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Material Behaviour

Novel cast polyetherurethanes based on dispersed polymeric polyols

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ABSTRACT

Our study was focused on obtaining polyetherurethanes synthesized with using polymeric polyether based polyols differing in dispersed copolymer content (10, 20 and 40 wt%). The polyetherurethane materials were synthesized via two step method. The influence of different polymeric polyether based polyols on the chemical structure, morphology, mechanical and thermal properties of the obtained polyetherurethanes was investigated. The Fourier transform infrared spectroscopy (FTIR) was used to analyze and confirm the chemical structure of synthesized materials. Analysis of thermal stability by thermogravimetric method (TGA) of polyetherurethanes indicated that the decomposition of all materials carried out in two steps. The results of the thermomechanical analysis (DMA) showed that the polyetherurethanes synthesized with using polymeric polyols containing 10 wt % of the copolymer characterized by the highest storage modulus of all materials. The same materials have got also the highest tensile strength value.

1. Introduction

Polymeric polyols (known as filled polyols) are defined as a polymer or copolymer dispersion in a flexible polyether polyol matrix. These kinds of polyols are often used as “reinforced polyols” for polyurethane foam synthesis (soft and semi-rigid foam) [1,2]. Polyether polyols containing polymers as fillers are a class of polymer polyols and are produced in a large industrial scale because they are one of the most important group of polyols used for high-performance flexible polyurethane (PU) foam and PU elastomers. Polymeric polyols are divided, by the nature of the polymer finely dispersed in the polyether matrix, into the following categories: graft polyether polyols also known as dispersion polymer or as dispersant polyol; polyurea dispersion - PHD polyols; polyisocyanate polyaddition PIPA polyols (polyurethane dispersion) and other polymeric polyols (epoxy or aminoplast dispersion) [3].

Commonly, the styrene/acrylonitrile copolymer dispersion (SAN) in the base polyether polyol is used. The polyether polyols technology based exclusively on ACN are commercialized because of the high glass transition temperature (T_g) of the polyacrylonitrile solid fraction. The disadvantage of this example of polymeric polyols is the higher cost of SAN in comparison with the cost of alternative polymers such as polyethylene and polypropylene. The methods of polymeric polyols preparation have been described in many patent applications. Process for preparing a stable dispersion of a preformed polymer in a polyol in a single mixer. A preformed polymer is mixed under sufficient heat and shear to reduce its particle size to the desired size in the presence of a polyol. The effect of the type, concentration and monomers ratio, the polyol - monomer ratio, of the chain transfer agent concentration, reaction temperature, the initiator type, reaction time on the polymerization system dispersion stability was described [1,2].

Generally, copolymer polyols are produced by polymerizing one or more ethylenically unsaturated monomers dissolved or dispersed in a polyol (carrier polyol) in the presence of a free radical polymerization initiator to form a stable dispersion of solid polymer particles in the polyol. Carrier polyols like can be both feedstock which are added to the reactor before and/or during the polymerization of the solid particles. and diluent polyol which is added to the feedstock polyol after this polymerization. The low viscosity polyol allows to increase the solid content when making the polymer polyol from the said polyol, keeping viscosity similar to other polymeric polyols [4]. Another potential approach to manufacturing polymer polyols is to polymerize the discontinuous phase polymer separately, and then disperse the polymer into the polyol [5,6].

Polymeric polyols, as stated earlier, can be used in polyurethane synthesis [7]. Polymeric polyols compositions, which are used in the preparation of polyurethane foams are based in known materials and were first disclosed in US Patents [8,9]. Such polymeric polyols are

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prepared by polymerizing one or more unsaturated monomers (styrene monomer, acrylonitrile, etc.), dissolved in the base polyol in the presence of a free radical catalyst. Thus, the produced polymer particles are stably dispersed in polyol liquid, and polyurethane foams prepared from this kind of polymeric polyol present higher hardness and greater physical properties compared to polyurethane foams prepared from conventional polyols [7]. In order to manufacture polyurethanes having further improved physical properties, several efforts to improve the properties of polymeric polyols have been made. Particularly, in order to prepare low-viscosity polymeric polyols, having high polymer content together with high dispersion stability, a method of introducing a reactive NAD (nonaqueous dispersant) stabilizer was suggested. The NAD stabilizer serves to introduce a small amount of unsaturation into polyol and contributes to increase the dispersion stability of solids, which are produced in the preparation of polymeric polyols [7].

Methods of preparing polymeric polyol composition and the grafted polyol-polyacrylate are also provided to have a low viscosity as well as high stability and may be prepared with high level of dispersed vinyl polymer and high styrene: acrylonitrile ratios in the dispersed vinyl polymer. This polymeric polyol composition is useful for the preparation of polyurethanes, particularly polyurethane foams and comprises a continuous phase, a disperse phase within the continuous phase and as a dispersant to enhance the stability of the polymer polyol a grafted polyol-polyacrylate dispersant comprising an isocyanate vinyl monomer/ethylenically unsaturated monomer random copolymer and a polyoxyethylene polyether which are connected through at least one urethane graft site [10].

Glycolysis of flexible polyurethane waste containing polymeric polyols can be conducted and recovered polyol can partially replace the commercial polyols in the novel process of polyurethanes synthesis. Influence of SAN content on the glycolysis processes kinetic rate was studied. It was found that lower SAN content caused increasing in rate of glycolysis reaction progress [11].

Polymer blends based on thermoplastic polyurethanes and polystyrene–co–acrylonitrile have different properties which derived from individual properties of a single polymer. This multicomponent composition leads to join different, usually contrary, properties of various polymers [12]. Vatalis et al. noted that SAN, as a polymer blend component, promotes microphase separation between hard segment (HS) and soft segment (SS) in polyurethanes materials. The microphase separation of PU/SAN blend was studied by differential scanning calorimetry (DSC), dielectric relaxation spectroscopy (DRS) and thermally stimulated depolarization currents (TSDC) [13]. The addition of SAN copolymer enhances mobility of hard segments (HS) at their microdomains region, visible as a decreasing of ΔCp [14].

The aim of this study was to investigate the influence of different SAN copolymer content in polyol used to the polyetherurethane synthesis on structure, morphology, thermal, thermomechanical and mechanical properties of produced materials. The aforementioned properties and parameters were determined by means of spectroscopy, and thermal methods and mechanical testing under static and dynamic conditions.

2. Experimental

The polyetherurethanes (PU) were synthesized by the prepolymer method. The prepolymer was prepared from diisocyanate 4,4′-diphenylmethane diisocyanate, MDI (BorsodChem, Hungary) and a polymeric polyol based on polytetrahydrofurane (PTHF, 2000 g/mol, BASF, Germany) containing dispersed copolymer SAN particles in an amount of 10, 20 and 40 wt % (Castilla La Mancha University, Spain). This reaction was conducted at 80 °C for 1 h. During the second step, the prepolymer chains were extended by using 1,4-butanediol (Brenntag, Poland) with 0.3 wt% of 1,4-diazabicyclo[2.2.2]octane (DABCO, Merck, Germany) as a catalyst. The molar ratio $[NCO]_{prepolymer}/[OH]_{chain\ extender}$ was equaled 1.05:1. All samples were molded by gravity casting to the forms and then cured at 100 °C for 24 h. Segmented structure of synthesized cast polyurethanes as a graphic scheme is presented below.

3. Measurement

3.1. FT-IR spectroscopy

The Fourier transform infrared spectroscopy (FTIR) of cast polyetherurethanes was carried out using a FTIR Nicolet 8700 spectrophotometer (Thermo Electron Corporation) and ATR technique; a Specac Heated Golden Gate single reflection diamond ATR accessory was used. Spectra were registered at room temperature for the wavenumbers ranging from 500 to 4500 cm^{-1} at 4 cm^{-1} nominal resolution. Each spectrum was an average of 64 independent scans.

3.2. SEM analysis

The microscopic analysis was conducted on the cross section of samples using a Phenom G2 PRO (Phenom- World) scanning electron microscope, with accelerating voltage of 5 kV.

3.3. DMA

Dynamic mechanical analysis of cast polyetherurethanes was performed using a DMA Q800 Analyzer (TA Instruments). The measurements were taken under the nitrogen atmosphere, at a temperature range from −100 to +100 °C, at an operating frequency of 10 Hz, with a heating rate of 4 °C/min. The values of storage modulus, loss modulus and glass transition temperature were also recorded. Rectangular samples with dimension 17.6 × 9.7 × 2.9 mm (length x width x thickness) were used to the measurement.

3.4. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed with the use of NETZSCH TG 209F3 analyzer. Samples about ca. 6 mg were measured in the temperature range from 35 to 700 °C with the heating rate of 20 K/min. Measurements were carried out under the nitrogen atmosphere. Thermogravimetric (TGA) and differential thermogravimetric (DTG) curves for each cast polyetherurethane were plotted. The temperature of mass loss 5, 10 and 50% were given as $T_{5\%}$, $T_{10\%}$ and $T_{50\%}$ respectively, while the maximum of rate decomposition temperature of the each stage were described as $T_{max\ I}$ and $T_{max\ II}$.

3.5. Mechanical analysis

3.5.1. Tensile test

The tensile strength (TSb) and elongation at break (Eb) were measured under static pressure by using a Zwick Z020 tensile-testing machine, in accordance with the EN ISO 527-1:1996 and EN ISO 527-2:1996 standards. The dumbbell-shaped samples of standard dimensions were tested at a rate of 100 mm per minute. The original gauge length (l_o) was equal 25 mm. The measurements were performed at room temperature.

3.5.2. Cyclic compression tests

The compression test were carried out by using a Zwick Z020 tensile-testing machine, in accordance with the EN ISO 604:2006 standards. The compression cylindrical shape specimens were measured 10 ± 0,5 mm in diameter and about 25 ± 1 mm in height. The cyclic compression tests consist of achieving three load–unload loops continuously up to the strain value of about 40% and successively up to 10% of the strain in order to calculate hysteresis. The samples were tested at a compression rate of 5 mm per minute. The measurements were performed at room temperature.

Hysteresis is expressed as a lost energy during deformation cycle and can be calculated by using equation (1), given below:

$$H = \frac{W_H}{W_{loading}} \cdot 100\% = 100\% - \frac{W_{unloading}}{W_{loading}} \cdot 100\% \quad (1)$$

where:

W_H – lost energy,
$W_{loading}$ – energy of loading (deformation),
$W_{unloading}$ – energy of unloading (compression).

3.5.3. Hardness

Hardness was measured according to the PN-EN ISO 868:2005 standard. The circular sample (ϕ56 × 6 mm) was placed on a flat surface, and 10 measurements were taken per sample by applying a Shore D durometer for 3 s.

3.5.4. Rebound resilience

Rebound resilience was determined by means of a Rebound Tester in accordance with the ISO 4662:2009 standard. Rebound resilience is measured by dropping a free-falling pendulum hammer from a given height, which impacts the sample. The amount of energy is shown on a pendulum scale. 10 measurements were recorded per sample.

3.5.5. Density

Density was determined according to the PN-EN ISO 1183-1:2013-06 standard. The measurements were performed in methanol at 23 ± 2 °C (see Fig. 1).

4. Results and discussion

4.1. FTIR spectroscopy analysis

The FTIR-ATR spectra of the polyetherurethane synthesized with using polyols containing different amounts of the copolymer are presented in Fig. 2. The wavenumber value of 3300 cm^{-1} and 1599 cm^{-1} corresponds to the vibration of NH bond. The peak of absorption at higher wave number is attributed to stretching vibration of NH bond and at the lower to the bending vibration of NH bond which is characteristic of the urethane group. The stretching vibration of CN was registered at 1533 cm^{-1}. The wavenumbers of 2852 and 2937 cm^{-1} correspond to the stretching vibrations of the CH_2 group, while the deformation vibrations were registered at 1414 cm^{-1}. The valent vibration of carbonyl group presented in the structure of synthesized polyurethanes and derived from the ether groups of the polymeric polyol, both for free and hydrogen bonded carbonyl groups manifests itself as a multiplet at a wavenumber range from 1701 to 1730 cm^{-1}, while the stretching vibration of C=O group occurs at 1225 cm^{-1}. At the wavenumbers 3300 cm^{-1} and 1701 cm^{-1} absorbance growth with increasing of SAN content in the polymeric polyols thereby increased amount of hydrogen bonds in the polyurethanes structure. The slight differences in band intensity at 1103 and 1082 cm^{-1} were observed which are attributable to resilience stretching vibrations of C-O-C group. For the wavenumbers 1103 and 1082 cm^{-1}, the vibrations corresponding to free C-O-C group and hydrogen-bonded C-O-C group were present, respectively. In the range from 500 to 900 cm^{-1}, the area characteristic for vibration of CH derived from the aromatic ring are visible [15–18] (see Fig. 3).

4.2. Scanning electron microscopy

The morphology of the polyetherurethanes was assessed by the scanning electron microscopy, SEM and presented in Figs. 4–6. The SEM images of the polyetherurethanes synthesized with using polymeric polyols show the uniform structure and distribution of copolymer particles. The polyetherurethanes continuous phase is represented by rest of polymeric polyol (ingredients of soft segments, SS), while dispersed phase as rest of diisocyanate and chain extender (ingredients of hard segments). The polyetherurethanes are characterized by ordered and regular structure regardless the content of copolymer in polymeric polyols. The particles of the copolymer are visible as well spheres shape and its distribution depends on the copolymer amount in the polymeric

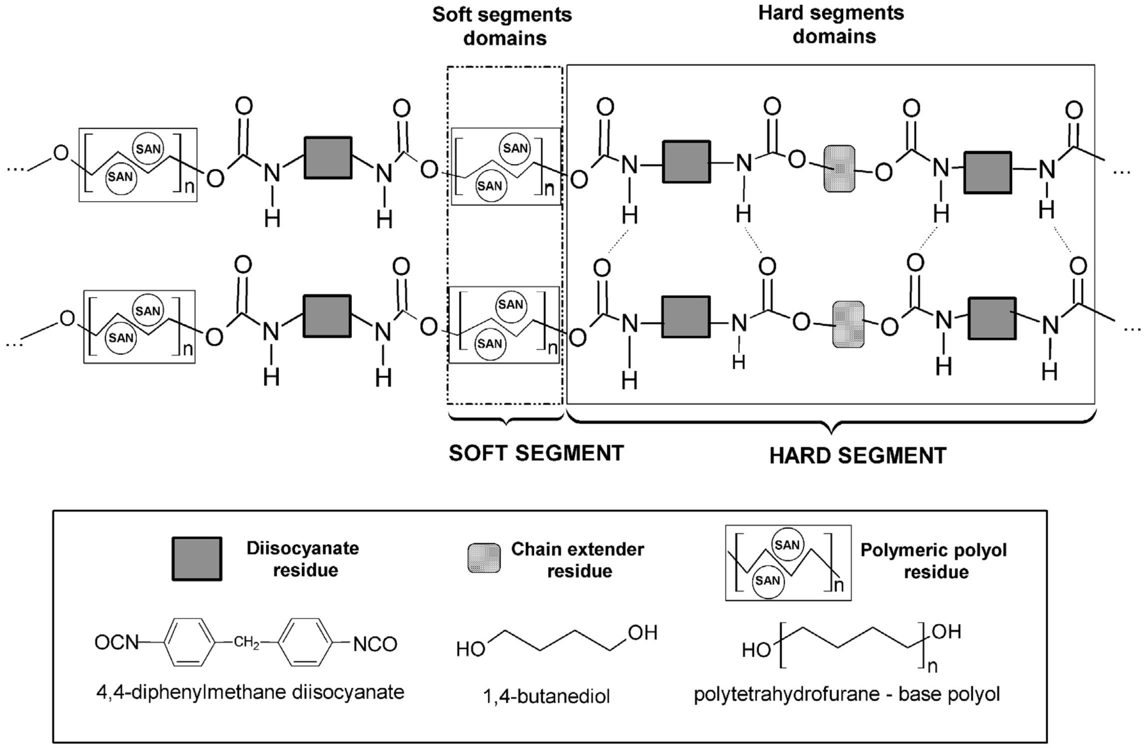

Fig. 1. Scheme of segmented structure of obtained cast polyurethanes based on polymeric polyols.

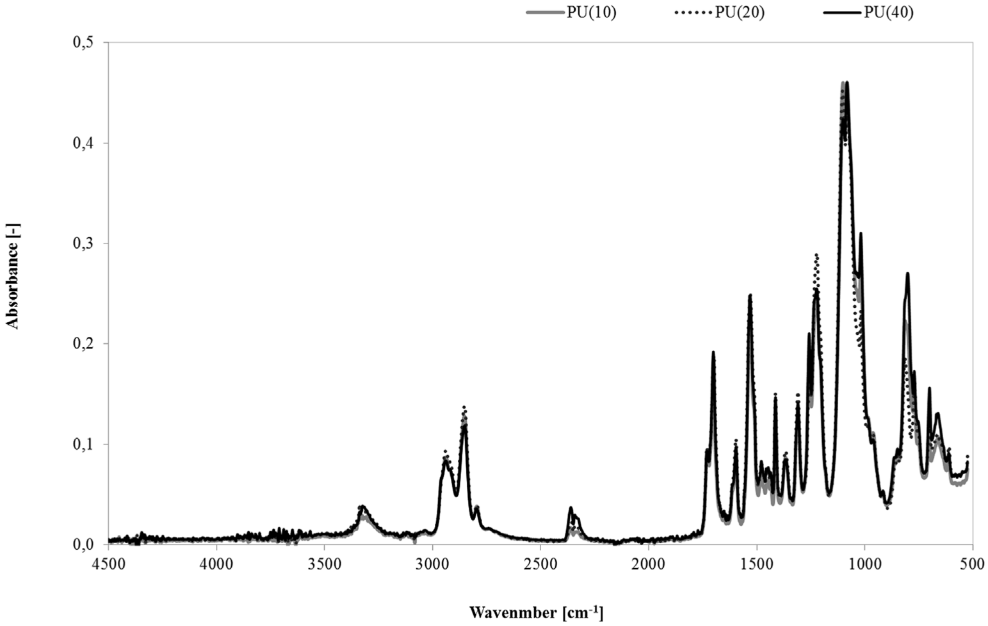

Fig. 2. FTIR-ATR spectra of bio-polyetherurethanes synthesized with polymeric polyols containing 10, 20 and 40 wt% of the copolymer.

polyols and seems to be a part of the HS (bright regions). Each sample characterized by good microphase separation between HS and soft segment SS in obtained polyetherurethanes materials what is visible as a two dominate bright and dark regions. The microphase separation of HS and SS domains is responsible for the versatile properties of polyurethanes [20,21].

4.3. Dynamic mechanical analysis

The results of dynamic thermomechanical analysis of the polyetherurethanes containing 10, 20 and 40 wt% of the copolymer (SAN) in PTHF polyol are shown in Figs. 7–9. Based on the analyzed data, it can be stated that the application of polymeric polyols to polyurethane synthesis had a positive effect if the copolymer content in the polyol is not higher than 20 wt%. The maximum E′ value was observed for the polyetherurethane containing 10 wt% of the copolymer in the temperature range from −100 to −32.8 °C and it is equaled 2776 MPa. At the soft segments glass temperature region, the value of E′ is 406 MPa. Over this temperature, it can be observed that the highest E′ was noted for polyetherurethanes containing 40 wt% of the copolymer into the polyol (MPa at $T_g = -37.5$ °C), below the glass temperature the highest value for PU(40) is 2452 MPa. At glass temperature region, the storage modulus of PU(40) is equal 945 MPa. In the case of PU(20) the E′ at the T_g point this parameter is 564 MPa, below glass temperature highest E′ value, is equal 2333 MPa. Generally, the polyetherurethanes samples were characterized by high rigidity due to the incorporation of hard copolymer particles into the polyols part (Fig. 7).

The loss modulus (E″) also depended on the amount of copolymer dispersed in the polyether polyol. The E″ values decreased with increasing amount of copolymer in the polyol (Fig. 8). The polyurethanes

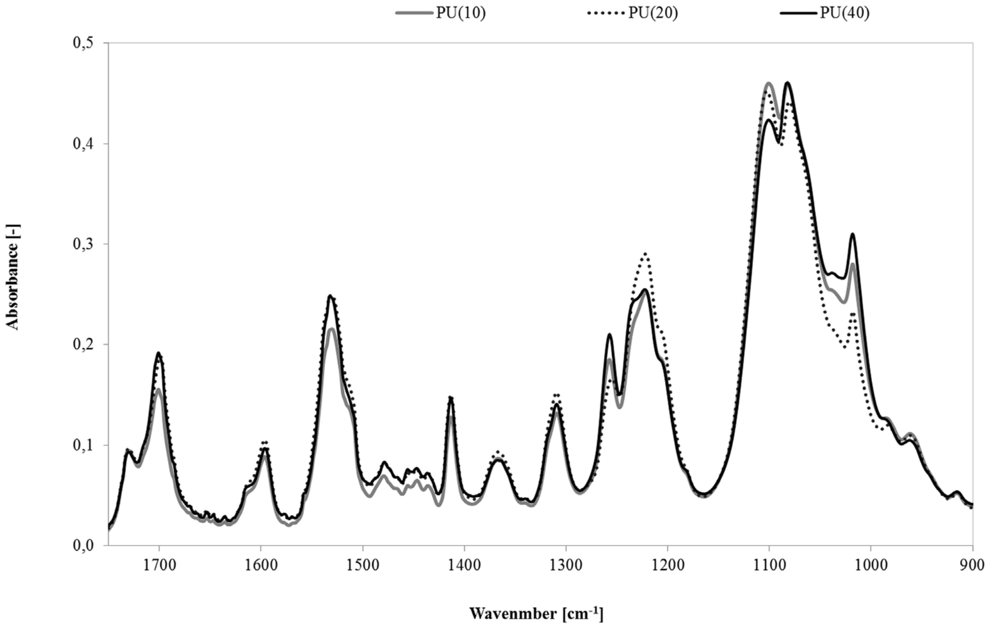

Fig. 3. FTIR-ATR spectra of bio-polyetherurethanes synthesized with polymeric polyols containing 10, 20 and 40 wt% of the copolymer at the range of wavnumber from 900 to 1750 cm^{-1}.

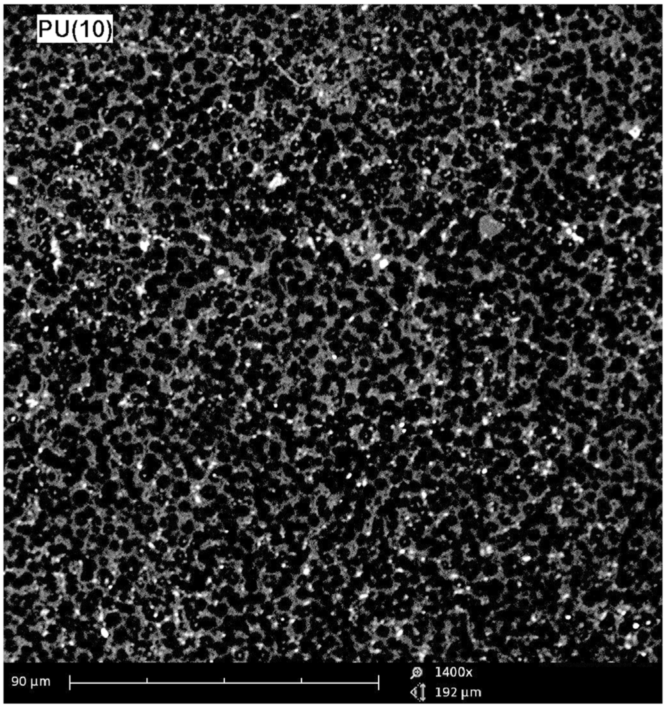

Fig. 4. SEM images of polyetherurethanes synthesized with polymeric polyols containing 10 wt% of the copolymer.

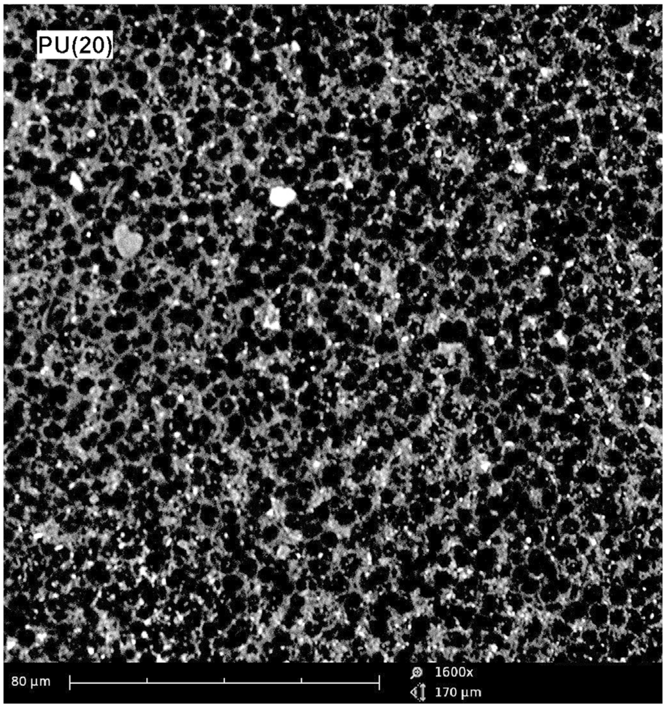

Fig. 5. SEM images of polyetherurethanes synthesized with polymeric polyols containing 20 wt% of the copolymer.

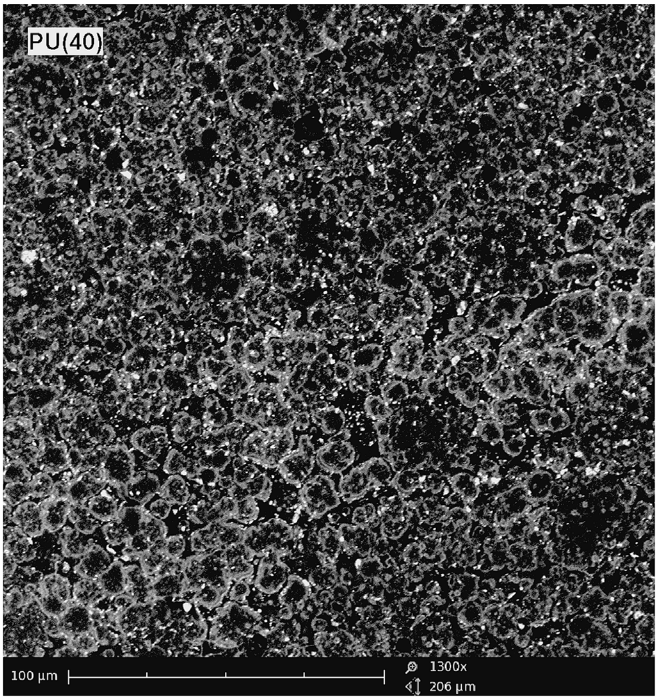

Fig. 6. SEM images of polyetherurethanes synthesized with polymeric polyols containing 40 wt% of the copolymer.

are characterized by the loss modulus in the range from 192 to 212 MPa. The elevated values of loss modulus of the PU(40) are advantageous because less energy is irreversibly lost by the materials. In the case of materials with the lower content of SAN – PU(10) and PU (20)- were characterized by similar dynamic mechanical behavior.

The values of glass transition temperature of soft segments (Tg_1 as α transition characteristic for soft segments) for different polyetherurethane samples ranged from − 40 to − 34 °C, while for the copolymer SAN glass transition (Tg_2) was registered at about from 110 to 127 °C (Fig. 9) what was also noticed and described in literature [1]. The melting temperature of soft segments is visible on the tan δ and loss modulus curves as a width shoulder around 0 °C, what is correlated with PTHF polyols with molecular weight about 2000 g/mol [19]. The values of $tan\delta_1$ of the PUs synthesized employing polyol containing the lower copolymer (10 or 20 wt%) amount were characterized by higher tanδ compared to the PU(40). With increasing of copolymer content in employing polymeric polyol, Tg_2 is slightly shifted to the higher temperature. However, the employment of the polymeric polyol with higher content of copolymer caused only a small decrease in the value of loss modulus, what means that the dissipation properties of the materials decreased slightly (Table 1). The coefficient values are characteristic of materials with good dissipation properties [22]. Analyzing the second pick of Fig. 9 it can be observed that the tanδ values increases with increasing copolymer content in the base PTHF polyol. The curve tan δ behavior is typical for polymer blends based on polyurethanes and SAN copolymer [14].

4.4. TGA

Thermal properties of obtained polyetherurethanes employing polymeric polyols containing different proportions of copolymer were determined by thermogravimetric analysis. Based on the obtained data, the effect of type of polymeric polyol on the thermal decomposition of the polyetherurethanes was below described (Figs. 10 and 11).

Thermal decomposition of polyetherurethanes took place in two main steps (Fig. 10) what confirms a good phase separation between polyetherurethanes hard and soft segments as well. The first step of thermal decomposition is related with urethane bonds dissociation derived from hard segments, while the second step is attributed to the soft segment decomposition. The thermal degradation curve curse seems to be similar for each measured sample. The differences caused by using polymeric polyols instead of commercial polyether polyol are visible as a shift of $T_{5\%}$ decomposition to the highest values what is resulted of different decomposition mechanism of these materials [23]. Generally, T5%, T10%, for each polyetherurethanes samples decreased

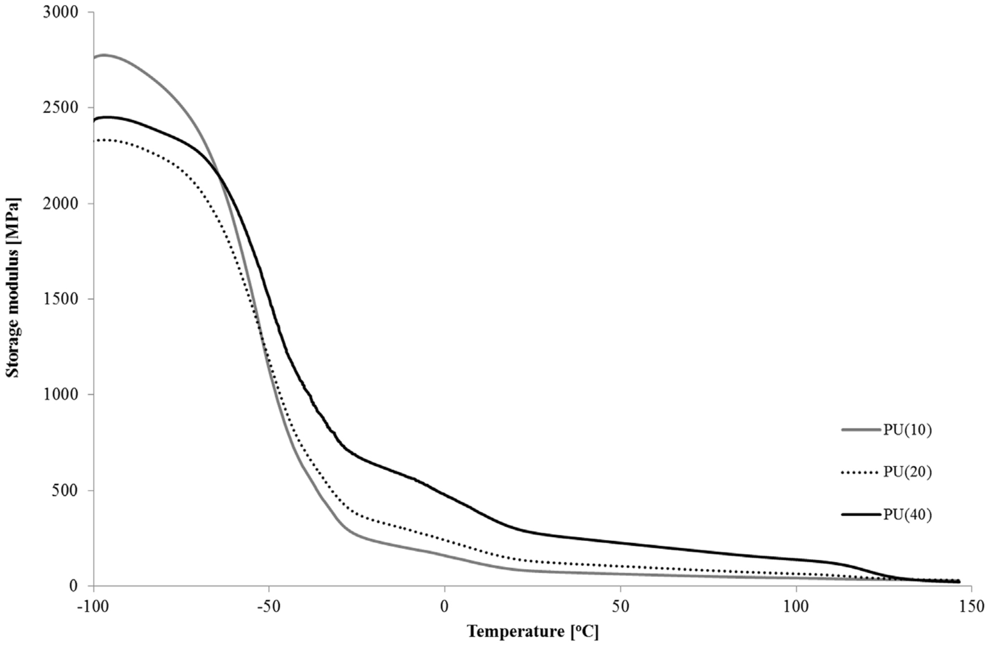

Fig. 7. The log E′ as a function of the temperature of polyetherurethanes.

with increasing copolymer content in polymer polyol. The beginning of thermal decomposition of polyetherurethane is correlated with urethane group thermal decomposition. The sample coded as PU(40) decomposed at the lower temperature (about 314 °C) than PU(10) and PU(20) what can be the result of interaction between the copolymer and hard segments of polyetherurethane. T50% values of polyetherurethanes were slightly increased with increasing copolymer content that is mean that the second step of decomposition at T50% have been already occurred (decomposition of the soft segments). Based on the literature, thermal decomposition degree of SAN copolymer takes a place in one step (ab 413.4 °C at the max rate of decomposition) [24] what is typical for PTMG polyols as well.

Based on the speed of the weight loss curves (DTG, %/min) analysis it was found that the decomposition depends on SAN content of the polymeric polyols used in the polyetherurethanes synthesis (Fig. 11). It is worth seeing that the thermal decomposition of the first stage with the highest rate occurred in the case of samples synthesized with using polymeric polyol with the lowest content of SAN copolymer while the lowest rate of this thermal decomposition stage was noticed for the polyetherurethane obtained with the polymeric polyol containing the highest content of SAN (Table 2). This phenomena of decreasing of the decomposition rate with increasing of SAN content in polymeric polyols can be result of the stabilizing effect of the aromatic chain derived from copolymer. At the second stage it can be observable that decreasing of temperature (at $T_{max\ II}$) at the highest rate of thermal decomposition is correlated with increasing of SAN content at the polymeric polyol.

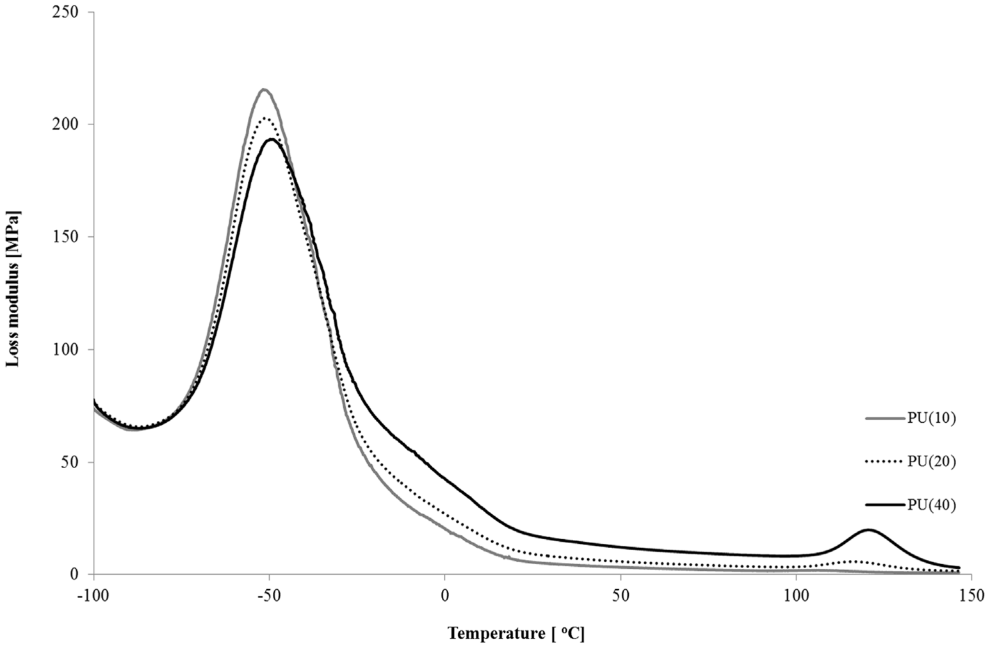

Fig. 8. The loss modulus as a function of the temperature of polyetherurethanes.

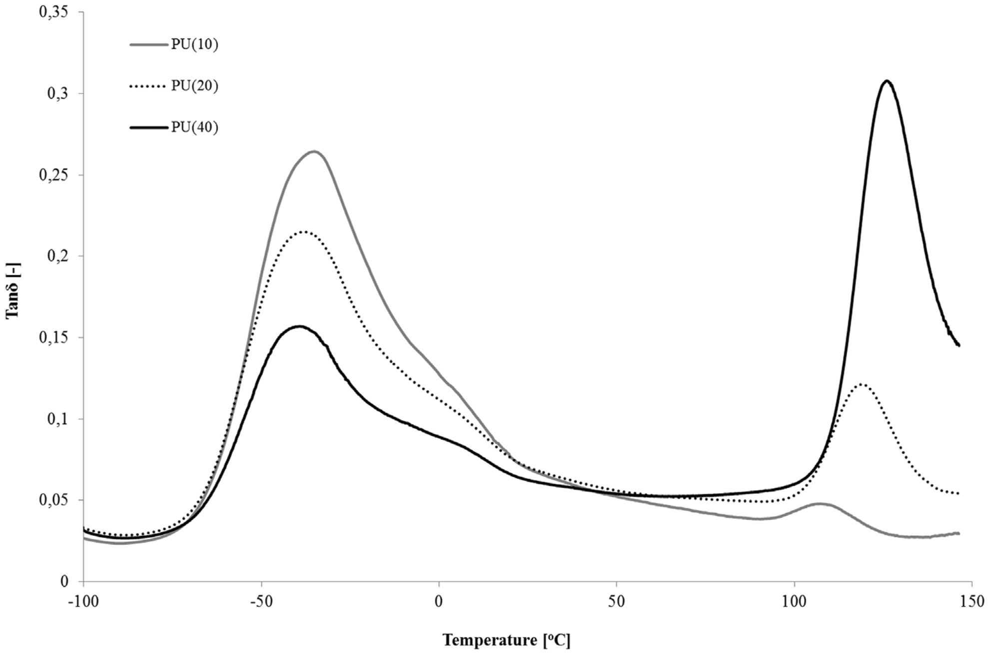

Fig. 9. The tanδ as a function of the temperature of polyetherurethanes.

Table 1
T_g, tanδ, storage and loss modulus of polyetherurethanes.

SAN content, wt%	$T_{g\ 1}$, °C	$T_{g\ 2}$, °C	Tanδ_1	Tanδ_2	E′, MPa	E″, MPa
PU(10)	− 32,8	110	0,26	0,05	2776	212
PU(20)	− 34,6	122	0,21	0,12	2333	200
PU(40)	− 37,5	127	0,16	0,30	2452	192

4.5. Mechanical properties: tensile test, cyclic compression test, hardness and elasticity

The results of tensile testing (tensile strength (TS_b)), elongation at break (E_b), compression test, hardness and elasticity of polyurethane are presented below in Table 2. Conducted measurements confirmed the strong influence of the copolymer amount in the polymeric polyol on mechanical properties of synthesized polyetherurethanes. It was noted that the polyetherurethanes containing 10 and 20 wt% of copolymer displayed TS_b values that were doubly higher to that of the polyurethane with 40 wt% copolymer into polyol (Fig. 10). It was observed that for the higher copolymer content in polymeric polyols the differences between the TS_b values were significant, i.e. ca. 16 MPa. For the samples, PU(10) and PU(20) same like in the case of DMA analysis, similar TS_b were noted. Increasing the copolymer content resulted in a rigidity increase of the composites, which was reflected in the values of elongation at break. For the sample with 40 wt% of the copolymer in the polymeric polyol, the E_b drastically decreased about 400% in comparison to the sample with 10 and 20 wt% copolymer content (Fig. 12). The decrease in elongation at break is a consequence of the

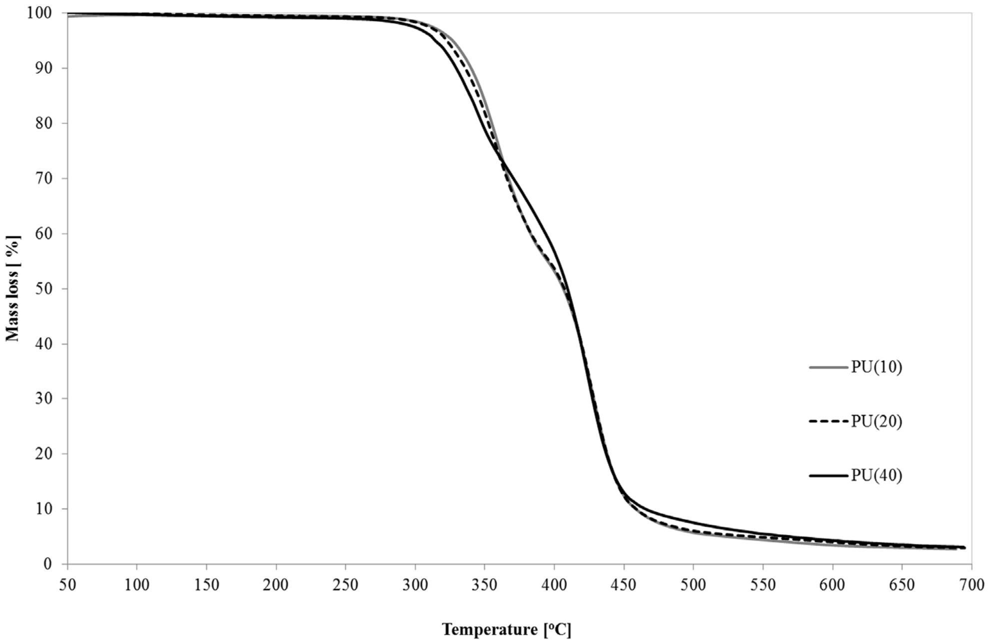

Fig. 10. Mass loss versus temperature plotted for the polyurethane materials.

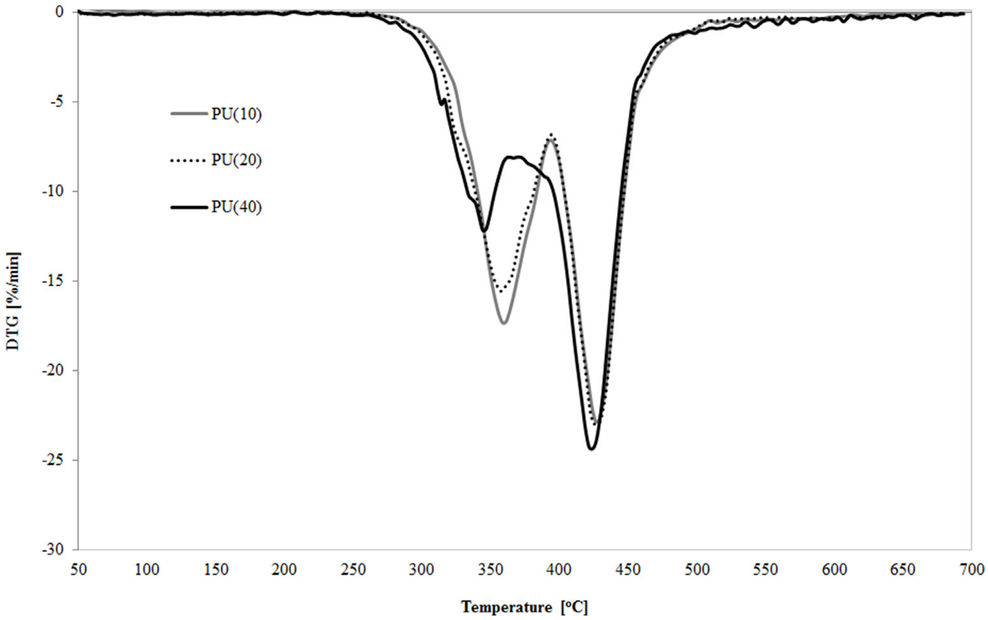

Fig. 11. DTG versus temperature plotted for the polyurethane materials.

Table 2
Thermal degradation temperatures of the polyetherurethanes containing copolymer.

Code of sample	$T_{5\%}$, °C	$T_{10\%}$, C	$T_{50\%}$, °C	$T_{max\ I}$, °C	DTG $_{I}$, %/min	$T_{max\ II}$, °C	DTG $_{II}$, %/min	Char at 700 °C, %
PU(10)	326	338	406	359	17.3	426	22.8	2.76
PU(20)	322	335	407	357	15.7	427	23.0	2.96
PU(40)	314	329	409	344	12.2	424	24.4	3.14

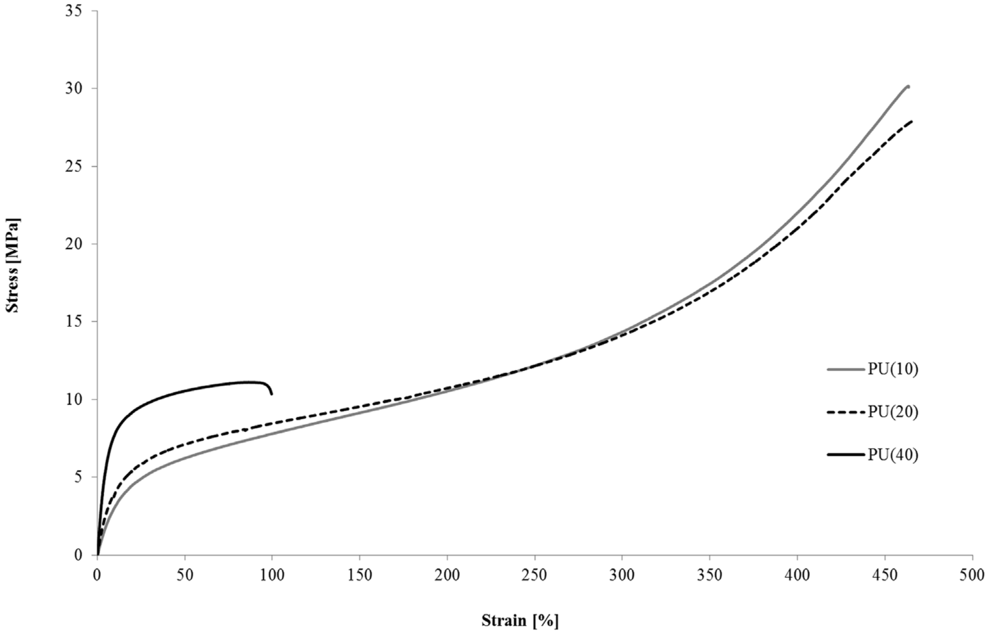

Fig. 12. Tensile strength as a function of elongation plotted for polyetherurethanes synthesized with polymeric polyols containing 10, 20 and 40 wt% of the copolymer.

lower mobility of the polyetherurethanes chains.

High copolymer content in the polymeric polyol did not affect to the polyetherurethanes elasticity, with values ranging from 55 to 56%. On the contrary, the hardness of the polyetherurethanes materials changed as a function of the copolymer particles dispersed in polyol; their hardness was increased 5 °ShD with increasing copolymer content about 10 wt%. Hence, the highest value of hardness was noted for PU (40), as itwas suspected. In a general way, it was found that increase the copolymer amount in the PTHF base polyol does have a significant impact on hardness. The hardness values of the PUs synthesized with the polymeric polyols are presented in Table 3.

The compression test results, expressed as deformation modulus 10,

Table 3
Selected mechanical and physical parameters of polyetherurethanes synthesized with polymeric polyols containing 10, 20 and 40 wt% of copolymer.

Code of sample	TS_b, MPa	E, %	H, °ShD	Rebound resilience, %
PU(10)	30.2 ± 0.4	459 ± 6	35 ± 1	55 ± 1
PU(20)	27.6 ± 0.9	460 ± 11	40 ± 1	56 ± 1
PU(40)	10.8 ± 0.3	98 ± 7	$51 \pm 4{\cdot}10^{-1}$	56 ± 1

Table 4
Results of compression at 10, 20, 30 and 40% deformation of polyetherurethanes.

Code of sample	Strain, %	Stress, MPa
PU(10)	10	3.3
	20	6.3
	30	9.2
	40	12.8
PU(20)	10	4.1
	20	7.5
	30	10.5
	40	14.2
PU(40)	10	8.7
	20	14.2
	30	19.3
	40	26.0

20, 30, 40%, were presented in Table 4. Based on the obtained results it was found that the copolymer content has a huge influence on the compressive stress. The difference between the stress values at a strain of 40% of the samples PU(10) and PU(40) is about 13 MPa. In a general way, it must be noted that the higher the copolymer content in the polymeric polyol, the higher the stress values as a consequence of the increase in hardness of the polyetherurethanes synthesized.

The compression cyclic test results during the cyclic loading/unloading tests are presented in Fig. 13 and in Table 5. Based on the obtained data, the hysteresis values for each sample were calculated. In the cyclic compression, the material absorbs energy when compressive loads are applied and they release energy when the loads are removed [25,26]. It was observed that polyetherurethanes coded as PU(40) needed the highest energy input to carry out the compression processes.

Table 5
Cycle compression test parameters of polyetherurethanes.

Code of sample	Cycle	Total force, kN	W loading, J	W remove, J	ΔW, J	Hysteresis, %
PU(10)	1	3.3	16.3	9.5	6.9	42
	2	3.2	12.6	9.2	3.4	27
	3	3.2	12.0	9.0	3.0	25
PU(20)	1	3.7	19.7	9.3	10.4	53
	2	3.6	13.6	8.9	4.7	35
	3	3.5	12.7	8.6	4.1	32
PU(40)	1	6.7	36.5	11.4	25.1	69
	2	6.3	20.2	10.7	9.5	47
	3	6.1	18.5	10.3	8.2	44

Analyzing Fig. 11, it can be observed that polyetherurethanes exhibited cyclic softening in its rubbery regime what indicates a good microphase separation [21]. The stress–strain cyclic loading curves show that, after a second cycle, the stress–strain curves follow to stabilization, what is confirmed by similar hysteresis values registered in second and third cycle. Generally, it was found that the higher the copolymer content in the base PTHF polyether polyol, the higher the hysteresis observed (Table 5).

5. Summary

FTIR spectroscopy, SEM microscopy, thermogravimetric analysis (TGA), thermomechanical analysis (DMA) and tensile test lead to confirm the strong influence of the copolymer content (SAN) in the PTHF polyols incorporated to the polyetherurethane materials. The morphological analysis of the obtained polyether-urethanes indicated an ordered and regular structure, regardless the copolymer content (SAN) of the polymeric polyols used in the polyurethane synthesis. Dynamic mechanical thermal analysis (DMTA) demonstrated that increases the copolymer content in the PTHF base polyol provokes a decrease in the polyetherurethane glass transition temperature of about 6 °C. Thermogravimetric analysis of polyetherurethanes indicated that the decomposition of all materials took place in 2 steps and that the decomposition rate depends on the copolymer amount in the polymeric polyol. Moreover, significantly changes in the polyetherurethanes hardness were observed, while the elasticity values for each sample was

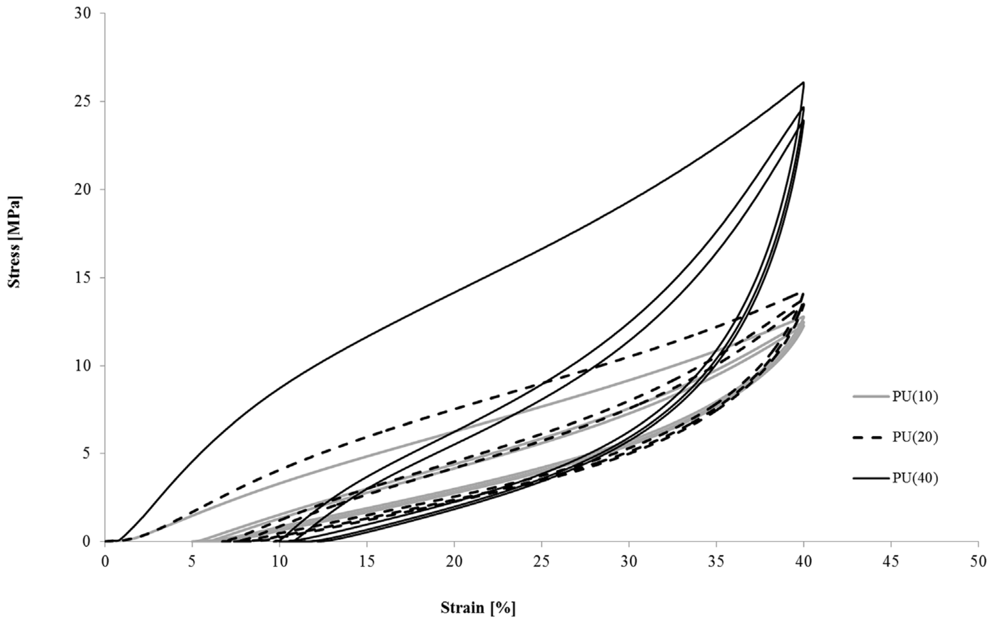

Fig. 13. Compression strength as a function of elongation plotted for polyurethanes synthesized with polymeric polyols containing 10, 20 and 40 wt% of SAN.

on the same level, regardless the copolymer content. Moreover, based on tensile test and compression test, it was noted a remarkable influence of the solids content (SAN). The obtained polyetherurethane with the highest content of copolymer was characterized by the highest hardness value. Polyetherurethanes synthesized by means of using polymeric polyols present significant potential uses, as a consequence of their thermal and mechanical properties.

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