activation decreased until a conversion.

An important depression in activation energy values versus conversion can be observed for a conversion $\alpha <$ 0.3. This behaviour was also characteristic to an autocatalytic reaction. In connection with this, one should note that the oxygen traces in the polymer act as a catalyst for the decomposition process [8].

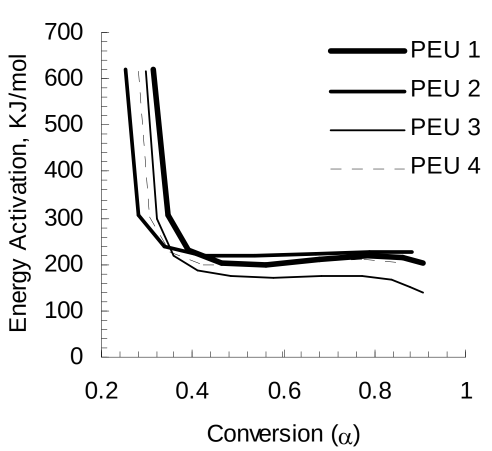


Fig. 8. Energy activation vs. conversion of PEU 1… PEU 4.

3.5 DSC behaviour

The thermal properties of the samples were studied too, by means of Differential Scanning Calorimetry (Figure 9). 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. So, the diisocyanate nature influence (aliphatic or aromatic), on the transition behaviour of polyetherurethane samples, may be studied by DSC analysis. The polyurethanes PU 1 and PU 3 based on MDI exhibit *Tg* at -44.19 respectively -46.65 ^{o}C, while the polyurethanes PU 2 and PU 4 based on HDI exhibit *Tg* at -73.23 respectively at -73.08 ^{o}C. Supplementary, the samples based on HDI exhibit ***Tmelt*** at +11.39 ^{o}C (PU 2) and respectively +10.44 ^{o}C (PU 4), while the samples based on MDI don't exhibit this comportment. The semicrystalline structure provided by diisocyanate component (HDI) provoke, to these samples, a decreased glass transition (*Tg*) in opposition with polyetherurethane samples based on MDI, which don't present crystalline structures.

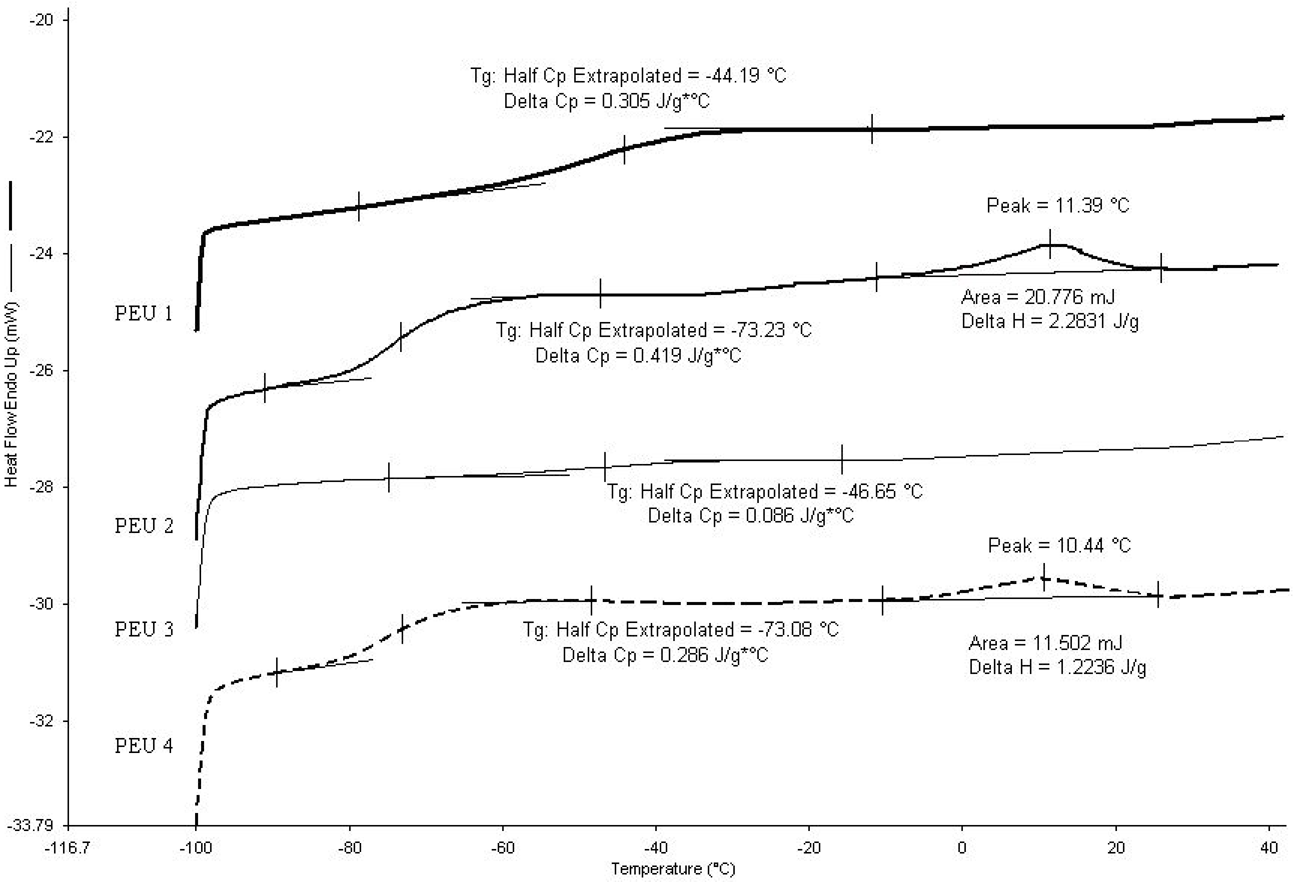


Fig. 9. DSC traces of polyurethanes based on PTMEG/MDI and PTMEG/HDI.

The transitions, which are observed to occur above 10-12 ^{o}C, for PEU 2 and PEU 4 based on aliphatic diisocyanate, are associated with the melting of hard segment domains. The melting behaviour of the hard segments can be seen as an endothermic peak in the DSC curve. From the heats of transition data (ΔH), it is clear that when the hard segment content is decreased, the energy associated with the melting of the hard segments is also decreased (ΔH-PEU 4< ΔH-PEU 2). In addition to this, the presence of amorphous hard segments appeared to decrease the melting temperatures of the crystalline hard segment. Higher hard segment transition in the DSC indicates higher thermal stability of the resulting polyurethane.

3.6 Mechanical properties

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 [17].

The results of mechanical properties are presented in Table 2 and Fig. 10.

When the amount of hard segments is greater, higher stress and modulus and lower elongations result. 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. This is because these polar groups, which have a high cohesive force, participate in intermolecular hydrogen bonding and restrict the rotation of polymer segments, resulting in a higher hardness.

Table 2. Physico-mechanical measurements of polyurethane samples based on PTMEG/MDI(HDI)/EG+Gly.

Sample code	Tensile strength, MPa	Elongation at break, %	Young's modulus, MPa	Remanent elongation, %	Hardness, °ShA	Abrasion, mm^3/mm^2
PEU1/MDI	24.8±0.25	105±1.00	53.0±0.50	1.33±0.03	60±0.60	33±0.35
PEU2/HDI	23.7±0.87	308±2.50	24.2±0.36	2.67±0.06	55±0.85	35±0.42
PEU3/MDI	52.6±0.35	115±1.52	155.0±0.76	0.67±0.02	70±0.47	31±0.29
PEU4/HDI	22.1±0.40	287±1.52	22.7±0.40	1.33±0.03	65±0.58	30±0.23

Table 3 . Distribution of hard and soft segments of polyurethane samples based on PTMEG/MDI(HDI)/EG+Gly.

Sample	Chain extender		Hard segments, %		Soft segments, %	Molar ratio, PTMEG:MDI(HDI): EG+Gly
	Ethanediol, %	Glycerine, %	Crystalline	Amorphous		
PEU 1/MDI	2.10	1.52	19.33	9.67	71.00	1:2:1
PEU 2/HDI	2.29	1.70	15.05	7.52	77.43	1:2:1
PEU 3/MDI	3.60	2.67	25.98	12.99	61.03	1:3:2
PEU 4/HDI	4.04	2.99	21.09	10.55	68.36	1:3:2

Physical and mechanical analyses evidence the extent of the supermolecular modifications of polyurethanes obtained as a function of their structural change [18]. From the results, it is evident that as the crystalline hard segment content of the elastomer is decreased, the elastomer hardness also decreases. Wherever, because of amorphous portion of the hard segments, the hardness of samples has appropriate values, less than for samples which don't have trifunctional chain extender in their structures. By analysing the soft and hard segments and their relation to hardness, it appears that the amorphous hard segment behaves like the polyether soft segment (Table 3).

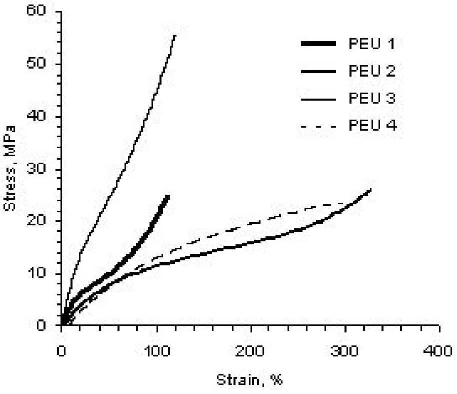


Fig. 10. Stress-strain of polyurethane samples.

In segmented polyurethanes, the mechanical properties were generally accredited to the result of a pseudo-crosslinking effect resulting from the hard-segment aggregation [19]. 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. In case of these polyurethanes, added of small quantities of glycerine have a crosslinking effect and diminish the concentration of crystalline hard segments.

4. Conclusions

In this study were synthesized and evaluated some polyurethane elastomers for resistance to different aggressive agents.

These results indicate that the chemical resistance and mechanical properties of these polyurethane materials can be improved by varying of the hard and soft segments amount.

We demonstrate that these polyetherurethane elastomers were suitable for oil and incidental gasoline exposure.

Polyether-based urethanes are more resistant to hydrolysis effects than polyester-based urethanes.

Evaluated polymers are recommended for hot water, steam and high humidity applications.

Acknowledgements

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