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The changes of crosslink density of polyurethanes synthesised with using recycled component. Chemical structure and mechanical properties investigations.

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Abstract

This paper aims at the utilisation of glycerolysate (Gly) obtained in polyurethane recycling process by means of crude glycerine, which has in its structure hydroxyl end groups that allow for further processing. Polyurethanes (PUs) were synthesised using prepolymer method with the mixture of neat polyol and glycerolysate, in different ratios, with 4,4-diphenylmethane diisocyanate (MDI). The prepolymer was subsequently extended using 1,4-butanediol (BD). The incorporation of glycerolysate caused the crosslinking of obtained polyurethane materials. The crosslink density was calculated from swelling measurements by means of Flory and Rehner equation. The effect of recycled component content on the structure, thermal and mechanical properties were investigated by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA) and mechanical tests, respectively. Morphology was also analysed by atomic force microscopy (AFM). As the content of recycled component increased, the swelling ratio decreased and simultaneously crosslink density increased, resulting in the increase of glass transition and storage modulus at room temperature. Thermomechanical stability, tensile strength, elastic modulus and hardness of PUs also increased with the incorporation of glycerolysate. Although elongation at break decreased, the recoverable deformation increased with the content of glycerolysate. Morphology reveals the transition from a microphase-separated microstructure to an interconnected hard segments domain structure with the incorporation of glycerolysate. These materials can be applied as protective coatings.

Keywords: polyurethanes, chemical recycling, crosslink density, thermal properties, mechanical properties

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1. Introduction

Polyurethanes (PUs) are versatile materials with properties and thus applications closely dependent on the used components. The main components for polyurethane formation are polyols, isocyanates, short chain extenders and catalysts. The structure and properties can be also changed by additives such as blowing agents, fillers, antioxidants, components containing ionic groups, etc. The primary reaction goes between hydroxyl groups (OH) of polyol and isocyanate group (N=C=O) of the isocyanate compound forming urethane linkages, and the reaction is an addition polymerisation [1]. The structure depends on the relative ratios of the main compounds. Due to those wide possibilities, polyurethanes can be obtained in the form of rigid or flexible foams, thermoplastics, CASE (coatings, adhesives, sealants and elastomers) and waterborne dispersions [2,3]. Polyurethane coatings are particularly recommended for application to surfaces subject to high levels of wear-and-tear, because they combine outstanding resistance to solvents and chemicals with good weather stability and they exhibit very good mechanical properties and provide the ideal balance of hardness and flexibility, even at low temperatures [4]. Such broad range of forms and properties result in a high interest from industry in these materials and nowadays are placed in 5th in European plastics demand [5] with CAGR (Compound Annual Growth Rate) of 7% from 2016 to 2025 [6]. Global PU market demand in 2013 was 15 million tons and it is expected to reach over 22 million tons by 2020. With such high production, there exists a problem of produced waste from PUs. Therefore a lot of recycling methods are developed for an accurate treatment route [7–9]. Moreover, there is a pressure on the plastic industry for implementing eco- or bio-based products [10]. Hence a lot of research works in polyurethane area concern on the usage of natural oils or fatty acids for the production of bio-based substrates [11–13]. The usage of different biobased, synthesised from vegetable oils, polyols on the properties of PU coatings were studied [14]. Another method for sustainability in polyurethanes is recycling, that can prevent from usage crude oils and reuse already produced articles and materials. In most methods of PUs chemical recycling, usually, the polyol can be recovered and further used in new polyurethane formulation, what was presented in the literature [15–17]. Similar topic to this paper was presented by Rane at el.[18]. They prepared polyurethane-urea coatings with usage a recycled component obtained from aminolysis of polyurethane foam.

The advantages of polyurethanes recycling are related to both, economic and environmental issues. Firstly, due to the recycling, the amount of polyurethane waste (and their volume) from the landfill is reduced and the costs of such disposal are minimised. Secondly, the recovered intermediates aren't waste, these are valuable components that can be used as raw chemicals in a new synthesis, reducing simultaneously the cost of usage of petrochemical components (even by partial replacement) and saving natural resources as polyols are made from gas and oil. Moreover, reducing landfilling of polyurethanes also contribute to the reduction of harmful substances emissions into the environment by reducing groundwater pollution, air and morbidity of civilization diseases.

As it was mentioned before, polyurethane properties can be tailored by changing the composition: either by means of substrates or varying the molar ratio of the components. Moreover,

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PU properties strongly depend on the crosslinking of the polymer chains and it can be modified by the crosslink density. The crosslinking can have dual origin namely physical or chemical crosslinking. Physical crosslinking is a result of the hydrogen bonding in hard domains of segmented polyurethanes. Hydrogen bonding causes relatively strong interactions and therefore the polar nature of the hard urethane segments causes a strong mutual attraction leading to domain formation [19]. Physical crosslinking disappears above their melting point and are restored under cooling. When the material is chemically crosslinked it cannot be easily destroyed by heating as in the case of physical crosslinks [20]. Chemical crosslinking can be obtained by using the following combination:

- Using polyols with f>2
- Substitution of glycols chain extender with polyfunctional alcohols or amines
- Using isocyanates with f>2
- Using NCO: OH ratio >1 (the excess of isocyanate can lead to forming of allophanate or biuret bonds causing branching and chemical crosslinking)
- Introducing of a crosslinker or crosslinking nodes in the form of rings of isocyanurate [21,22].

The thermal stability of crosslinked polyurethanes is proved to be higher and depends more on crosslink density than on molecular weight. Not only the crosslink density influence on polyurethane properties but also cure conditions. It happens because more thermal energy is needed to break the additional bonds with increasing crosslink density before the breakdown of the total network takes place [21]. The molecular weight between crosslinks (M_c) can be used to characterise crosslinked PU as it is the parameter characterising macromolecule architecture [23]. The glass transition of polyurethanes (regardless their chemical composition) depends on the polyol hydroxyl number and hence crosslink density. The higher molecular weight in PUs which poses branched and/or crosslinked structure also gives the result in improvement of mechanical properties. However, chemical crosslinking can have various effects on tensile properties according to the network chain molecular weight compared to the molecular weight between crosslinks [20].

The application of new, recycled component into polyurethane synthesis was investigated. The aim of this work was to apply the recycled polyurethane component in solvent-free polyurethane coating synthesis. Firstly, polyurethane foam recycling was carried out by means of crude glycerine, where a homogenous intermediate (glycerolysate) was obtained. In this one reaction, two types of waste, polyurethane foam and crude glycerine, will be utilised to obtain valuable components for further usage. The goal was to examine the effect of crosslinking occurring due to the presence of glycerolysate on the thermal and mechanical properties of synthesised materials. The crosslink density was estimated through swelling properties and using Flory-Rhener equation. The crosslink density was in accordance with DMA results. Obtained materials exhibit properties suitable to act as protective coatings [24].

2. Experimental

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2.1. Polyurethane synthesis

Polyurethane materials were synthesised by solvent-free, two-step bulk polymerisation. In the first step the prepolymer was obtained by the reaction of difunctional poly(ethylene-butylene)adipate diol (Polios 55/20 macrodiol, Purinova, OH_{number} = 58, M_w~2000, information given by the company) and recycled glycerolysate component (OH_{number} = 369.7 mg KOH g^{-1} in accordance to standard ASTM D 4274-99) with 4,4'-diphenylmethane diisocyanate (MDI, Desmodur 44, Bayer). The reaction was carried out at 80 ^oC for 5 h under a nitrogen atmosphere in a three-necked glass reactor equipped with mechanical stirrer and nitrogen inlet. In the second step, the chain extender 1,4-butanediol (BD, Sigma-Aldrich) was added and stirred for 10-15 min in order to homogenise. The molar ratio of NCO to OH was kept constant for all PUs, 1.05. Finally, the viscous mixture was poured into a mould and pressed at 100 ^oC under 50 bar for 10 h. Polyurethanes with different molar ratios of glycerolysate and macrodiol were prepared, as a polyol part of the system. However, the polyol part: diisocyanate: chain extender molar ratio of the system was kept constant at a ratio of 1:3:2 (polyol part: MDI: BD). Polyurethanes were coded as PU0 to PU5, where the number determines the percentage of glycerolysate in PU. The two-step synthesis reaction scheme of polyurethanes obtained with glycerolysate was presented in our previous research [25].

Glycerolysate was obtained in the chemical recycling process of polyurethane foam, which was originally prepared from a trifunctional polyol. The foam was reacted with crude glycerine in 3 to 1 weight ratio at 220 ^oC. The used catalyst was potassium acetate. A detailed procedure was described in a previous paper [26].

2.2. Characterisation techniques

2.2.1. 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° 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}.

2.2.2. Equilibrium swelling properties and crosslink density

The crosslink density and swelling parameters of obtained polyurethanes were determined by employing the equilibrium swelling method according to the procedures described in the literature [27–29]. The rectangular specimens with average dimensions 10 x 10 x 1.4 mm^3 were immersed in dimethylformamide solvent (DMF, purchased from Chempur). The equilibrium point was obtained after 72 h. When the samples reached equilibrium, they were removed from the solvent, patted with paper and weighted again. The crosslink density (v_c) (mol cm^{-3}) and average molecular weights between the chains (M_c) were estimated using following equations, which were introduced by Flory and Rhener Eq.[30]

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$$M_c = \frac{\overline{V_s} d_p (V_r^{\frac{1}{3}} - \frac{V_r}{2})}{-[\ln(1-V_r)+V_r+\chi V_r^2]} \quad (1)$$

where: V_s – molar volume of solvent (77.42 cm^3 mol^{-1}), χ- the polymer-solvent interaction parameter (0.49) [28], V_r- equilibrium volume fraction of polymer in the swollen network calculated according to Eq. 2, where w_o is the initial weight of the network and V_{equil} (Eq.3) is the equilibrium volume of the swollen network assuming additivity of volumes, where w_s is the weight of the swollen network, d_p is the density of polymer and d_s of DMF.

$$V_r = \frac{w_0}{V_{equil}\, x\, d_p} \quad (2)$$

$$V_{equil} = \frac{w_0}{d_p} + \frac{w_s - w_0}{d_s} \quad (3)$$

$$v_c = \frac{1}{M_c} \quad (4)$$

The swelling ratio was calculated according to the following Eq. 5:

$$SR = \frac{w_s - w_o}{w_o} x\ 100\% \quad (5)$$

2.2.3. 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 °C at a scanning rate of 20 °C min^{-1} under a constant nitrogen flow. The inflexion 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).

2.2.4. Thermogravimetric analysis (TGA)

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

2.2.5. 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 a static strain of 0.10%. The temperature was varied from -100 to 200 °C at a scanning rate of 2 °C min^{-1} and at a fixed operating frequency of 10 Hz. Approximate dimensions of samples were 22 mm× 5 mm×1.5 mm (length ×width ×thickness). Glass transition temperature (T_g) was determined as the maximum of the loss factor peak.

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2.2.6. Mechanical properties

Mechanical tests were carried out at room temperature using a 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.

2.2.7. 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.

2.2.8. Atomic Force Microscopy (AFM)

AFM was used to characterise polyurethanes morphology by imaging the cross-section of the samples cut with a Leica EM FC6 cryo-ultramicrotome equipped with a diamond knife at -120 ºC. This temperature was chosen in order to attempt to cut the samples in the glassy state, to obtain an adequate surface. Images were obtained in tapping mode at room temperature with a Bruker Dimension ICON scanning probe microscope equipped with a Nanoscope V Controller. Samples morphology was examined using TESP-V2 type silicon tips having a nominal resonance frequency of 320 kHz and a cantilever spring constant about 42 N m^{-1}.

3. Results and discussion

3.1. Structure characterisation

The chemical structure of synthesised polyurethanes was analysed by FTIR spectroscopy (Fig. 1). There were not observed remarkable changes caused by the replacement of polyol with glycerolysate, in comparison to the reference sample. It demonstrated that the usage of the recycled component does not introduce any new bands and the chemical structure characteristic is very similar to reference PU. Moreover, the complete reaction of substrates was confirmed as there is a lack of peak at 2270 cm^{-1} associated with NCO groups. Furthermore, all of them show a broad band centred at ca. 3334 cm^{-1}, ascribed to the N-H stretching vibration of urethane groups [31]. It is well known that the infrared absorbance of N-H groups in polyurethanes shifts to different wavenumbers depending on whether they are free or hydrogen bonded [32]. The band is shifted to lower wavenumbers (from 3334 to 3329 cm^{-1} for PU0 and PU5) and the intensity increases slightly for polyurethane with glycerolysate. The highest value is achieved for PU5 sample. In the range from 1730 to 1700 cm^{-1}, a double peak attributed to the stretching vibrations of C=O groups from ester bond in polyol and urethane bond can be observed. One peak is connected with hydrogen bonded carbonyl groups (ca. 1700 cm^{-1}) while the other one with ester carbonyl group and free urethane carbonyl group (at 1727cm^{-1}) [33]. The peak at 1700 cm^{-1} increases with increasing content of recycled component and that can be explained by the hydrogen bonding interactions (the same case as the stretching vibration bands of amine group at 3334 cm^{-1}). The peak at ca. 1600 cm^{-1} is attributed to aromatic ring constituted in the hard segment

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(HS). The characteristic peaks associated with bending vibrations of N–H bond and stretching vibration of C-N bond appear at 1530 and 1308 cm^{-1}, respectively. All polyurethanes displayed bands at 2872 (symmetric stretching) and 2918 cm^{-1} (asymmetric stretching) which correspond to the $–CH_2–$ group. The bands indicating urethane and ester bonds of C-O-C are present at following wavenumbers 1167 and 1134 cm^{-1} (stretching vibrations of C-O) and 1073 cm^{-1} (bending vibration of C-O) [34].

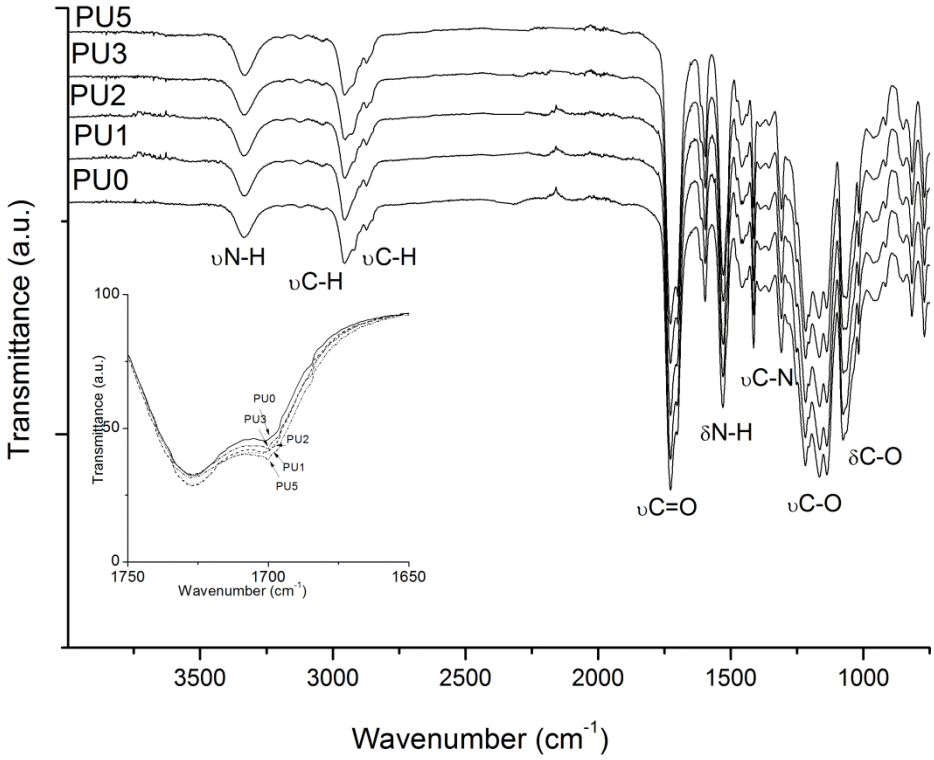

Fig. 1. FTIR spectra of prepared polyurethanes containing the recycled component. In the inset the carbonyl stretching region.

3.2. Swelling properties and crosslink density

In Table 1 the results of equilibrium swelling in DMF are presented. The swelling ratio (*SR*), the volume fraction of a rubber network in the swollen phase (V_r), the molecular weight of the polymer between crosslinks (M_c) and crosslinking densities (v_c) were calculated from Eqs. 1-5. First of all, it can be noticed, that the reference sample (PU0) was dissolved (after one day) in DMF. It is a proof that the reference material is not crosslinked and even can be considered as a thermoplastic one. With the incorporation of glycerolysate to the system, the structure becomes more branched and even crosslinked due to the presence of compounds with different chain-length in glycerolysate and functionality of Gly. The small addition of Gly (PU1 or PU2) still allows sample for high absorption (ca. 1600 and 1100%, respectively) of the solvent and that can be a hint that material is crosslinked. The swelling ratio is the weight of solvent uptake per weight of material [35]. SR is decreasing with the

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higher replacement of commercial polyol with a recycled component from 1600 to ca. 250% after 72h when the equilibrium was obtained. The determination of crosslink density from swelling behaviour is valuable and can be considered as a structural parameter which can help to explain other properties (i.e. mechanical or thermal) of obtained polyurethanes.

The average molecular weight between the crosslinks (M_c) and the crosslink density (v_c) was obtained from equilibrium swelling measurements. It was found that with increasing content of glycerolysate, M_c is lower and simultaneously indicating the higher crosslink density. This is connected with forming more number of linkages between glycerolysate and MDI and BD components, since the amount of MDI and BD is higher to keep the NCO/OH ratio constant, equalled 1.05. That shows that more linkages and bonds are formed. Moreover, as the original polyol used for the preparation of foam was three functional, therefore there can be even more linkages per glycerolysate molecule than per Polios (f=2) molecule. In addition, more networks can be created in this material as its structure is more branched. That all can result in a reduction in polymer chains movement and lower amount of DMF can penetrate into the polymer structure. The M_c and v_c values of PU5 are comparable to the crosslinked structure of a rubber [36].

Table 1. Effect of glycerolysate content on swelling properties and crosslink densities of prepared polyurethanes

Sample	SR (%)	V_r (-)	M_c (g mol)	v_c x 10^4 (mol cm^{-3})
PU0	∞(dissolved)	-	-	-
PU1	1631 ±20	0.045±0.001	603542±2889	0.016±0.001
PU2	1118±32	0.065±0.002	241919±4198	0.041±0.001
PU3	324 ± 2	0.193±0.001	14161±91	0.706±0.005
PU5	259 ± 2	0.231±0.001	8486±147	1.178±0.020

3.3. Thermal properties

Fig. 2 shows the thermograms of polyurethanes and in Table 2, the results of thermal transitions from DSC are summarised. The thermograms obtained in the first heating scan (Fig. 2) for all of the analysed PU materials showed inflexion corresponding to the glass transition temperature of soft segments (*Tg*). The glass transition of synthesised polyurethanes is in the range from -35 to -25 ^{o}C. Incorporation of glycerolysate caused shifting glass transition to higher temperatures and it can be associated with increasing crosslink density (Table 1) with a higher concentration of glycerolysate in the prepolymer system. Higher crosslinking is causing the restriction on molecular motions and therefore *Tg* of prepared polyurethanes is increasing. Similar findings were presented by Campanella et al. [37]. The signal from the melting of the soft phase (Tm_{SS}) occurs at 16 ^{o}C for pure polyol as it was a semi-crystalline polyester. For Gly, a broad endothermic peak occurs (T_I) and is ascribed to the

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disruption of the short-range order of the urethane rests in glycerolysate [38]. No endotherms related with soft phase were observed in synthesised polyurethanes. Regarding polyurethane DSC thermograms above room temperature, it has been observed that it is a function of hard segment length. At the lowest temperatures, endotherms ascribed to the dissociation of small, unstructured hard segments have been observed, while the endotherms observed at the highest temperatures were related with ordered structures formed by longer segment length [39,40]. Laity et al. [41] report that peak observed by DSC at around 50 ^{o}C for polyurethanes with high HS content (71%) can be assigned as glass transition due to departure from thermodynamic equilibrium when the polymer is cooled from the rubbery to the glassy state. Different thermal transitions occurred above room temperature for prepared polyurethanes. PUs show an enthalpic relaxation (disruption of the short-range order) which might evolve to a glass transition temperature (*Tg*) related to the amorphous phase of the hard segment for PUs with higher Gly content, as the Tg_{HS} for pure MDI/BD can occur around 108 ^{o}C as has been reported [42]. Other transitions at higher temperature are associated with melting endotherms resulting from different crystal structures, domain sizes or different degrees of order and reorganisation in the crystalline structure of hard segment [43]. The increase of hard segment content caused by incorporation of the recycled component and thus the increase of hydrogen bonds between urethane groups results in higher melting enthalpy ΔHm_{HS} values and Tm_{HS} shifted to higher temperatures around from 155 to 175 ^{o}C. These values are in agreement with FTIR were higher hydrogen bonding was observed as glycerolysate content increases.

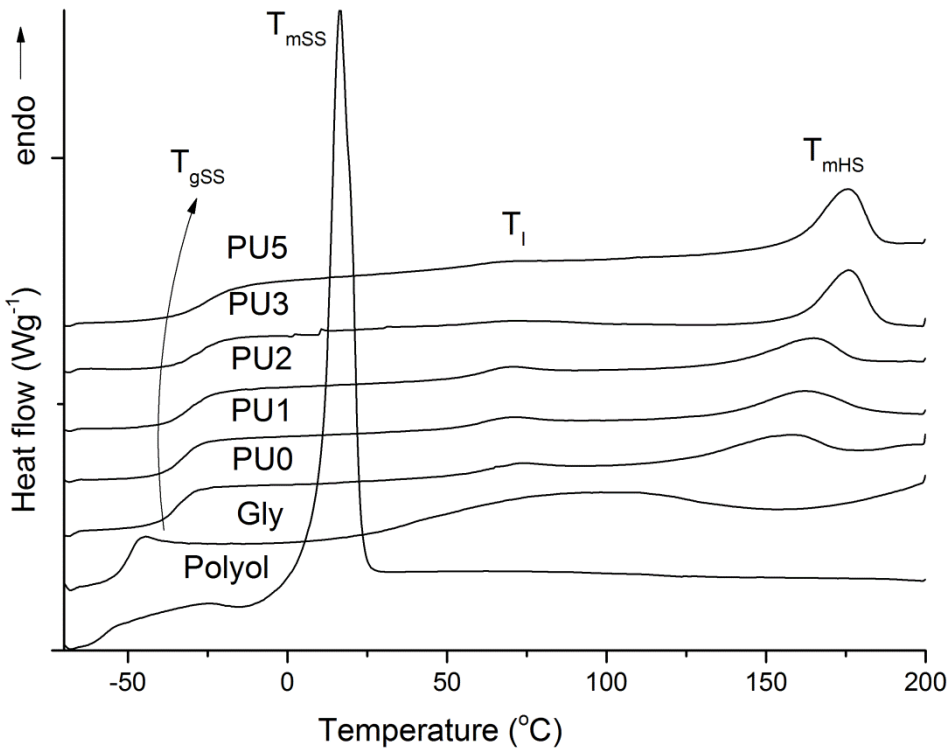

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Fig. 2. Thermograms of synthesised polyurethanes, pure polyol and glycerolysate (first heating scan at 20 $^{o}C\ min^{-1}$).

Table 2. Summary of DSC results of polyurethanes, pure polyol and glycerolysate. HS- calculated theoretical hard segment content.

Sample	HS (wt.%)	Tg_{SS} (^{o}C)	Tm_{ss} (^{o}C)	ΔHm_{SS} ($J\ g^{-1}$)	T_I (^{o}C)	ΔHm_I ($J\ g^{-1}$)	Tm_{HS} (^{o}C)	ΔHm_{HS} ($J\ g^{-1}$)
Polyol	-	-56.2	16.3	62.8	-		-	-
Gly	-	-50.6	-	-	85.6	30.3	-	-
PU0	32	-34.9	-	-	72.6	1.9	156.8	6.7
PU1	34	-32.9	-	-	68.9	2.1	161.9	8.2
PU2	37	-30.5	-	-	68.9	2.2	164.8	7.8
PU3	40	-27.4	-	-	71.9	1.5	175.8	11.1
PU5	44	-25.5	-	-	58.6*	-	175.7	12.5

*Tg of hard segment

Thermogravimetric and DTG curves of polyurethanes PU0 and PU3 and glycerolysate are shown in Fig. 3. The presented polyurethanes are stable up to 300 ^{o}C and the initial weight loss (temperature taken at the 5 wt.% of weight loss, $T_{5\%}$) for PU0 and PU3 appears at 301.4 and 301.8 ^{o}C, respectively. The thermogravimetric curves for the reference sample and with the recycled component are similar. Therefore it can be stated that both materials have similar thermal stability and that the incorporation of glycerolysate does not worsen this property. From the literature, it is known that thermal decomposition of crosslinked PUs starts preferentially via degradation of side chains. The following step is scission and depolymerisation resulting in weight loss and degradation of mechanical properties [21].

In general, thermal degradation of polyurethanes occurs in two steps. DTG curves of synthesised materials show typical run for polyurethanes. The first step is related to the decomposition of hard segments i.e. urethane groups (for PU0 T_{step1} = 327.2 ^{o}C, PU3 T_{step1} = 323.9 ^{o}C) and an intensity increase is observed for PU3, probably due to the higher content of urethane coming from the stoichiometry and from the glycerolysate. The second step is attributed to soft segments (ether or ester bond) (PU0 T_{step2} = 405.4 ^{o}C, PU3 T_{step2} = 402.6 ^{o}C).The result of the first step degradation is the formation of isocyanates, amines or CO_2 [44]. With the increasing temperature, the decomposition of soft segments starts, this step is slower and it depends on the polyurethane structure [24]. In DTG curve of glycerolysate, the first peak at 196.1 ^{o}C can be associated with evaporation of the residual glycerine [16] while the second peak at 397.4 ^{o}C is related to the polyol. The residue is ca. 9 and 11%

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for PU0 and PU3, respectively. The higher residue for PU3 is probably related to the presence of Gly, which is a mixture of compounds with different chains length and in addition, more, MDI was added to the formulation to maintain NCO/OH ratio constant and hence, the higher residue was observed [45].

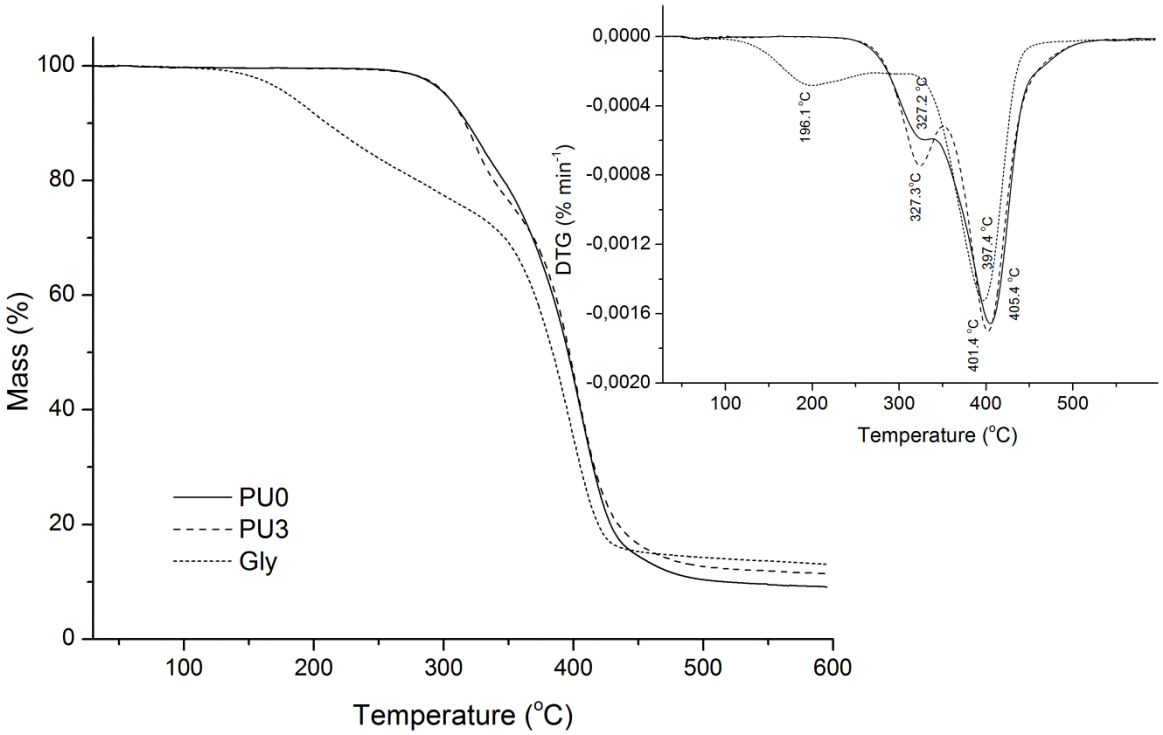

Fig. 3. Thermogravimetric curves and DTG of prepared polyurethanes and glycerolysate for comparison.

3.4. Dynamic-mechanical and mechanical characterisation

In Fig. 4 the dynamic-mechanical curves registered during DMA tests were presented, where the dependence of storage modulus and loss factor versus temperature is shown. The storage modulus (E') values in the glassy state are in the range of 2083 – 2285 MPa and it was not noticed any significant changes in E' values with increasing content of glycerolysate in the formulation. However, it can be found that in the viscoelastic state (above glass transition temperature *Tg*) polyurethanes with glycerolysate show higher E' values than reference polyurethane and moreover the difference is increasing with the rising content of the recycled component in prepolymer system. That trend confirms and is in accordance with results from equilibrium swelling ratio (Table 1) as the increasing crosslinking of polyurethanes occurs with a higher concentration of glycerolysate. High storage modulus at room conditions allows for the application of materials of high mechanical demanding. The decreasing of storage modulus has a maximum rate at the region connected with the glass transition temperature of soft segments. The glass transition of this series is in the range from -22 to -6 °C, going to higher temperatures with higher content of the recycled component. These results are in

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compliance with DSC results (Table 2) which confirms higher crosslinking of these materials. Nevertheless, the *Tg* is below 0 °C and hence the material should behave as an elastic material in room conditions. Regarding thermomechanical stability, it increases as glycerolysate content increases, which could be attributed to the higher crosslink density, as well as to the higher melting temperature and enthalpy as the content of Gly increases.

Variation of tanδ as a function of temperature is shown in Fig. 4. The tanδ trend is indicative of energy dissipation with regards to the changes in the physical properties and tells how good material will be at absorbing energy, therefore, peaks in the tanδ plots are often referred to as damping peaks [46]. The width of the tanδ peak becomes broad with higher Gly content in comparison to the reference sample which peak is narrow [47]. The narrow areas of loss factor curves can be associated with higher purity and good phase separation of PUs hard and soft phases. The incorporation of Gly also modifies the structure of the domain responsible for this transition that, according to the wider relaxation observed in the temperature DMA scan, presents a less homogeneous structure, which is in accordance with Fig. 5. The obtained polyurethanes exhibit loss factor in the range 0.38-0.55, decreasing with higher content of the recycling component and the results suggest that the PU with glycerolysates are less ductile and exhibit lower ability for vibration damping (absorption) than PU0 [48] which is in agreement with the increasing crosslinking density.

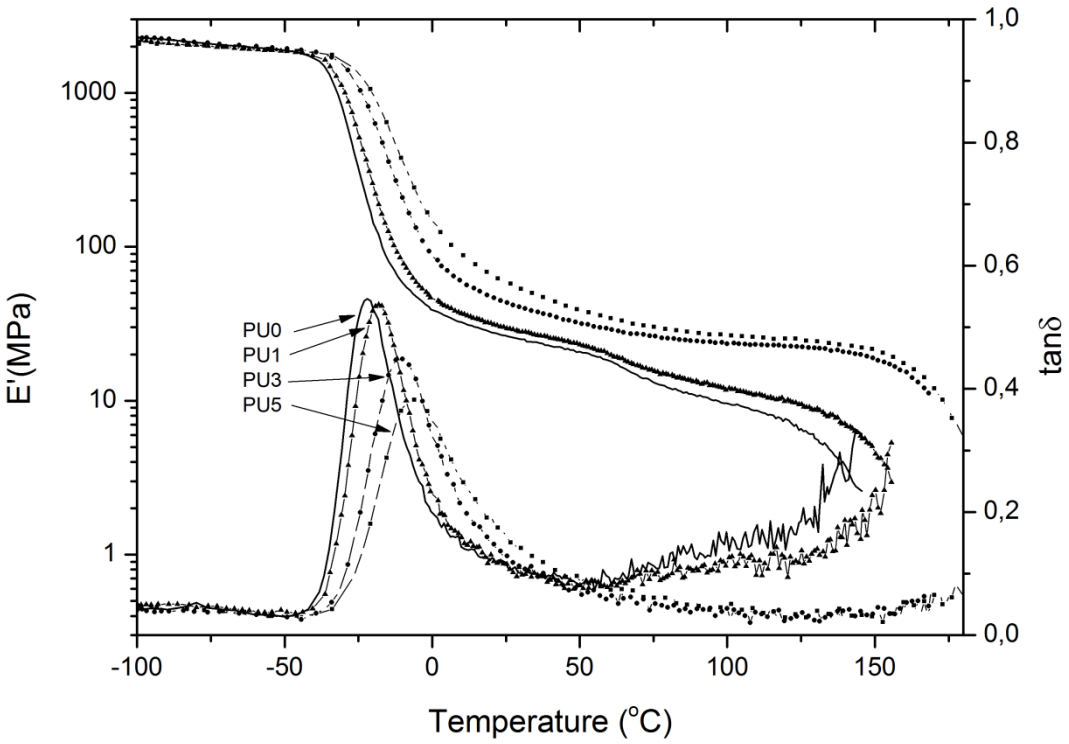

Fig. 4. Storage modulus (E') and loss factor (tan*δ*) as a function of temperature for synthesised polyurethanes.

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In Table 3 summary results from static mechanical test and hardness are presented. It can be noticed that with higher content of glycerolysate (as well the higher crosslink density) the higher tensile strength, except PU5 sample, and Young modulus are obtained. This trend is highly related to the crosslinking in materials as the crosslinked network requires more force to break formed bonds, especially chemical linkages. However, as a result of that, the elongation at break value is decreasing almost three times from 890% to 290%. In any case, this deformation can be considered high. Permanent elongation is a very important parameter which characterises returning the material to its original state. For reference sample that value is ca. 47% and for polyurethanes with recycled component, these values are lower (from 37 to 8 %), what is a favourable phenomenon. Hardness is in accordance with the strength and modulus values and with higher content of recovered intermediates and also crosslinking, the hardness values increased.

Table 3. Static mechanical properties (tensile strength - TS; elongation at break - ε_b, permanent elongation after break – ε_p, Young modulus - E) and hardness of prepared polyurethanes

Sample	TS (MPa)	ε_b at break (%)	ε_p after break (%)	E (MPa)	Hardness(°ShA)
PU0	24.6±1.5	892±40	46.9±1.8	16.5±0.7	81.0±0.2
PU1	34.8±0.9	758±14	36.7±1.2	16.6±0.1	83.1±0.5
PU2	29.7±1.2	641±26	34.7±1.8	17.3±0.2	84.9±0.3
PU3	32.2±1.6	434±10	14.9±1.5	20.8±0.4	87.6±0.3
PU5	25.9±1.2	293±11	8.2±1.1	31.8±0.4	89.9±0.3

3.5. Morphology

The morphology of polyurethanes with different crosslinking density was imaged by using tapping mode AFM, which allows simultaneous detection of phase and height features. Fig. 5 shows phase and height images of the PU0 (a) and PU5 (b). The synthesised polyurethanes are distinguished by the heterogeneous structure. In the phase image (right), the light regions indicate hard phase material (hard ordered domains or crystalline regions in polyurethane) and the darker regions correspond to soft phase material (polyol) [49]. Significant differences can be observed between PU0 and PU5 polyurethanes surfaces. For sample PU0 (Fig. 5a) there is visual evidence of a microphase-separated structure with well-defined hard segments domains. The addition of glycerolysate influences the morphology, more bright regions were observed and the formation of an interconnected hard segments domains structure can be appreciated, thus increasing hard-soft segments interaction, which agrees with previous DSC and DMA results [50].

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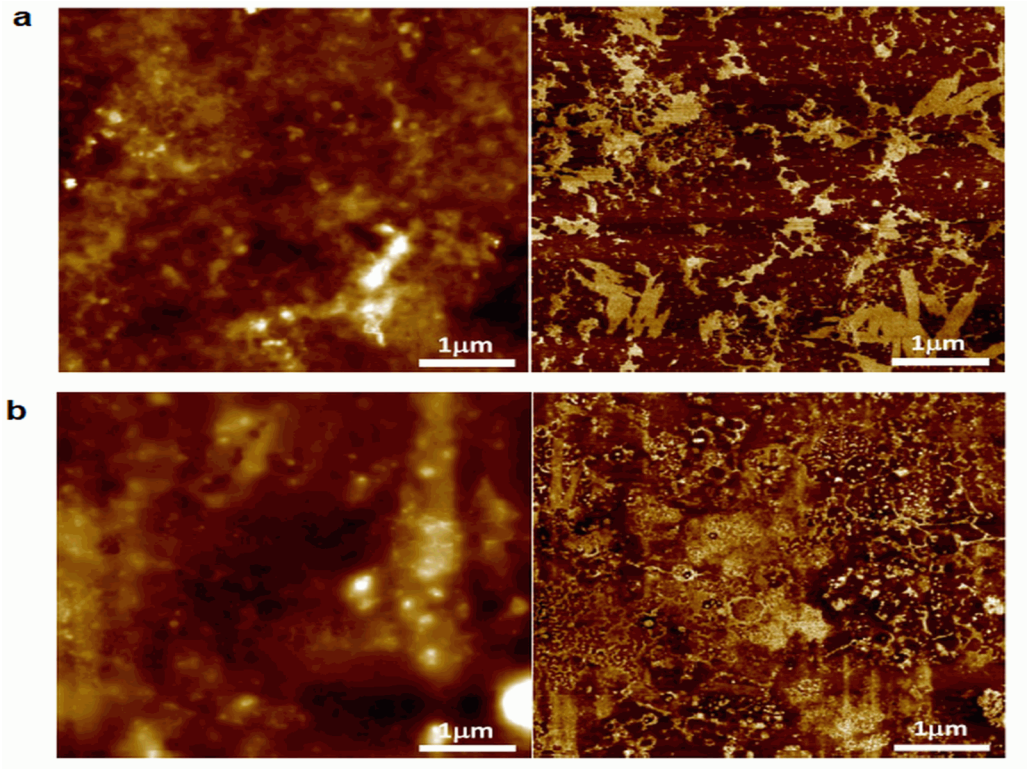

Fig. 5. AFM height (left) and phase (right) images showing the bulk morphology of: (a) PU0 and (b) PU5. Scan size of 5 μm × 5 μm.

4. Conclusions

A recycled component (glycerolysate), obtained by glycerolysis of polyurethane process, was applied in cast polyurethane, replacing part of commercial polyol and simultaneously increasing the crosslinking of the material. Polyurethane material was synthesised by two-step bulk polymerisation using a mixture of commercial polyol and glycerolysate, 4,4-diphenylmethane diisocyanate and 1,4-butanediol as a chain extender. The crosslink densities of polyurethanes were calculated from the results of swelling behaviour in DMF using Flory and Rehner equations. It was established that the incorporation of a higher amount of recycled component is causing the decreasing of swollen solvent volume from 1600 to ca. 250% and increasing crosslink density. PU5 indicated a crosslink density on the level of a crosslinked rubber. The effect of crosslinking was noticeable in FTIR spectrum where bonds associated with urethane group were shifted to lower wavenumbers marking that more hydrogen bonding interactions were formed. The glass transition determined by DSC of polyurethanes was in the range from -35 to -25 ^{o}C, increasing with the higher incorporation of glycerolysate and it can be caused by the restriction on molecular motions due to higher crosslinking. Obtained materials are stable up to 300 ^{o}C and show two-step degradation typical for polyurethanes. The crosslink density was in accordance with DMA results, as higher storage modulus were registered for polyurethanes with the recycled component. Moreover, the crosslinking trend was confirmed by mechanical properties, as the elongation of polyurethanes decreased with more content of glycerolysate with the remaining or even higher level of tensile strength and Young modulus values. According to the AFM results, the PU5 (with Gly) reveals the formation of an interconnected hard segments domain

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structure. The usage of glycerolysate as a part of polyol mixture allowed for obtaining crosslinked polyurethane coatings.

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