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Synthesis and characterisation of polyurethane elastomers with semi-products obtained from polyurethane recycling

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Abstract

In this work polyurethane elastomers were synthesised by using different mixtures of a petrochemical and glycerolysate polyols and 4,4-diphenylmethane diisocyanate (MDI). Glycerolysate polyol was produced from polyurethane foam decomposition using crude glycerine as a decomposition agent. The structure and thermal properties of obtained semi-product were similar to the polyol used in the synthesis of original foam. Glycerolysate polyol was incorporated into polyurethane formulation as soft segment (SS). Since polyol is one of the major component in polyurethane system (>70%) introducing recycled components leads to lowering of consumption of petrochemicals and valorisation of recycled products. Polyurethane elastomers containing up to 16.4 wt.% of glycerolysate polyol were synthesised, soluble in dimethylformamide (DMF) up to ca. 12 wt.%. The effect of glycerolysate polyol content on the structure and properties was analysed by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA) and mechanical tests. Thermal properties did not worsen after using glycerolysate into polyurethane formulation. A slight increase in glass transition temperature is observed with the incorporation of glycerolysate polyol. Elastic modulus, tensile strength and hardness of polyurethane elastomers increased with recycled polyol content. Moreover they showed high elongation at break values.

Keywords: chemical recycling; crude glycerine; semi-products; polyurethane elastomer

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1. Introduction

Plastics production is increasing yearly on the level of 9.9%. Such high growth is connected with their diversity, low-cost of production and an ability to replace conventional materials such as metal, glass or wood. However, this growing trend causes also huge amount of waste which needs to be managed that may not spread on the landfills. Therefore in the recent years to prevent the environmental damage, the international regulations were introduced. In accordance to European Directive 2008/98/EC, the waste management should be in order of importance as follows [1,2]:

1. Prevention,
2. Reuse,
3. Recycling,
4. Other recovery as energy recovery,
5. Disposal.

When the first two principle are not suitable for specific plastic waste, recycling is a suitable option after which useful products can be received. Recycling can be divided into two main groups (excluding energy recovery): mechanical recycling and chemical recycling [3,4]. During mechanical recycling the polymer waste is very often subjected to the following procedure: collection, separation, purification, shredding, melting, extrusion and re-granulation. This option is mainly suitable for thermoplastic polymers such as polyethylene (PE), polypropylene (PP) or polystyrene (PS), while for thermoset polymers i.e. polyurethanes (PUs) mechanical recycling is limited to changing its physical form and instead of re-granulation can be used as fillers, bonded with adhesives, hot pressed or extruded in order to reduce the molecular chain to obtain thermoplastic material [5]. Chemical recycling allows to depolymerise polymers to starting monomers or into basic oil and hydrocarbons [1,6]. Thus, the majority of research on polyurethanes recycling describes methods of chemical recycling due to the possibility of obtaining starting substrates [3,7–9]. Thereby the reduction of plastic waste (recycling) remains and it helps to conserve commercially used substrates by production reduction (prevention).

Growing interests of polyurethane chemical recycling is related with their increasing production (currently is on the level of 15 million tonnes [10]) and quite expensive starting substrates which translates to their higher price in comparison with more conventional polymers as PE, PP. Success of polyurethanes in the plastic market is associated with their variable structure and broad spectrum of forms (rigid, elastic, viscoelastic foams; elastomers; sealants; adhesives; coatings) and hence wide range of application starting with mattresses sponges, shoe soles, paints, insulating materials, adhesives and even in medical application [7,11].

In a view of chemical variety, chemical recycling of PUs can be carried out in different ways that starting substrates can be received. The idea of PUs chemical recycling it to treat PU waste at increased temperature with a decomposing agent which allows to break the biuret, urea and urethane bond [12]. As a decomposing agents, in the literature, were used substances as follows: water [13], glycols [14], pure and crude glycerines [15,16], alcohols [3], acids and amines [3]. Very well and broad described method of polyurethane recycling is glycolysis [12,17,18]. In general, glycolysis carries out in the reaction with glycols at high temperatures, ca. 200 ^{o}C and the PU structure is decomposed in a transesterification reaction [19]. As the main idea of this process is to recover constituent polyols, many researchers surveyed on valorisation of that intermediates in synthesis of polyurethanes because they show similar properties to original, commercial substances [20]. Hence, the concept to implement semi-products obtained from the chemical recycling looks like a good way of managing recycled substances and simultaneously reducing the usage of petrochemicals and the cost of material production. Recycled polyol (in the case of glycolysis known as glycolysate) can be introduced to polyurethanes system to obtain rigid [21–23] or flexible[24,25] foams, elastomers [26,27] and adhesive [28]. Most of the works are concerned with the appliction of recovered polyol in the synthesis of flexible and rigid polyurethane foam synthesis. In the work of Benes et al. [29], rigid high density polyurethane foams were synthesised using 100% recycled polyol obtained from PU decomposition by fish oil-based polyol. Recovered and purified polyol from glycolysis of PU was used to prepare flexible polyurethane foams replacing 25 and 50% of origin polyol [30]. In another three works of Simon et al. [31–33], the upper and bottom phase of recovered polyol were incorporated into flexible and rigid polyurethane foam synthesis, respectively. The concept of using recovered polyol in polyurethane elastomer synthesis was proposed by Datta and Haponiuk [34]. Synthesis was carried out by an one-step method in which polymeric 4,4- diphenylmethane diisocyanate, the selected glycolysate, polyol (an elongation agent) and phosphoric acid (an inhibitor of side reactions) were mixed. Materials were thermally stable up to 300 ^{o}C and tensile strength was in the range of 3.6-5.4 MPa.

With respect to the “green chemistry” trend, oil industry also became interested in renewable resources and tries to replace crude oil with i.e. biodiesel which is created in a transesterification reaction of vegetable oil or animal fat with methanol (mostly) in the presence of catalyst. Besides the ester phase, the by-products in the form of glycerol phase are obtained. The crude glycerol is separated from esters, which are in sequence purified from catalyst and methanol. Crude glycerine can be purified and then used in pharmaceutical, chemical industry and also in alkyd resins, cellulose coatings, but the cost of purification and refining are high and the use of crude glycerine has been less exploited [15,35].

In this study crude glycerine was used in flexible polyurethane foam decomposition, as a reactant agent in the transesterification reaction, to obtain valuable semi-product - glycerolysate. Glycerolysis was performed in the "split-phase" condition resulting in two phase semi-product, viz. upper phase (liquid one, considered as a re-polyol) and bottom phase (solid one, residues from the disrupted urethane bond). The semi-product was tested by Fourier transform infrared (FTIR) spectroscopy, and gel permeation chromatography (GPC) and differential scanning calorimetry (DSC). The main goal is to demonstrate the feasibility of incorporate the obtained glycerolysate in standard polyurethane elastomer as a part of polyol system. The glycerolysate was used to replace commercial polyol up to ca. 26% in new polyurethane elastomers synthesis. The synthesis was carried out in a two-step bulk polymerisation process without catalyst. The effect of glycerolysate content on synthesised polyurethanes physicochemical, mechanical and thermal properties was studied, using FTIR, DSC, TGA, DMA and mechanical testing.

2. Material and methods

2.1. Chemical recycling of polyurethane foam by crude glycerine- Glycerolysis

Flexible polyurethane foams waste based on polyether polyol (Rokopol F 3600, PCC Rokita, Poland: M_n= 3600 g mol^{-1}, OH_{number}= 50 mg KOH g^{-1}, acidity 0.1 mg KOH g^{-1}) and polymeric 4,4-diphenylmethane diisocyanate (pMDI, Borsodchem, Hungary) was reacted in 3 to 1 mass ratio with crude glycerine with purity 84% (Rafineria Trzebinia S.A., Poland). Stannous octoate (Sigma Aldrich, Poland) was used as catalyst in the amount of 0.5 wt.% on polyurethane amount. It was reported by Molero et al. that active catalyst allows to obtain high decomposition rates and a great purity of recovered polyol [19]. Glycerolysis was carried out in a 1 L steel reactor equipped with a mechanical stirrer and reflux condenser in the temperature of 225 – 230 °C. Temperature was maintained constant during the reaction. Glycerine was not separated from the product after the process of glycerolysis. After the reaction, the upper phase (liquid) of glycerolysate was decanted and separated from bottom phase (solid), which was used in the polyurethane elastomers synthesis. The weight ratio between upper and bottom phase was approx. 3:2. Fig.1 shows a scheme of the glycerolysis process and possible resulting products.

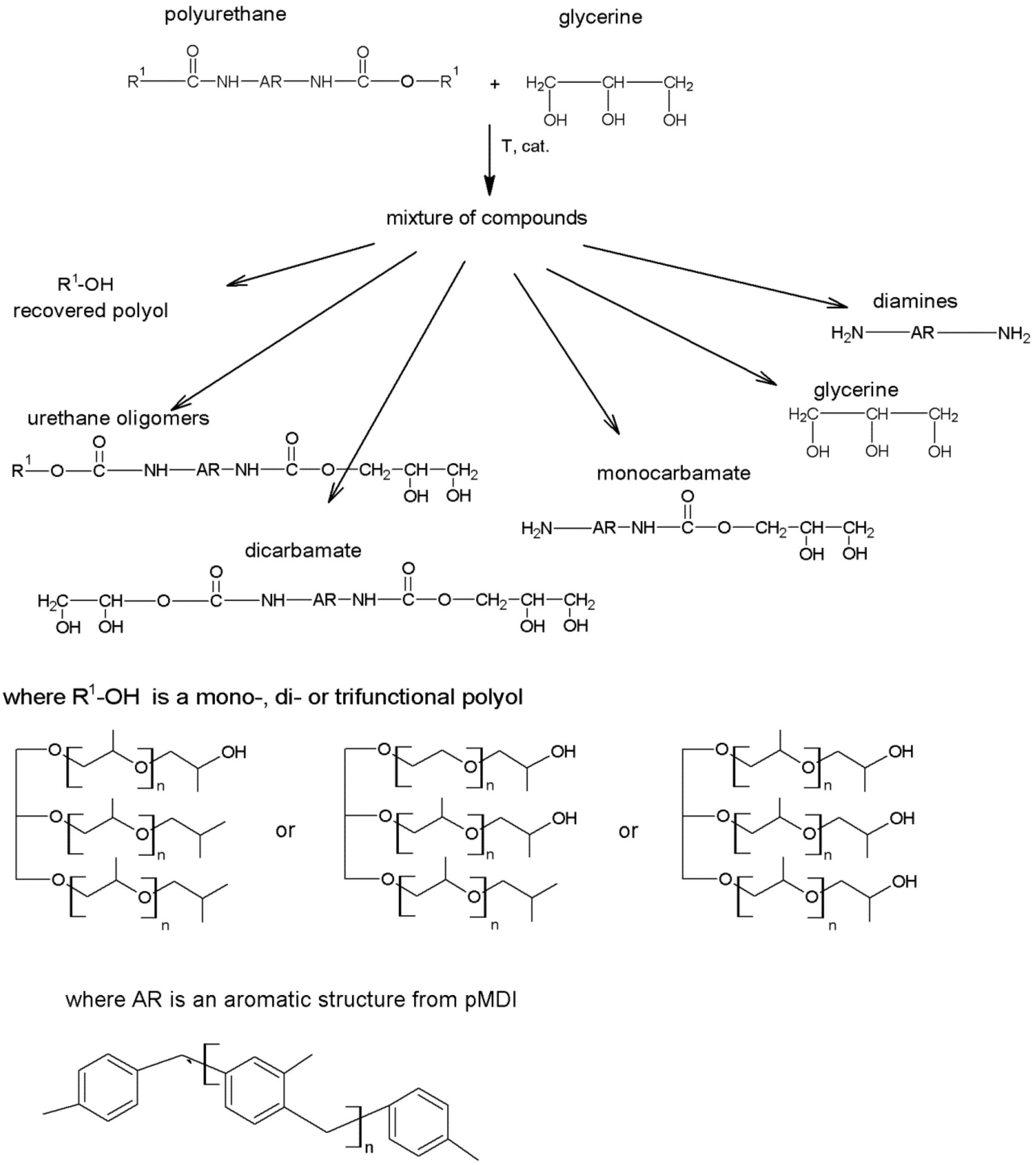

Fig. 1. A scheme of glycerolysis process and the resulting products.

2.2. Polyurethane synthesis

Polyurethane elastomers based on a mixture of glycerolysates - recovered intermediates and poly(ethylene-butylene)adipate diol (macrodiol) as a polyol component were synthesised in two step bulk polymerisation under nitrogen atmosphere in a three necked glass reactor equipped with mechanical stirrer. The dried macrodiol (Polios 55/20, Purinova, OH_{number} =58) and upper phase of glycerolysate (GLStOc, obtained by the method described in 2.1., OH_{number} = 103,75 mg KOH/g in accordance to standard ASTM D 4274-99) were first premixed for 30 min in different macrodiol /glycerolysate ratios (up to 16.4 wt.% of glycerolysate in polyurethane). Thereafter, the 4,4'-diphenylenemethane diisocyanate (MDI, Desmodur 44, Bayer) was added. The prepolymerisation step was carried out at 80 ^{o}C for 5 h. In the second stage the 1,4-buthanodiol (BD, Sigma-Aldrich) was added to the prepolymer as chain extender and stirred for 10-15 min in order to homogenise the mixture before pouring into a mould, where reaction was completed under pressure. The pressing conditions were as follow: 100 ^{o}C under 50 bar for 10 h. The NCO to OH group molar ratio of all polyurethanes was kept constant at 1.05. For comparison a polyurethane without glycerolysate was synthesised (PU REF). Polyurethane samples were soluble in DMF up to 11.9 wt.% glycerolysate. The molar ratios and samples codes are presented in Table 1. Higher content of glycerolysate was not incorporated due to that with a higher re-polyol content, cross-linked materials would be obtained and the characterisation would be completely different from the reference one.

Table 1. Designation, molar ratio of substrates, hard segment (HS) and glycerolysate content of the synthesised polyurethanes.

Code of sample	Polios 55/20	GLStOc	MDI	BD	%HS	% GLStOc in respect to polyol	Wt. % of GLStOc in PU formula
PU REF	1.0	0.0	3	2	32	0	0
PU GL4	0.9	0.1	3	2	33	5.5	3.7
PU GL8	0.8	0.2	3	2	34	11.6	7.6
PU GL12	0.7	0.3	3	2	35	18.4	11.9
PU GL16	0.6	0.4	3	2	37	25.9	16.4

2.3. Characterisation techniques

2.3.1. Fourier transform infrared spectroscopy (FTIR)

FTIR was used to identify glycerolysate and polyurethane characteristic functional groups. Spectra were recorded using a Nicolet Nexus FTIR spectrometer, equipped with a MKII Golden Gate accessory (Specac) with diamond crystal at a nominal incident angle of 45^{o} and a ZnSe lens. The spectra were obtained after 32 scans in a range from 4000 to 750 cm^{-1} with a resolution of 2 cm^{-1}.

2.3.2. Gel permeation chromatography

GPC was used to determine the molecular weight distribution of polyol and glycerolysate. Measurements were performed using a Thermo Scientific chromatograph, equipped with an isocratic

Dionex UltiMate 3000 pump and a RefractoMax 521 refractive index detector. The separation was carried out at 30 ^{o}C within four Phenogel GPC columns from Phenomenex, with 5 μm particle size and 10^5, 10^3, 100 and 50 Å porosities, respectively, located in a UltiMate 3000 Thermostated Colum Compartment. Tetrahydrofuran (THF) was used as mobile phase at a flow rate of 1 mL min^{-1}. Samples were prepared by dissolving first in DMF and then in THF at 1.6 wt.% and filtering using nylon filters with 2 μm pore size.

2.3.3. Differential scanning calorimetry (DSC)

DSC measurements were carried out in a Mettler Toledo 822e equipment, provided with a robotic arm and with an electric intracooler as refrigerator unit. PU samples with a weight between 5 and 10 mg were encapsulated in aluminium pans and were heated from −70 to 200 ^{o}C at a scanning rate of 20 ^{o}C min^{-1} under a constant nitrogen flow. The inflection point of heat capacity change observed was chosen as glass transition temperature (T_g). Melting temperature (T_m) was settled as the maximum of endothermic peak taking the area under the peak as melting enthalpy (ΔH_m).

2.3.4. Thermogravimetric analysis (TGA)

Analysis was performed on a TGA/SDTA851 Metler Toledo equipment to evaluate thermal stability of polyurethanes. Samples were heated from room temperature to 650 ^{o}C at a heating rate of 10 ^{o}C min^{-1} under a nitrogen atmosphere.

2.3.5. Dynamic mechanical analysis (DMA)

The dynamic mechanical behaviour of the polyurethanes was analysed by DMA in tensile mode on an Eplexor 100 N analyser from Gabo, using an static strain of 0.10%. The temperature was varied from -100 to 200 ^{o}C at a scanning rate of 2 ^{o}C min^{-1} and at a fixed operation frequency of 10 Hz. Approximate dimensions of samples were 22 mm× 5 mm×1.5 mm (length ×width ×thickness).

2.3.6. Mechanical properties

Mechanical tests was carried out at room temperature using an Universal Testing Machine (MTS Insight 10) with a load cell of 10 kN and pneumatic grips. Samples were cut into dog-bone shape according to ASTM D1708-93 standard procedure. Tests were performed at a crosshead rate of 50 mm min^{-1}. Elastic modulus (E), tensile strength at break (σ) and elongation at break (ε) were averaged from five test specimen data.

2.3.7. Hardness

Hardness was determined according to PN-EN ISO 868:2005 standard using an electronic durometer type A Zwick/Roell Shore A durometer perpendicularly applied for 3 s.

3. Results and discussion

3.1. Characterisation of glycerolysate

The chemical structure of upper phase of glycerolysate GLStOc was confirmed by FTIR spectroscopy (Fig.2) and compared with starting, commercial polyol (Rokopol F 3600) and crude glycerine used as a decomposing agent.

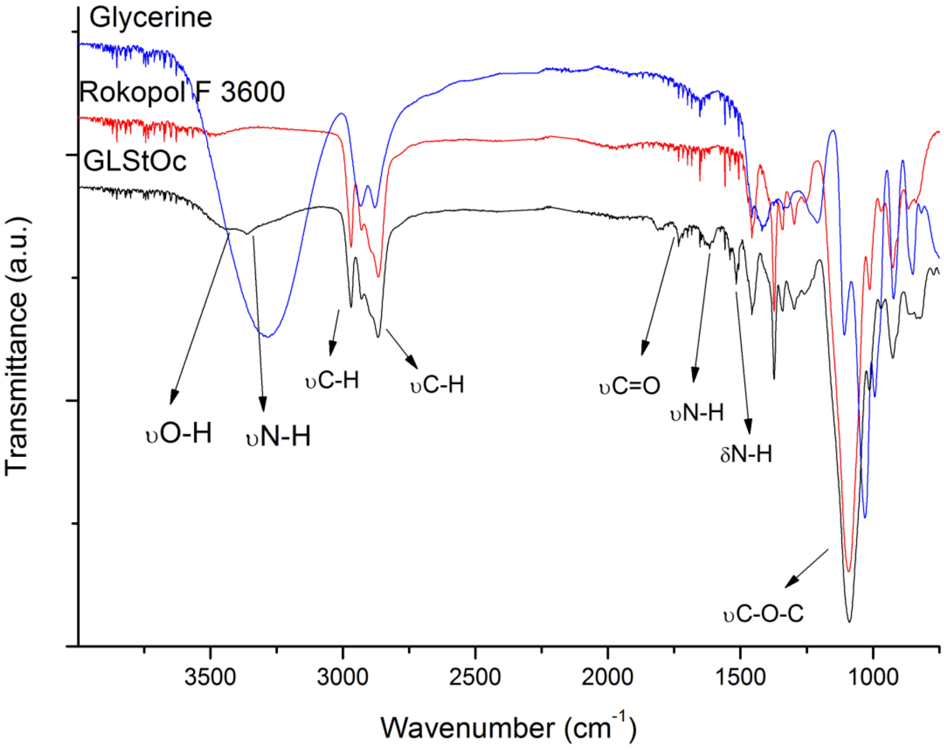

Fig. 2. FTIR of glycerolysate (GLStOc), original polyol (Rokopol F 3600) and crude glycerine.

The similarity of glycerolysate spectrum to virgin polyol can be seen. However in the glycerolysate spectrum a broad band at 3500-3200 cm^{-1} wavenumber appears and corresponds to OH group from the remains of glycerine. At 3363 cm^{-1}, the characteristic stretching vibrations of -NH bond, coming from urethane bond, occurs. Intensive absorption bands at wavenumber 2950 - 2870 cm^{-1} correspond to symmetric and asymmetric stretching vibrations of –CH$_2$ and –CH$_3$ groups. For glycerolysate in comparison with Rokopol F 3600, appear additional small peaks at 1730, 1611 and 1511 cm^{-1}. The peak at wavenumber 1730 cm^{-1} is characteristic for carbonyl group C=O and corresponds to transesterification products [21]. The absorption bands at 1611 cm^{-1} and 1511 cm^{-1} correspond to aromatic ring stretching and–NH bending vibrations, derived from pMDI and urethane coming from the starting foam, which has been dissolved within the semi-products [15]. Therefore, it can be concluded that in the upper glycerolysate obtained with crude glycerine, the by-products are present in a minor quantity. The absorption bands observed at 1456 and 1371 cm^{-1} are characteristic of bending vibrations of methylene and methyl groups in the polyol chain [36]. One narrow peak at wavenumber 1081 cm^{-1} was observed and marks the presence of stretching vibrations of C-O-C bond [37]. This stretching vibration is characteristic for ether group in the polyol.

GPC chromatograms of glycerolysate (GLStOc) and virgin polyol used for polyurethane foam forming (Rokopol F 3600) are presented in Fig. 3.

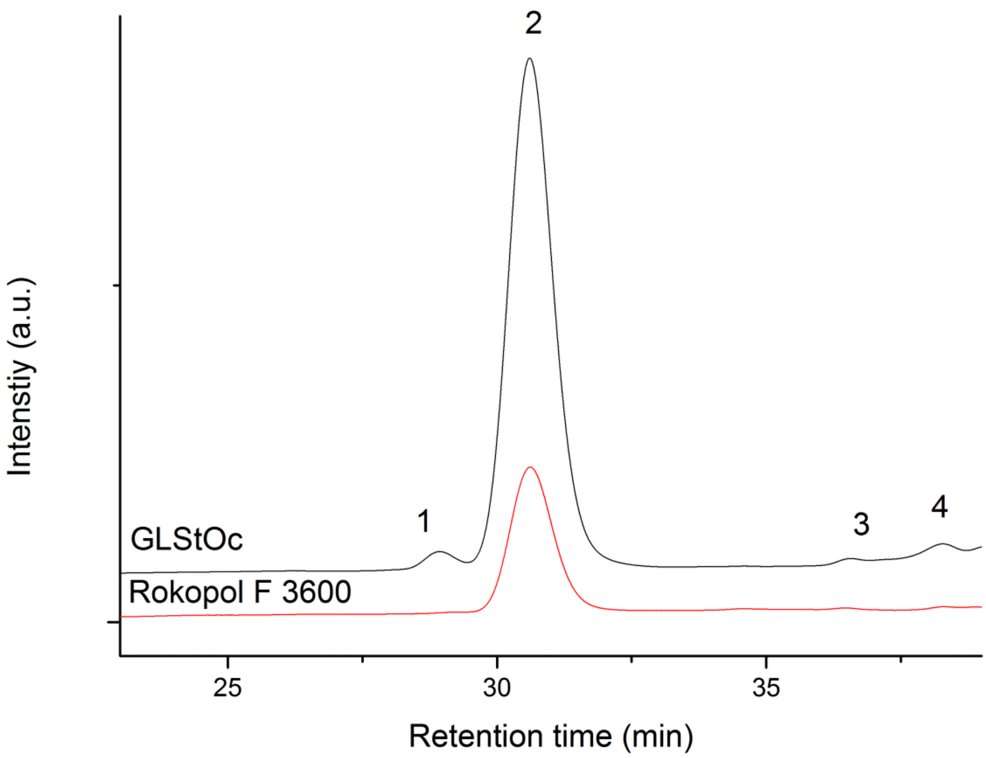

Fig. 3. GPC chromatograms of glycerolysate (GLStOc) and original polyol (Rokopol F 3600).

Polyurethane is decomposed by the glycerine and converted into smaller fragments (urethane oligomers) and releasing polyol into reaction media [38]. For the glycerolysate four different peaks can be observed. First peak, appearing ca. 29 min retention time can be assigned to urethane oligomers, with representing a high molecular weight. Second peak, at 30.6 min retention time, also observed for neat polyol, is associated with recovered polyol. The two last peaks can respond to by-products as carbamates and aromatic amines derived from the glycerine substitution in the urethane bond [16]. The percentage by weight (% by weight) was obtained by integration of peaks from glycerolysate chromatogram. The glycerolysate (upper phase) is recovered with 99% of purity. The main peak in glycerolysate sample appears at the same position that the peak observed for original polyol, so it is expected to have a very similar molecular weight. In conjunction with similiarity of glcyerolysate to original polyol and also using glycerine (f=3) it can be assumed that functionality (f) of GL-StOc is approximately 3.

Hydroxyl number of glcyerolysate according to standard ASTM D 4274-99 is 103.75 mg KOH g^{-1}, and this value is two times higher than for Rokopol F 3600 (I_{OH}~50 mg KOH g^{-1}). This feature can be a result of the presence of by-products and remaining glycerine, what was demonstrated in GPC and FTIR results.

DSC thermo-grams were recorded for neat polyol and recycled polyol. The glass transition of glycerolysate ($Tg \approx -61$ ^oC) is similar to neat polyol ($Tg \approx -66$ ^oC) and this value is characteristic for polyurethane polyol used for polyurethane synthesis [39]. The slightly higher value of re-polyol could be due to the urethane oligomers in the sample. No melting peak was observed in both samples, which denote that they both are amorphous.

The thermal behaviour of the glycerolysate and original polyol is shown in Fig. 4. A small inflection in glycerolysate curve at 180 ^oC can correspond to evaporation of glycerine remained in the sample, which is around 2.2 %.

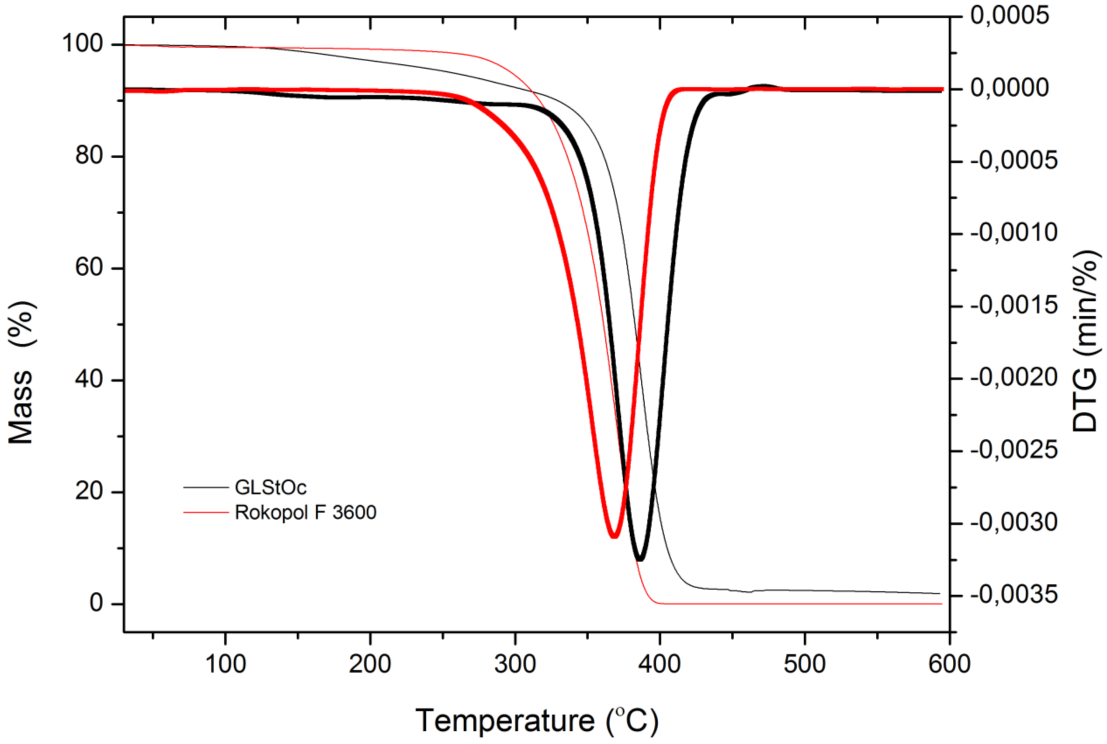

Fig. 4. Mass and DTG as a function of temperature for glycerolysate and original polyol.

The beginning of mass loss ($T_{5\%}$) starts earlier for glycerolysate than for neat polyol (257 ºC vs. 297 ºC), but glycerolysate stays more stable at higher temperatures and the maximum degradation is shifted to higher temperatures (386 ºC vs. 367 ºC). Probably that is related with the presence of high molecular weight urethane oligomers. It is also possible that rests remaining from urethane bonds and by-products have in its structure aromatic rings which provide higher stability [40]. However, the amount of residue is higher for glycerolysate (~2 wt.%) than for neat polyol not only due to the remaining by-products in glycerolysate but also because of the inorganic contamination of crude glycerol (MONG and sulphated ash).

3.2. Characterisation of polyurethanes

The FTIR spectra of synthesised polyurethanes (PUs) containing 4, 8, 12, and 16 wt. % of glycerolysate GLStOc are shown in Fig. 5. These spectra were compared to the spectrum of PU REF in order to determine how the presence of glycerolysate affects the chemical structure of polyurethane.

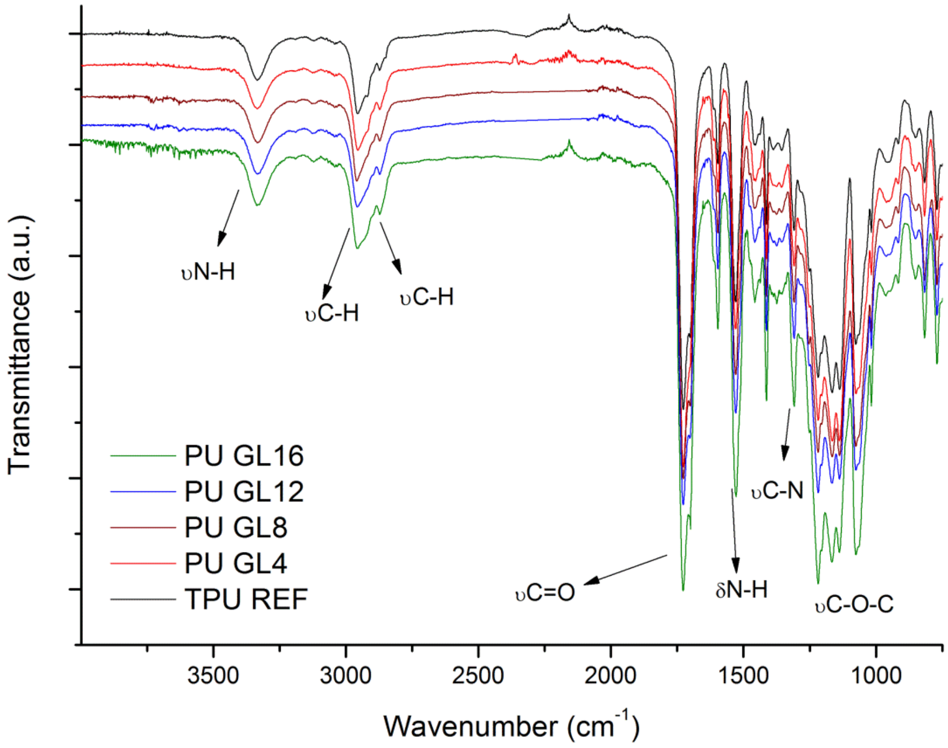

Fig. 5. FTIR spectra of the synthesised polyurethanes.

The spectra of PUs, despite of using glycerolysate acting as polyol, were similar. The lack of the stretching vibrations of the isocyanate group (N=C=O) of MDI at 2270 cm^{-1} confirms that reaction was carried out successfully [41]. At 3317 cm^{-1} appear the band associated to N-H stretching vibration of urethane group. The other bands related with urethane bonds occur at following wavenumber: 1727 and 1700 cm^{-1} (C=O, free and hydrogen bonded urethane carbonyl occurring as double peak [42]), 1527 (N-H bending vibration) and 1306 (C-N, the stretching vibration). Absorption at 1594 cm^{-1} is characteristic for aromatic groups, derived from MDI [43,44]. The wavenumbers of 2854 and 2918 cm^{-1} correspond to the stretching vibrations of CH_2 group, while the wavenumber value of 1412 cm^{-1}, to the deformation vibrations of the same group. Several bands occurring at 1165, 1138 and 1075 cm^{-1} are associated with stretching vibration of C-O-C. Those peaks appear as result of the presence of ether, urethane and ester bonds in the structure of prepared polymers [11,45].

Thermal properties of PUs were analysed by differential scanning calorimetry as shown in Fig.6. The glass transition occurs as a step increase in the heat capacity of the sample during the heating, which is because an enhancement of molecular motion in the polymer [46]. Glass transition temperature for all prepared samples is in the range -36.2 to -32.6 ^{o}C, shifting to higher temperatures together with higher amount of glycerolysate replacing commercial macrodiol. In view of glycerolysate chemical structure, which has functionality of 3 and is a mixture of compounds with different chain length (Fig.1), it can be assumed that the presence of that recovered polyol will cause higher branching and even partially crosslinking of prepared materials, because of increased possibility of bonding i.e. with isocyanate. Additionally, on account of higher hydroxyl number of glycerolysate than commercial macrodiol, the amount of used MDI and BD, in order to maintain constant molar ratio of [NCO]/[OH]=1.05, was higher, what at the same time is causing higher hard segment content (Table 1). These reasons are causing lower mobility of polymer chains and therefore *Tg* is shifted to higher temperatures. On the curves are also noticeable peaks from melting of hard segment (HS) of polyurethanes. Melting temperature of HS is shifted to lower temperatures due to the higher restriction to hard segment ordering imposed by branched chains of glycerolysate.

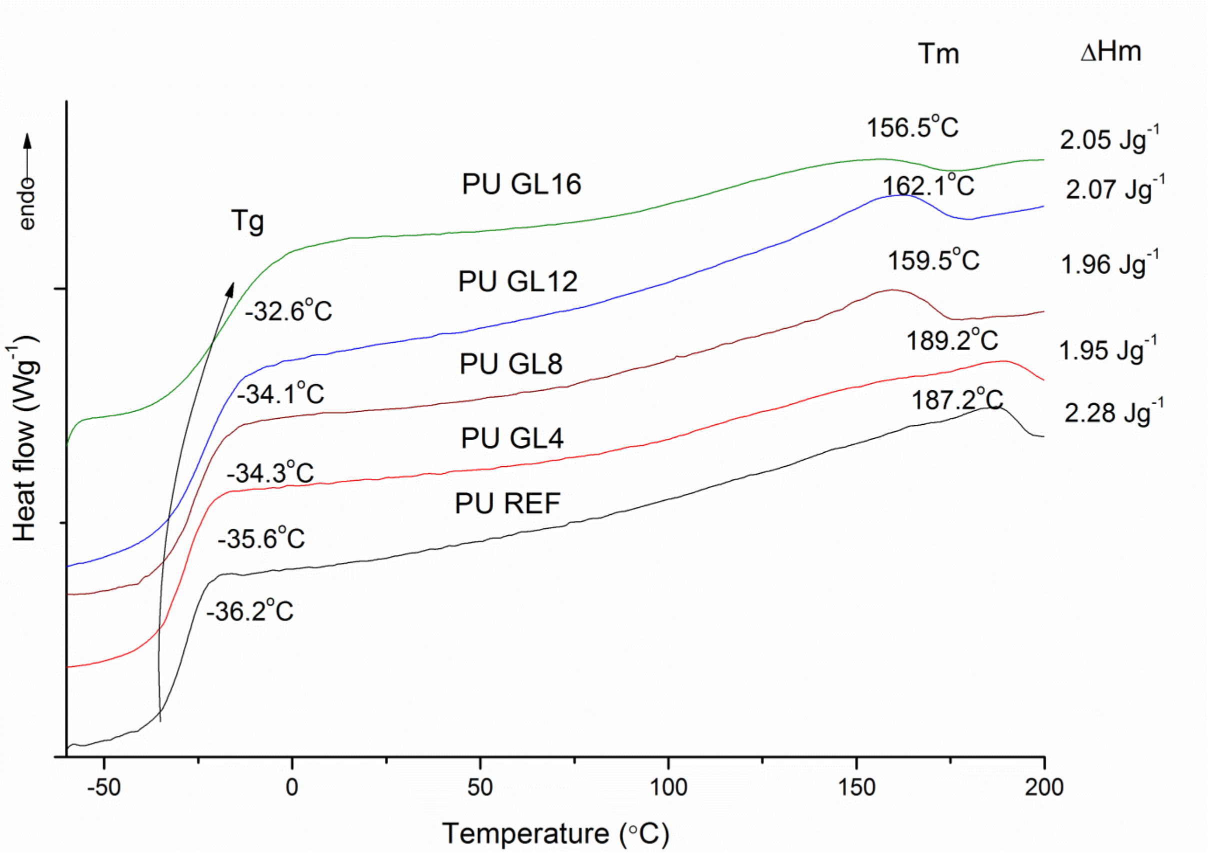

Fig. 6. Heating DSC thermo grams of the synthesised polyurethanes.

Thermal degradation of PU is a multi-stage process which depends on physical and chemical phenomena. The PUs stability is linked to the hard (HS) and soft segment (SS) nature, isocyanate and chain extender type and also the molar ratio of HS to SS. The first stage of degradation is caused by urethane bond decomposition to yield diisocyanate and polyols. The second stage of degradation corresponds to soft segment and sometimes in the third stage it is possible to observe another weight loss at higher temperatures associated with others segments of the remaining structure or it might be due to a probable C=C bond cleavage [47–49].

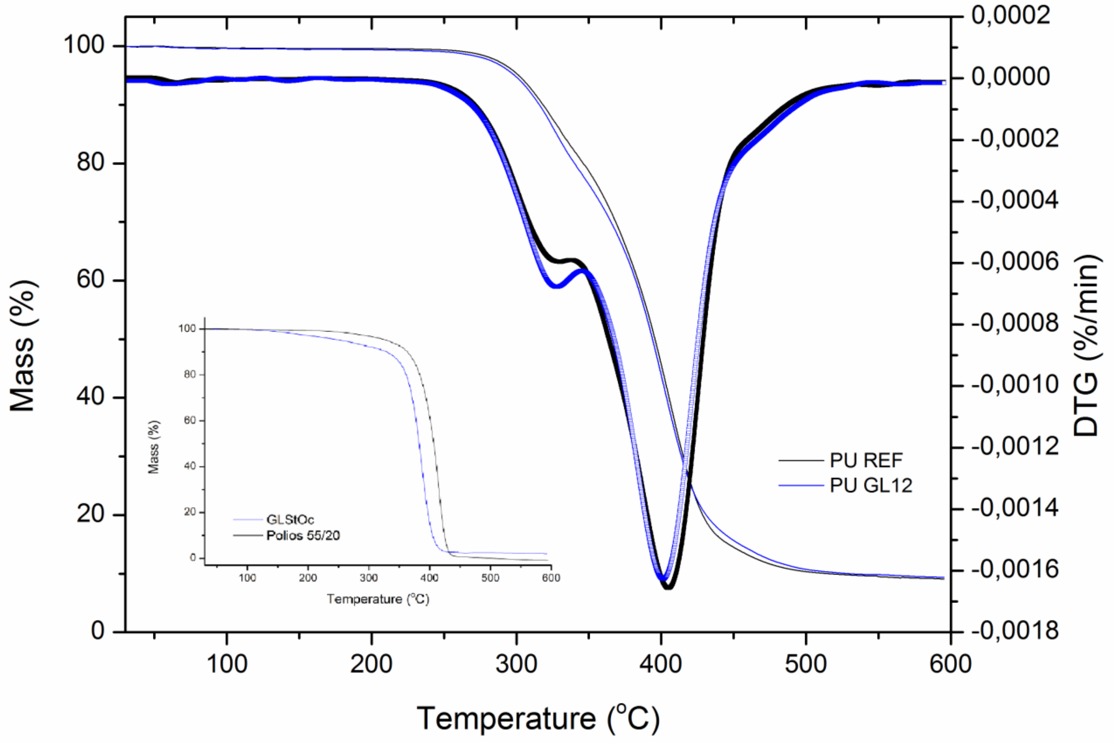

Fig. 7. TGA thermograms and DTG curves of reference polyurethane and PU with 12 wt.% ofglcyerolsyate.

The thermal stability of polyurethanes depends on the crosslink density, cure conditions and the structure of the network. The thermal stability of glycerolysate, commercial macrodiol and polyurethanes obtained with 100% of macrodiol and containing 12 wt.% of glycerolysate replacing macrodiol was analysed using TGA. Fig. 7 shows the results from TGA of previously stated samples [48].

TGA curve of polyurethane elastomer synthesised from glycerolysate (GLStOc) was similar to the reference sample based on the curves depiction the relationship between the mass loss and temperature. The beginning of mass loss ($T_{5\%}$) starts at similar temperature, 301.4 and 298.6 °C for PU REF and PU GL12, respectively. No weight loss related with evaporation of glycerine is observed. As can be observed, thermal degradation takes place in two stages. The first stage takes place at 327 °C in both PU REF and PU GL12 and is associated with the decomposition of urethane rich domains, whereas the second stage occurs around 400 °C (405.4 °C for PU REF, 401.4 °C for PU GL12) and is related to the polyol rich phase. This behaviour is typical for polyurethane elastomers as observed by Corcuera et al. [49]. The remaining residue is around 9 wt.%, and is insignificantly higher for PU GL12 than for PU REF. Taking into account TGA results, it can be concluded that the use of glycerolysate in polyurethane formulation up to 12 wt.% did not worsen thermal properties and the mechanism of degradation is similar as for polyurethane obtained from petrochemical substrates.

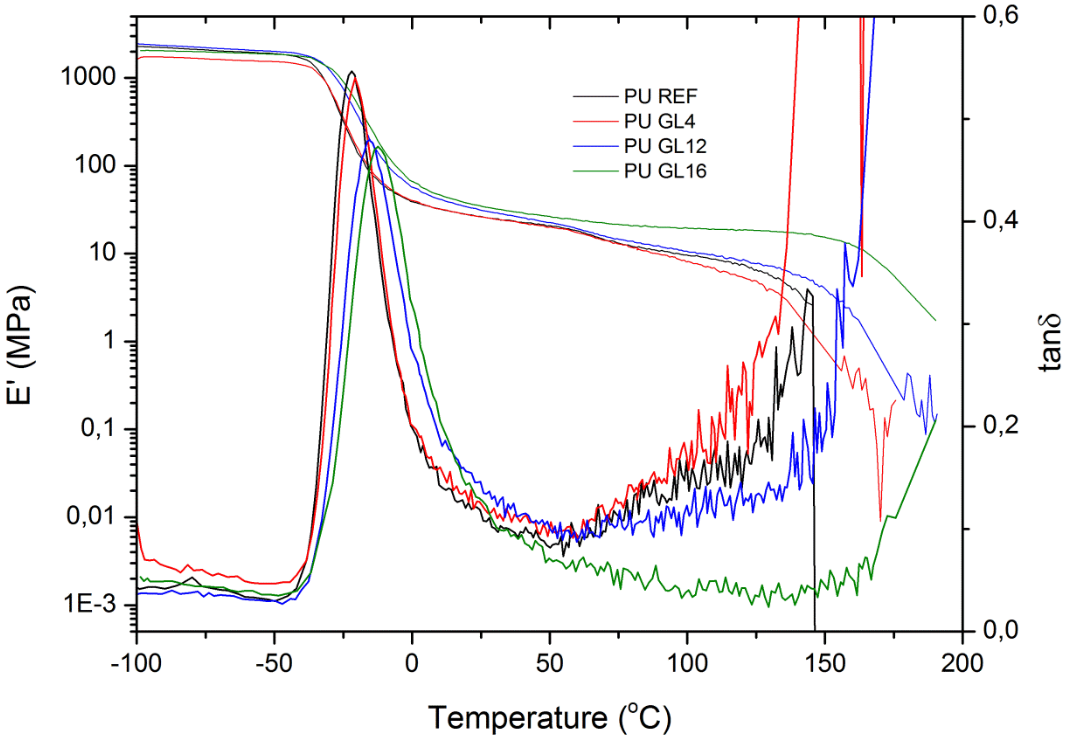

Fig. 8. Storage modulus (E') and loss factor (tanδ) as a function of temperature for prepared polyurethanes.

DMA results of synthesised polyurethane elastomers are shown in Fig.8 and Table 2. The general statement, based on analysed data, is that partial replacement of commercial macrodiol with glycerolysate does not worsen thermo-mechanical properties. At low temperatures up to -35 °C the storage modulus was similar for all presented materials in the range from 1,8 to 2,5 GPa and constant because in the glassy state at very low temperature molecular motions are limited. Sharp decrease of E' with increasing temperature, in the rage of -35 to 5 °C is caused by relaxation process of the soft segments in polyurethane and is related to the glass transition temperature. Values of glass transitions were derived from loss factor curves, usually interpreted as the peak of tanδ. *Tg* of all materials is in the range of -22 to -12 ^{o}C. The tendency is similar as in DSC result, where the *Tg* values are shifted to higher temperature as more glycerolysate is used in the system. It can be result, as mentioned before, of branching or partially crosslinking which is caused due to diverse chemical structure of recovered polyol, higher content of hard segment what causes limitation of molecular movements and as a result glass transition increased. The narrow areas of loss factor curves can be associated with good phase separation of PUs hard and soft phases [47]. Above this temperature, E' reached rubbery plateau whose value increased with higher concentration of glycerolysate in the formulation. This general characteristic can be result of few effects: higher amount of glycerolysate in the formulation increases the branching or even crosslinking, because the functionality of the re-polyol is ca. 3 and hence to maintain the same [NCO]/[OH] molar ratio, the higher percentage of MDI and BD has to be used [50]. According to a more branched structure, which can be formed due to greater possibility of bonding, can provides significant structural reinforcement [51].

Table 2. Summary of DMA results of polyurethanes.

Sample	E'(MPa)	E"(MPa)	T_g (^{o}C)
PU REF	2284	247	-22.0
PU GL4	1748	212	-20.7
PU GL8	2444	232	-15.7
PU GL12	2055	213	-12.4

Around 130-135 ^{o}C, the dramatic decrease starts of storage modulus associated with hard segment melting temperature indicating the change in properties [52]. Loss moduli (E") (Table 2) for all prepared PUs are in the range 210-250 MPa, but for polyurethanes obtained with glycerolysate, E" indicates a bit lower values. This can be considered as an advantage of using glycerolysate due to less energy is lost [53].

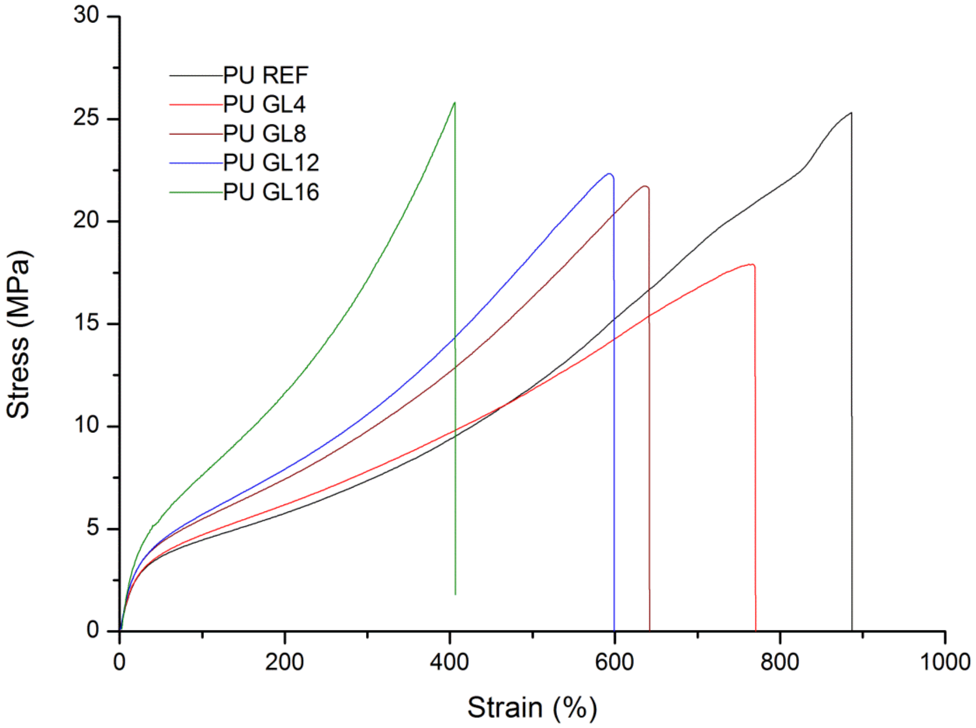

Fig. 9. Stress-strain curves of the synthesised polyurethanes.

Fig. 9 shows stress-strain curves of obtained polyurethanes and results derived from static mechanical test (ultimate tensile strength, elongation at break, modulus of elasticity) and hardness (Shore A) are summarised in Table 3. In general synthesised polyurethane elastomer based on glycerolysates showed properties comparable to petroleum derived polyurethanes [54].

Table 3. Comparing the tensile strength (TS), elongation at break (ε), Young moduli (E) and hardness of PUs.

Samples	TS (MPa)	ε(%)	E (MPa)	Hardness (°ShA)
PU REF	24.64±1.50	891.50±39.85	16.54±0.75	81.03±0.21
PU GL4	17.75±0.85	728.82±29.55	16.12±0.64	81.71±0.51
PU GL8	21.27±1.52	625.24±22.23	18.72±0.35	82.30±0.52
PU GL12	22.58±0.40	597.31±9.91	18.29±0.19	82.79±0.37
PU GL16	25.90±1.54	406.80±13.77	18.73±0.40	84.40±0.38

The overall trend is as follows: for higher macrodiol replacement with glycerolysate, the elongation at break decreases from ca. 890 to 406%, as incorporation of glycerolysates into system increases and as well as branching. However, even 400% deformation is associated with high extension, typical for elastomers. The branching and partially crosslinking for PU GL16, which is caused due to higher functionality of glycerolysate and the presence of compounds with different chain length (by-products) decreases the chain mobility, resulting lower elongation at break values, as observed with higher glycerolysate content. It is also connected with higher hard segment content, as higher percentage of isocyanate and chain extender was used, when higher concentration of glycerolysate was added to formulation, in connection with higher hydroxyl value of GL-StOc than macrodiol. The tensile strength (TS) slightly decreases with replacement of petrochemical macrodiol with re-polyol in comparison with reference sample (from 24.6 to 17.7 MPa), but that can be related with lower deformation. Although TS for PU GL16 reaches 25.9 MPa and thus it can be assumed that even more glycerolysate content will result with higher tensile strength. It can be also observed, that the Young modulus is increasing with higher replacement of commercial macrodiol, probably due to higher branching what causes stiffness of material.

Hardness (Table 3) of synthesised polyurethanes slightly increases with higher glycerolysate concentration. It is related with higher chemical branching and even crosslinking due the presence of glycerolysate.

4. Conclusions

From decomposition of polyurethane waste, glycerolysate - a useful semi-product for new polyurethane system was obtained. In that process the management of polyurethane foam waste and crude glycerine from biodiesel production was achieved. Obtained re-polyol indicated quite similar structure and thermal properties as original polyol used in polyurethane foam system. In FTIR spectrum, the peak from hydroxyl group connected with glycerine can be seen. Also additional compounds as urethane oligomers, carbamates were dissolved in glycerolysates, what was confirmed by FTIR and GPC. Glass transition of glycerolysate was similar to original polyol (-66 ^{o}C, -61 ^{o}C. Thermal stability, confirmed by TGA, was slightly improved in comparison to virgin polyol. To conclude, the general characteristic of glycerolysate GLStOc is similar to starting polyol and therefore re-polyol was successfully used as partial replacement of petrochemical macrodiol in polyurethane elastomer synthesis. The replacement of petrochemical macrodiol by glycerolysate in concentration from 5 to 26 % did not caused dramatic changes in PU characteristic, however some properties were strengthen and some weaken. Spectroscopic analysis did not indicated any differences between spectra of all polyurethanes. Glass transitions confirmed by DSC for PUs were in the range from -36 to -32 ^{o}C, increasing with higher concentration of glycerolysate in the formulation. Thermogravimetric curves of PU GL12 runs similar to reference sample what proves that replacing even 12 wt.% of macrodiol with glycerolysate does not influence much the thermal stability, what was confirmed by TGA. From DMA analysis the glass transitions were in the range from -22 to -12 °C, showing the same trend as data obtained from DSC. This shifting in *Tg* can be result of a higher branching in polyurethane based on glycerolysate, due to its higher functionality (f≈3), which can further restrict molecular motion. The storage modulus reaches higher values for polyurethanes with higher concentration of glycerolysate. Deformation decreases from 890 to 406% due to higher branching of PU containing glycerolysates, however the tensile strength is on acceptable level (in the rage 17.7 to 25.9 MPa). For the same reason the hardness slightly increases in comparison to neat polyurethane.

To sum up the general characteristic of glycerolysate GLStOc is similar to original polyol and that re-polyol was successfully used as replacement of petrochemical macrodiol in polyurethane synthesis. Such synthesised polyurethanes can result with good thermal and mechanical properties materials, which can be used in typical for polyurethane elastomers application.

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