Thermoplastic polyurethanes with glycolysate intermediates from polyurethane waste recycling

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ABSTRACT

The polyol is a major component in polyurethane formulations and therefore introducing to the formulation recycled polyol (obtained during decomposition process) allows decreasing the usage of pure petrochemical components. In this work, thermoplastic polyurethanes were prepared using various mixtures of a petrochemical macrodiol (poly(ethylene-butylene adipate)diol (PEBA) and a recycled glycolysate intermediate, called glycolysate polyol, in a two-step synthesis procedure with 4,4-diphenylmethane diisocyanate (MDI) and 1,4-butanediol (BD). The glycolysate polyol was obtained during glycolysis process of polyurethane elastomer using ethylene glycol as a decomposing agent. Glycolysate polyol showed a higher hydroxyl value (199 mg KOH g^{-1}) and glass transition temperature (Tg, -50.1 ^{o}C) than pure macrodiol (PEBA). The maximum concentration of glycolysate polyol was 25 wt% over the total polyol. Synthesized polyurethanes had similar chemical structure compared to the polyurethane synthesized without glycolysate polyol, confirmed by Fourier transform infrared spectroscopy. On the one hand, higher contents of glycolysate polyol resulted in higher T_g and a slightly lower thermal stability analyzed by thermogravimetric analysis. On the other hand, improved thermomechanical and mechanical properties were obtained in polyurethanes with partial replacement of pure macrodiol.

Keywords: chemical recycling, glycolysis, glycolysate polyol, thermoplastic polyurethanes

INTRODUCTION

Global production of polyurethane materials is currently on the level of 15 million tons and is growing due to the big interest in these materials [1]. Because of such high production and simultaneous consumption, a great amount (volume) of these materials is landfilled. Therefore, scientists have been searching suitable and efficient routes for polyurethane waste recycling for many years. The methods of recycling polyurethane waste include energy recovery [2], physical recycling [3,4] and chemical recycling [5–7], among which chemical recycling is the most efficient way to regain the raw materials for preparation of new polyurethanes. The term of chemical recycling is defined as the process leading to complete depolymerization of polymers to monomers. The monomers could be re-polymerized to regenerate the original polymer. The regeneration process may involve a variety of monomer/polymer purification steps in addition to different purification processes such as distillation, crystallization, and additional chemical reaction [8–10].

Chemical recycling of polyurethane has its origin in 70's, where first articles and patents were published [11–13]. Since then the topic of polyurethane feedstock recycling has been continuously developed by researchers, and various methods were proposed [14–16]. The most common methods include glycolysis using small molecular weight glycols [17], hydrolysis using water or steam [18], methanolysis by methanol [19], aminolysis using aliphatic or aromatic amines [20,21]. In the last decade the most studied process was glycolysis where scientists examined the influence of chosen glycols [22], catalysts [23], temperature, reaction time [24], microwave irradiation [25], mass ratio of polyurethane waste to glycol [26], type of waste (foam, elastomeric, thermoplastic [27–31]) on the process itself and the resulting products. The main products from mentioned methods are mostly polyols, amines, isocyanates (in the case of aminolysis), glycols or oligomeric compounds ended with functional groups (i.e. hydroxyl groups) [32]. The glycolysis process consists of a transesterification reaction, in which the ester group joined to the carbonyl carbon of the urethane is interchanged by the hydroxyl group of the glycol [33].

As the main concept of chemical recycling is to recover monomers, several papers dealing with the utilization of recovered monomers can be found in the literature. In the case of polyurethane recycling, the recovered products are mostly used for polyurethane materials synthesis in the form of foams [28,34–37] or elastomers [30,38–40]. Such recycled products are used to replace the polyol component in the formulation, which constitutes the soft segment (SS) of the polyurethane and confers extensibility, ductility and recovery ability to the material. Apart from this, urethane rich hard segments (HS) complement the microstructure of polyurethanes acting as reinforcements of high modulus.

The main goal of this study was to utilize the glycolysis product in thermoplastic polyurethane synthesis. Glycolysis using low molecular weight ethylene glycol was carried out with a high excess of polyurethane waste to decomposition agent (10:1), what can contribute to the faster reduction of waste. Glycolysate polyol was used in polyurethane synthesis and played as a macrodiol, replacing even up to 25 wt% of total polyol. The effect of increasing the content of
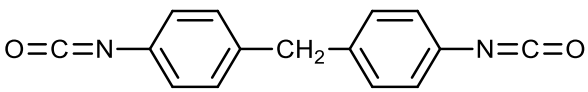
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glycolysate polyol over the properties of polyurethane materials was studied using Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA) and mechanical testing. Differences between pure and glycolysate polyol were analyzed by gel permeation chromatography (GPC) and nuclear magnetic resonance (NMR) techniques.

EXPERIMENTAL

Materials

The used macrodiol was the bifunctional poly(ethylene-butylene adipate)diol (PEBA), Polios 55/10) provided by Purinova (Poland), with a hydroxyl number of 54.48 mg KOH g^{-1} determined in accordance with ASTM D 4274-88 and a number-average molecular weight of 2060 g mol^{-1}. 4,4'-Diphenylmethane diisocyanate (MDI) (Desmodurd 44) and 1,4-butanediol (BD) were provided by Covestro and Aldrich, respectively. Glycolysate (Gly) polyol was obtained and prepared as it is described in the section *Glycolysate polyol preparation.* Before use, the macrodiol and Gly polyol were vacuum dried for 6 h at 80 ºC while BD was vacuum dried for 6 h at 40 ºC. The chemical structures and characteristics of the polyol, diisocyanate, and chain extender are shown in Table 1.

Table 1. Chemical structure and characteristics of the macrodiol, diisocyanate and chain extender.

Chemical structure	M_n (g mol^{-1})	T_g (ºC)	T_c (ºC)	T_m (ºC)
HO$-$[C$_4$H$_8$-O$-$C($=$O)$-$C$_4$H$_8$-C($=$O)$-$O$-$C$_2$H$_4$-O$-$C($=$O)$-$C$_4$H$_8$-C($=$O)]$_n$-OH Poly(ethylene-butylene adipate)diol	2060	-65	-17	20
HO$-$CH$_2$-CH$_2$-CH$_2$-CH$_2$-OH 1,4-Butanediol	90			16
O$=$C$=$N$-$C$_6$H$_4$$-CH_2$$-C_6H_4$$-N=C=$O 4,4'-Diphenylmethane diisocyanate	250			40

Glycolysate polyol preparation

Polyurethane (PU) elastomer with known chemical structure was recycled by glycolysis reaction. In this study, glycolysis was carried out with ethylene glycol (EG) (POCH, Poland) and potassium acetate (KAc) (POCH, Poland), which were used as a decomposing agent and a catalyst, respectively. The reaction was carried out in a 2 L steel reactor with a mechanical stirrer and reflux condenser. The reaction conditions were as follows: mass ratio of PU

elastomer/EG amounted 10:1, the concentration of catalyst equaled 0.5 wt% of the PU elastomer, the temperature was maintained in the range from 180 to 190°C and the total time of the process was about 40 min. Gly polyol samples were characterized by hydroxyl value (199 mg KOH g^{-1}) according to ASTM D 4274-88, the viscosity measured by Brookfield Rheometer R/S-CPS+ (2000 mPa s, 25 °C) and pH (9.17). Number average molecular weight was calculated from hydroxyl value, considering functionality equal to two as later confirmed by solubility analysis (564 g mol^{-1}).

Synthesis of polyurethanes

Polyurethanes were synthesized using a two-step bulk polymerization procedure. The reaction was carried out in a 250 mL five-necked round-bottom flask equipped with a mechanical stirrer and dry nitrogen inlet. Firstly, a mixture of PEBA and Gly and MDI were placed in the flask and heated in a thermo-regulated silicone bath at 80 °C for 5 h. Secondly, dry BD chain extender was added to the prepolymer at 60 °C while rapidly stirring for 10-15 min to homogenize the mixture. The resulting viscous liquid was quickly poured between two Teflon® coated metal plates separated by 1.5 mm and left to cure at 100 °C under 50 bar for 10 h. The NCO to OH groups molar ratio of all polyurethanes was kept constant at 1.05. TPU consist of two segments, one formed by a macrodiol, called as the soft segment (SS), and the other formed by a diisocyanate and a chain extender, known as the hard segment (HS). The designation of samples named as PU-XGly, where X denotes the wt% of Gly with respect to the total weight of polyol, PBEA/Gly/MDI/BD molar ratios and hard segment content of the polyurethanes are shown in Table 2. As a reference pure MDI/BD segment (PUBD100) was also synthesized. The exact composition of 100 g PU-10Gly sample was: PEBA = 55.0 g, Gly = 6.5g, MDI = 31.6g and BD = 6.9g.

Table 2. The designation, molar ratio of used components and hard segment content of synthesized polyurethanes.

Sample	PEBA/Gly	MDI	BD	HS (wt%)
PU-0Gly	1/0	3.15	2	32
PU-5Gly	0.85/0.15	3.15	2	35
PU-10Gly	0.7/0.30	3.15	2	38
PU-15Gly	0.6/0.4	3.15	2	40
PU-20Gly	0.5/0.5	3.15	2	42
PU-25Gly	0.45/0.55	3.15	2	44

Characterization techniques

Fourier transform infrared spectroscopy (FTIR)

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The identification of polyurethane characteristic functional groups and hydrogen-bonding formation was carried out by FTIR in attenuated total reflectance (ATR) mode using a Nicolet Nexus FTIR spectrometer equipped with a MKII Golden Gate accessory 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 600 cm^{-1} with a resolution of 4 cm^{-1}.

Nuclear magnetic resonance (NMR)

Differences in the chemical structures of PEBA macrodiol and Gly polyol were analyzed by proton (^{1}H NMR) nuclear magnetic resonance. ^{1}H NMR spectra were registered in a Bruker Avance 500 equipment, using a 125.77 MHz resonant frequency. Acquisition time was set at 3 s. For the analysis, samples of PEBA and Gly were diluted in deuterated chloroform (CDCl$_3$) at a concentration of 10 mg mL^{-1}.

Gel permeation chromatography (GPC)

Molecular weight distribution of PEBA macrodiol and Gly polyol were determined by GPC 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 °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 the polyol in THF at 1 wt% and filtering using nylon filters with 2 µm pore size.

Differential scanning calorimetry (DSC)

Thermal properties were investigated by DSC using Mettler Toledo DSC822e equipment, equipped with a robotic arm and an electric intracooler as refrigerator unit. Samples with a weight between 5 and 10 mg were sealed in aluminum pans and heated from -75 °C to 220 °C at a scanning rate of 20 ˚C min^{-1}, using N$_2$ as a purge gas (10 mL min^{-1}). The inflection point of the heat capacity change observed was chosen to evaluate 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).

Thermogravimetric analysis (TGA)

The thermal stability of samples was analyzed in a Mettler Toledo TGA/SDTA851 thermogravimetric analyzer. The samples were scanned from room temperature to 700 °C at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere.

Dynamic mechanical analysis (DMA)

The dynamic mechanical behavior of the polyurethanes was analyzed by DMA in tensile mode on an Eplexor 100N analyzer from Gabo, using a static strain of 0.10%. The temperature was varied from -100 to 150 °C at a scanning rate of 2 °C min^{-1} and a fixed operation frequency of 10 Hz. Samples were cut into strips of 22 mm x 5 mm x 1.5 mm (length x width x thickness).

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Mechanical properties

Mechanical testing was carried out at room temperature using a Universal Testing Machine (MTS Insight 10) with a load cell of 10 kN. Pneumatic grips were required to hold the test specimens. Samples from compression-molded polyurethanes were cut into dog-bone shape according to ASTM D1708-93 standard procedure. Tests were performed with a crosshead rate of 50 mm min^{-1}. Elastic modulus (E), tensile strength (σ_t) and elongation at break (ε_b) were averaged from five test specimen data. Shore D hardness of polyurethanes was determined according to ASTM D 2240-15 standard, using a MD-202 DuroTECH durometer applied perpendicularly for 3 s. The values were determined from the average of five measurements performed in different areas of the sample.

RESULTS AND DISCUSSION

To confirm that Gly polyol was bifunctional and hence the synthesized polyurethanes thermoplastic, polyurethane samples were dissolved in DMF. All samples were soluble in DMF at 70 ºC, the ones with low Gly content even in THF at room temperature. This confirmed that the obtained polyurethanes were thermoplastic. Moreover, Gly polyol and PEBA macrodiol were analyzed by GPC. Gly showed a more heterogeneous nature than PEBA, with a broader distribution of sizes as observed in GPC curves. Besides the main peak attributed to polyol, additional peaks come from the by-products present in glycolysate such as carbamates, amine and unreacted glycol. As they are lower molecular weight compounds, the molecular weight of Gly is lower than PEBA. (Figure 1).
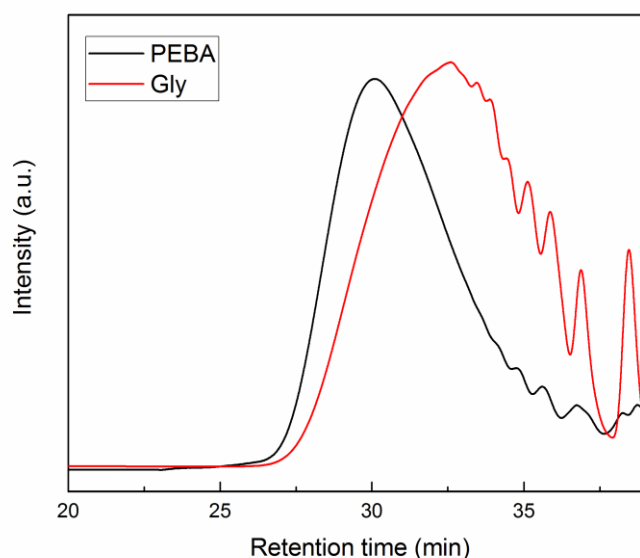

Figure 1. GPC curves of PEBA macrodiol and Gly polyol

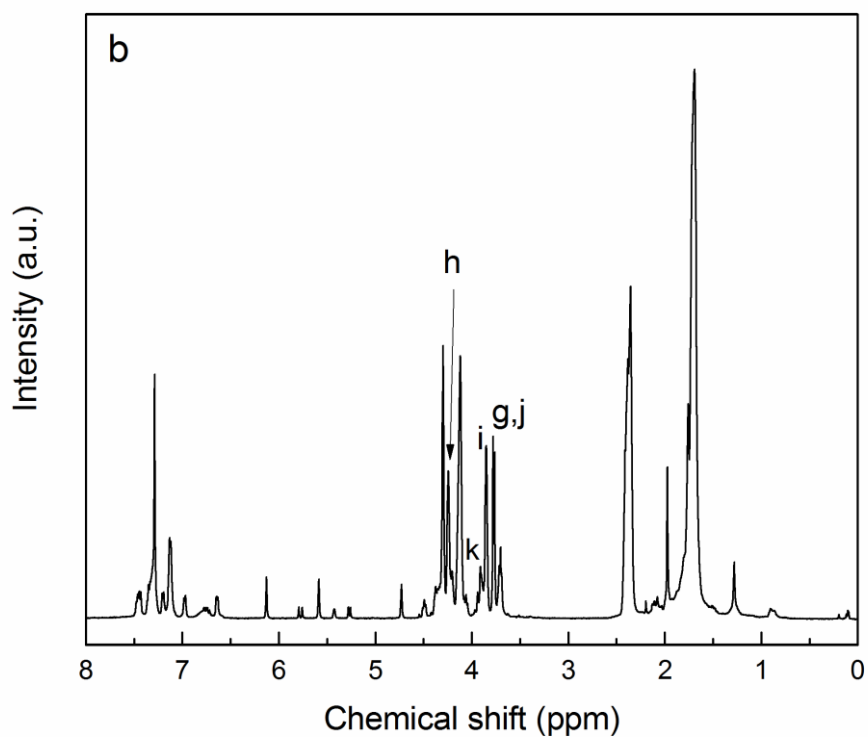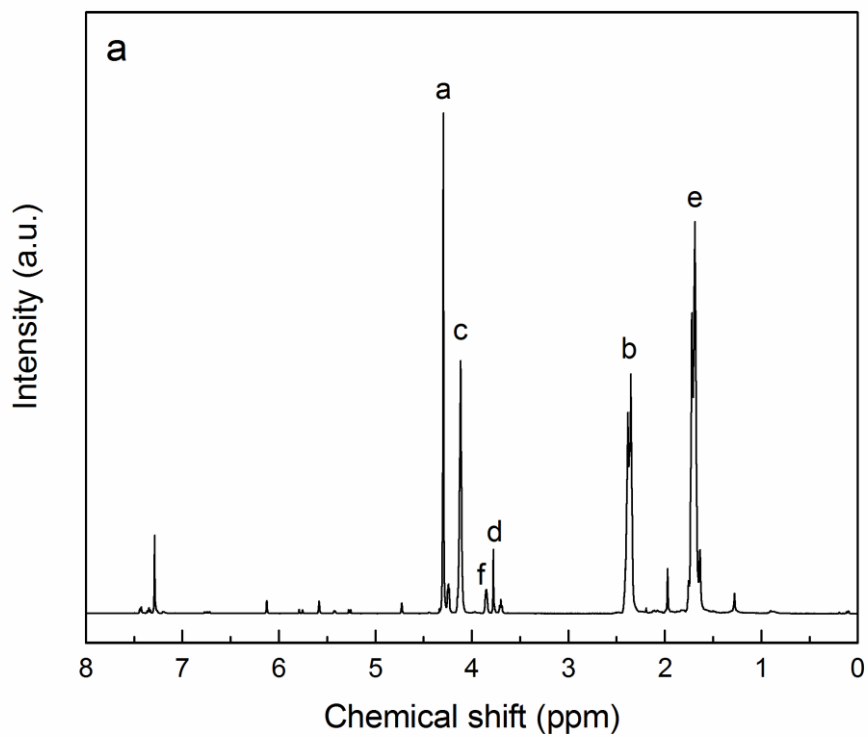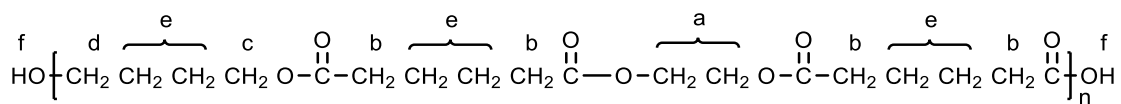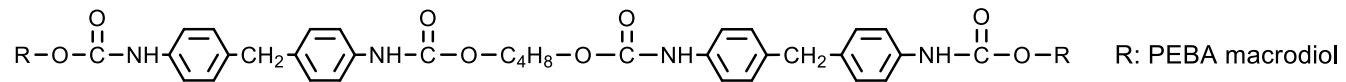The differences between the structure of PEBA and Gly were analyzed by ^{1}H NMR (Figure 2)

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Figure 2. Chemical structure and ^{1}H NMR spectra of PEBA macrodiol (a) and ^{1}H NMR spectra of Gly polyol.
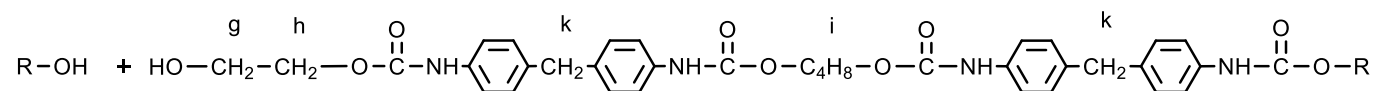
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The peak located at 7.23 ppm in both spectra was attributed to the solvent CDCl$_3$ used for sample preparation. Concerning the spectrum of PEBA macrodiol (Figure 2a), the peak observed at around 4.29 ppm was assigned to the protons of ethylene units in the polyol (a protons). Concerning the butylene units, the peak at 4.10 ppm was related to the protons next to oxygen (c protons). The CH$_2$ protons adjacent to the hydroxyl group were identified at around 3.75 ppm (d protons). Moreover, the CH$_2$ protons next to carboxyl group were identified at 2.35 ppm (b protons). Finally, the peak at 1.65 ppm was assigned to intermediate CH$_2$ protons of butylene unit (e protons). The single peak observed at 3.85 ppm (f protons) evidenced the presence of OH groups. Furthermore, the small peaks observed in the spectra were attributed to impurities.

Concerning the spectrum of Gly polyol (Figure 2b) the same peaks corresponding to impurities were observed as well as the peak corresponding to the solvent. Apart from these, the presence of some new peaks was noticed. Considering that the transesterification process affects the ester groups of the urethane bonds, different polyol structures might be obtained depending on the position of the ester group involved in the transesterification reaction. Thus, the simplified structures shown in Scheme 1 were proposed, considering that the ester group involved in the transesterification reaction was the one corresponding to the urethane bond between the polyol and the isocyanate (case 1) or to the urethane bond between the isocyanate and the chain extender (case 2).
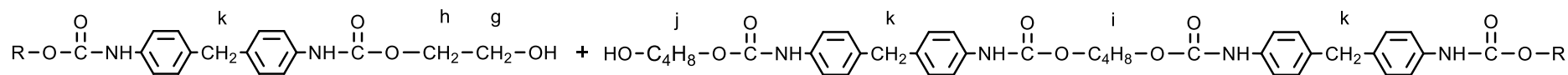
R—O—C—NH—⬡—CH₂—⬡—NH—C—O—C₄H₈—O—C—NH—⬡—CH₂—⬡—NH—C—O—R   R: PEBA macrodiol

+   HO—CH₂-CH₂-OH   (transesterification)

(case 1)

R—OH   +   HO—CH₂—CH₂—O—C—NH—⬡—CH₂—⬡—NH—C—O—C₄H₈—O—C—NH—⬡—CH₂—⬡—NH—C—O—R

(case 2)

R—O—C—NH—⬡—CH₂—⬡—NH—C—O—CH₂—CH₂—OH + HO—C₄H₈—O—C—NH—⬡—CH₂—⬡—NH—C—O—C₄H₈—O—C—NH—⬡—CH₂—⬡—NH—C—O—R

Scheme 1. Chemical structures proposed for Gly polyol due to the glycolysis process.

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The peak at 4.24 ppm was attributed to CH_2 protons of ethylene glycol units, used in the glycolysis process, adjacent to the oxygen of urethane bonds (h protons), whereas the peaks at around 3.6-3.7 ppm were attributed to the CH_2 protons of ethylene glycol (g protons) or butanediol (j protons) adjacent to hydroxyl groups. Moreover, the peak at around 3.95 ppm was assigned to CH_2 protons of the MDI units (k protons). The new peaks observed at around 3.85 ppm were assigned to CH_2 protons from PEBA or chain extender adjacent to urethane bonds (i protons). Finally, the new peaks observed in the range of 7-7.5 ppm evidenced the presence of aromatic structures derived from the isocyanate. These results suggested that some urethane groups remained after glycolysis process.
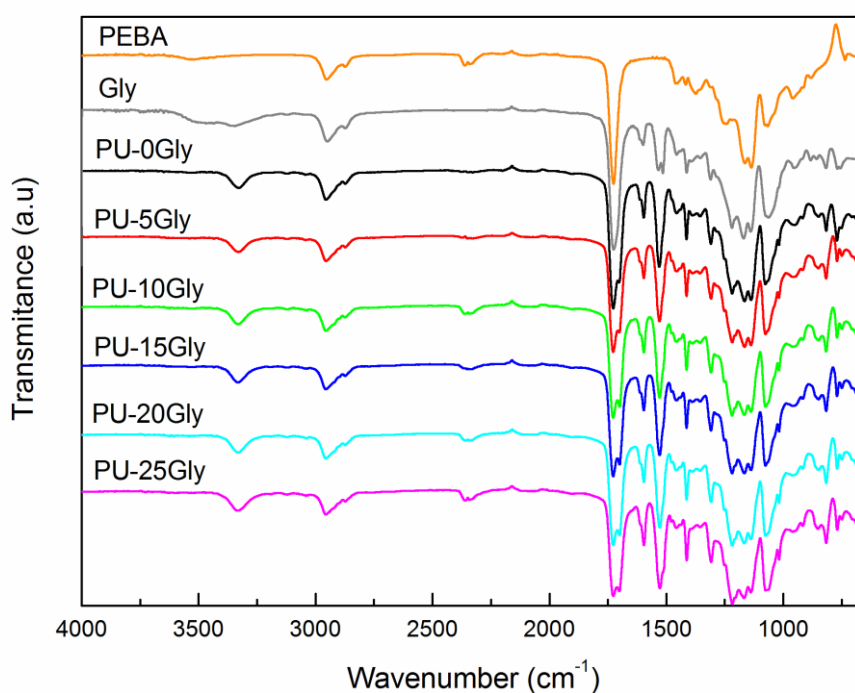

Figure 3. FTIR spectra obtained for thermoplastic polyurethanes, PEBA macrodiol and Gly polyol.

The IR spectra of all the synthesized polyurethane samples together with PEBA and Gly are shown in Figure 3. On the one hand, Gly polyol presented a band about 3500 cm^{-1} associated with O-H stretching vibration, and it was overlapped with stretching vibrations of N-H groups occurring at 3363 cm^{-1} from urethane groups remaining after glycolysis. On the other hand, concerning polyurethane samples, the absence of the stretching vibration band at 2270 cm^{-1}, referred to NCO group, indicated that all isocyanate groups reacted during the polymerization [41]. Moreover, in the spectra, different regions were differentiated. The region between 3200 - 3400 cm^{-1} is characteristic of the N-H stretching vibration in the urethane group [42], which was present in all the synthesized polyurethane samples. In this case, this band was centered at 3334 cm^{-1} and slightly increased in intensity as the Gly polyol content increased.

That can be due to the increase of hard segment content of the samples as well as the urethane groups remaining after glycolysis in the recycled polyol.

The region among 1900 - 1000 cm^{-1} is shown in Figure 4. PEBA showed a peak at 1730 cm^{-1} associated with carbonyl groups (C=O) stretching vibration of ester group while in the Gly polyol the same peak appeared but slightly wider, probably due to the overlap of carbonyl groups from ester and urethane. In the case of synthesized polyurethane samples, the apparition of a band at 1700 cm^{-1} was observed, related to hydrogen bonded urethane groups [43]. Its intensity increased in good agreement with the increased Gly polyol and urethane content of the samples. There could also be distinguished bands at ca. 1615 and 1595 cm^{-1} associated with the aromatic groups present in the material (derived from MDI) [44]. The peaks corresponding to N-H bending and C-N stretching vibrations of urethane bonds were identified at 1527 and 1306 cm^{-1}, respectively [42]. These bands were present also in Gly sample in comparison PEBA macrodiol suggesting the presence of urethane groups as confirmed by NMR analysis. Moreover, all the samples except PEBA showed an absorbance band at 1220 cm^{-1} corresponding to the C-O bond in urethane group. It is important to mark that in this work a high excess of polyurethane waste was used in the glycolysis process, which could influence the amount of existing urethane and by-products.
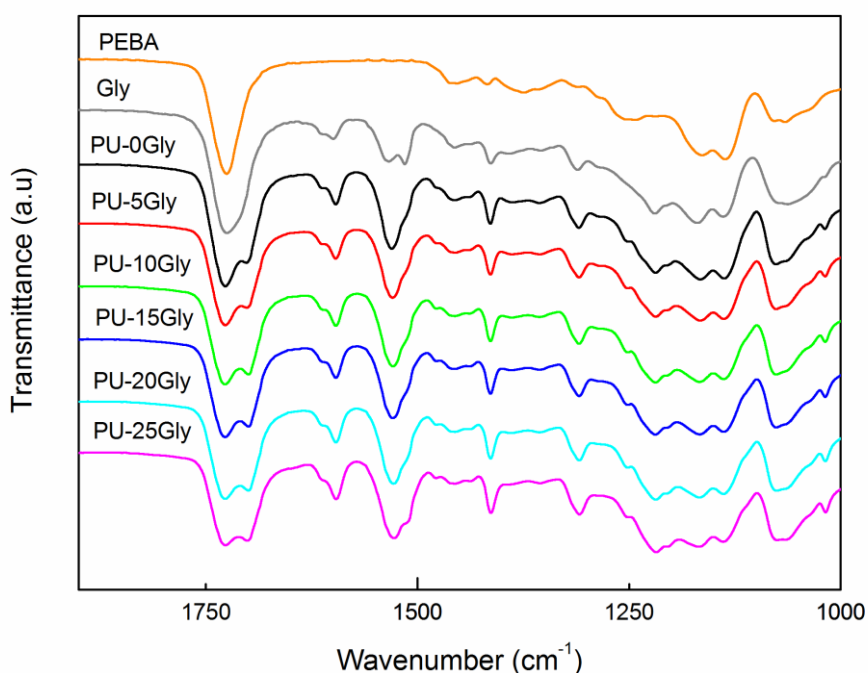

Figure 4. FTIR spectra in 1900-1000 cm^{-1} region.

Thermal properties of the synthesized polyurethanes, PEBA macrodiol and Gly polyol were analyzed by DSC. The obtained thermograms are presented in Figure 5 and the thermal transition values as a function of Gly polyol content are shown in Table 3. PEBA is a semi-crystalline macrodiol presenting a glass transition temperature (T_{gSS}) of -59.5 ºC and a melting temperature (T_{mSS}) and melting enthalpy (ΔH_{mSS}) of 16.3 ºC and 49.7 J g^{-1}, respectively, being a viscous liquid at room temperature. Gly polyol is an amorphous viscous liquid with a T_{gSS} of -50.1 ºC. Polyurethane

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samples presented two T_gs, one associated with the soft segment (T_{gSS}) and the other associated to the hard segment (T_{gHS}), indicating that phase separated polyurethanes were obtained. A melting endotherm related to hard segment was also observed. The T_g value can be taken as an indicative of the purity of different phases [45]. In fact, the purity will be higher as the T_{gSS} and T_{gHS} of the polyurethane are closer to those of pure segments. Concerning PU-0Gly sample, a deviation in both T_{gSS} and T_{gHS} was observed (Tg_{HS}(MDI-BD): 100 ºC [46]), indicating that there was some degree of phase mixing. The same effect was observed in polyurethanes containing Gly polyol. As can be seen in Table 3, as Gly polyol percentage increased the T_{gSS} also increased presumably due to the higher T_{gSS} of Gly polyol sample or to an increase in phase mixing. Similarly, T_{gHS} decreased with glycolysate content. Such results suggested that the incorporation of Gly hindered phase separation, especially at high contents.

Regarding the melting transition of the hard segment, $T_{mHS,}$ values shifted to lower temperature with respect to PU-0Gly with the addition of Gly polyol while ΔH_{mHS} increased, as a generall tendency. The incorporation of Gly polyol, containing residual urethane groups, together with the increase in hard segment content might have increased the interactions between hard segments resulting in an increase of melting enthalpy. However, the heterogeneity of the Gly polyol may have resulted in a broader distribution of crystal size, observed as a broadening of the melting endotherm, lowering the melting temperature. In PU-5Gly and PU-10Gly samples, a small melting endotherm was observed at higher temperatures than T_{mHS} (PU-0Gly), denoting that the incorporation of low Gly polyol contents did not hinder the formation of a small portion of purer crystals presumably due to the increase in hydrogen bonding between urethane groups. At higher Gly polyol contents, this small peak dissapeared probably due to the increased heterogeneity of the polyol component hindered phase separation, in accordance with T_g values.
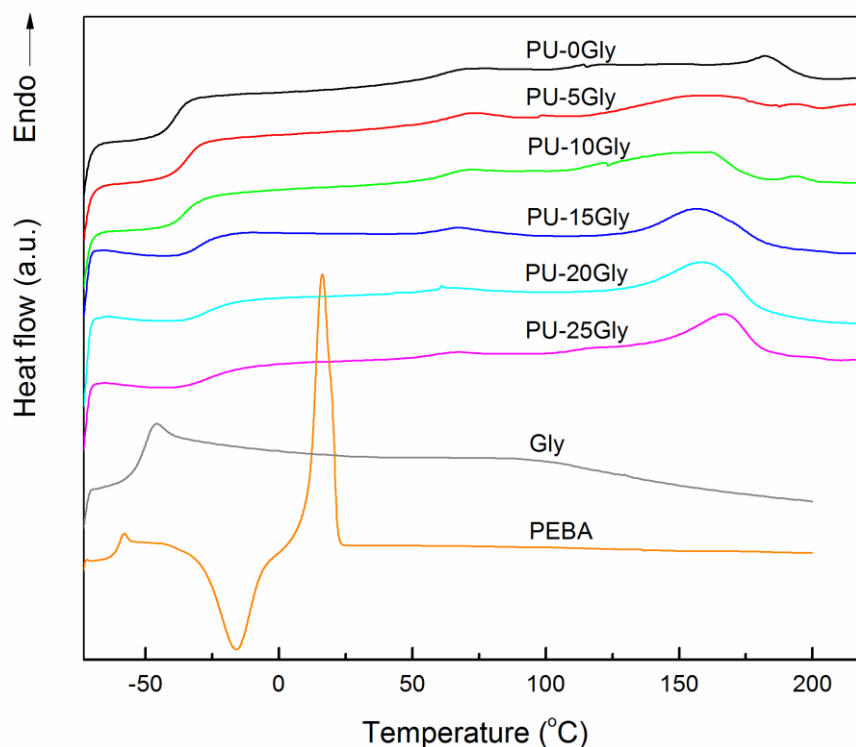
Figure 5. Heating DSC thermograms of synthesized thermoplastic polyurethanes, Gly polyol and PEBA macrodiol

Table 3. Thermal transition values of the synthesized polyurethanes.

Sample	T_g (SS) (ºC)	T_g (HS) (ºC)	T_m (HS) (ºC)	ΔH_m (HS) (J g^{-1})
PU-0Gly	-36.3	62.3	181.6	6.9
PU-5Gly	-34.0	63.7	145.6/195.6	7.9/0.4
PU-10Gly	-34.0	63.3	160.6/197.3	8.8/0.4
PU-15Gly	-30.0	61.3	157.6	12.6
PU-20Gly	-27.7	59.9	159.9	14.9
PU-25Gly	-26.1	58.3	166.8	12.9

Thermal stability of polyurethanes containing Gly polyol, PU-10Gly and PU-20Gly, as well as the reference PU-0Gly was analysed by TGA. The results from the thermogravimetric analysis are shown in Figure 6 (TG curves) and Figure 7 (DTG curves). The synthesized reference polyurethane was stable up to 270 ºC, where the mass loss began, whereas Gly polyol was less stable starting to degrade at 210ºC. Therefore, PU-10Gly and PU-20Gly were slightly less stable than PU-0Gly. It is worth noting that neat Gly started to degrade at lower temperature than synthesised polyurethanes, due to the lower thermal stability of urethane and by-products, and that would be the main reason why the incorporation of Gly polyol slightly decreased

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thermal stability. All TG curves of polyurethanes have similar trends. All synthesized polyurethanes and Gly polyol showed two stage thermal decomposition, characteristic for polyurethane materials as the first is related to decomposition of the hard segment and the second with the decomposition of the soft segment [47]. The first peak broadened and increased in intensity with increasing the Gly polyol content, related to residual urethane and by-products present in the Gly polyol and increasing hard segment content in PUs with glycolysate.
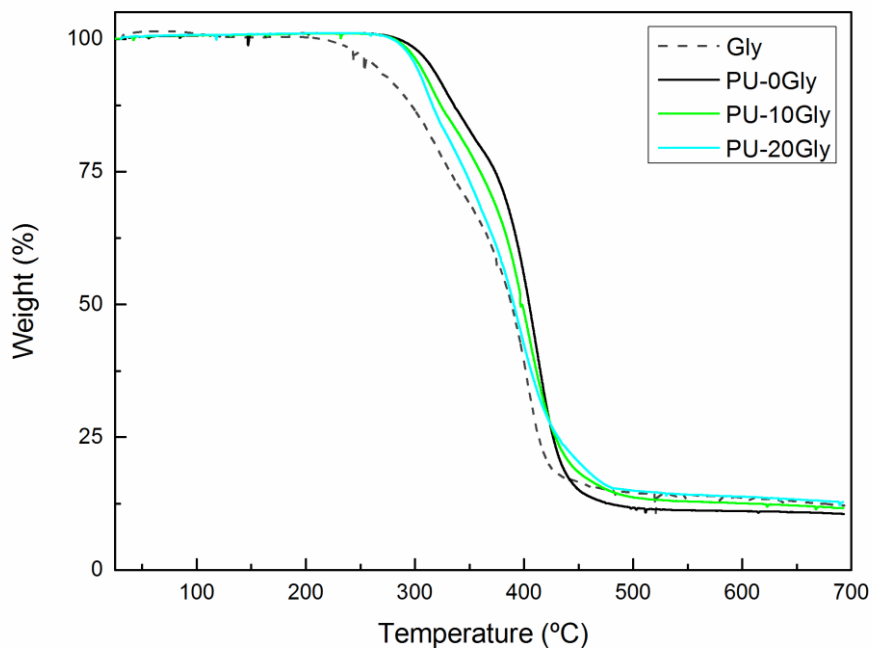

Figure 6. TG curves obtained for synthesized thermoplastic polyurethanes and Gly polyol
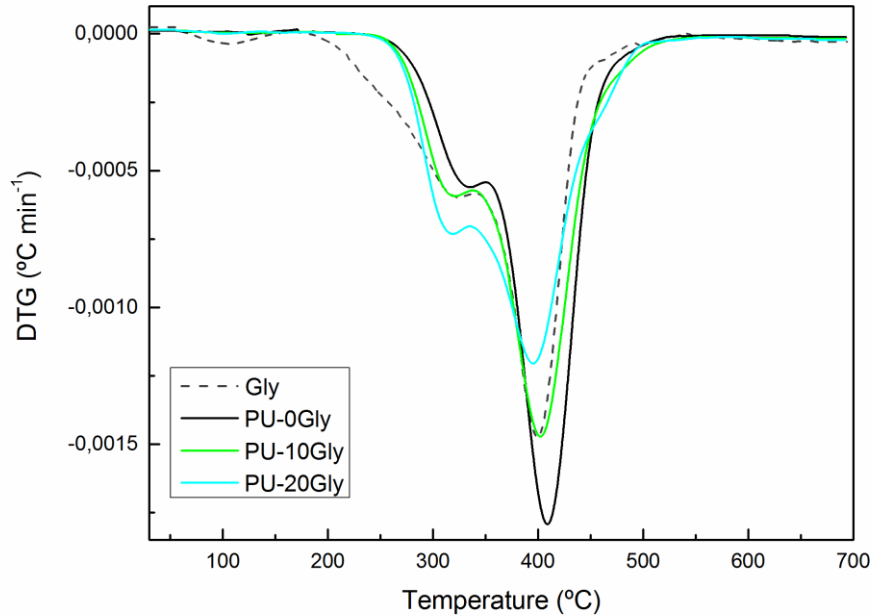
Figure 7. DTG curves obtained for synthesized thermoplastic polyurethanes and Gly polyol.

Figure 8 shows the evolution of storage modulus (E') and loss factor (tanδ) with temperature for the synthesized polyurethanes. At low temperature, all polyurethanes showed similar storage modulus. At a temperature about –45 ºC there was a drop in the storage modulus, being more pronounced for PU-0Gly presumably due to the lowest urethane content of this sample. At the same time tanδ presented a maximum indicating the α relaxation phenomenon of the soft segment, associated with the glass transition temperature. The temperature of the maximum presented the same trend as observed by DSC. An increase of T_{gSS} values as well as a broadening of tanδ peak was observed with the incorporation of Gly polyol. These suggested that the mobility of the soft segments was restricted, probably due to hydrogen bonding associations occurring as a consequence of the residual urethane groups in the Gly polyol. Moreover, the decrease in tanδ intensity observed with the addition of Gly polyol was associated with a smaller proportion of soft segment participating in the glass transition. At room temperature samples presented higher storage modulus values as the content of Gly polyol increased, in good agreement with a higher hard segment content. As heating continued, the values of storage modulus decreased until the onset of a second softening around 60 ºC related with the glass transition of hard segments, in accordance with DSC analysis. Also, a shoulder was observed in tanδ curve at this temperature. Finally, a dramatic decrease of modulus associated with the disruption of hard segment crystalline domains was observed. Samples showed higher thermo-mechanical stability with increasing Gly polyol content, as a general tendency. Despite PU-0Gly presented hard ordered domains with higher T_m (HS) values, lower thermo-mechanical stability was observed. The lower melting enthalpy may indicate that the smaller amount of crystalline structures was not able to act as an effective reinforcement.
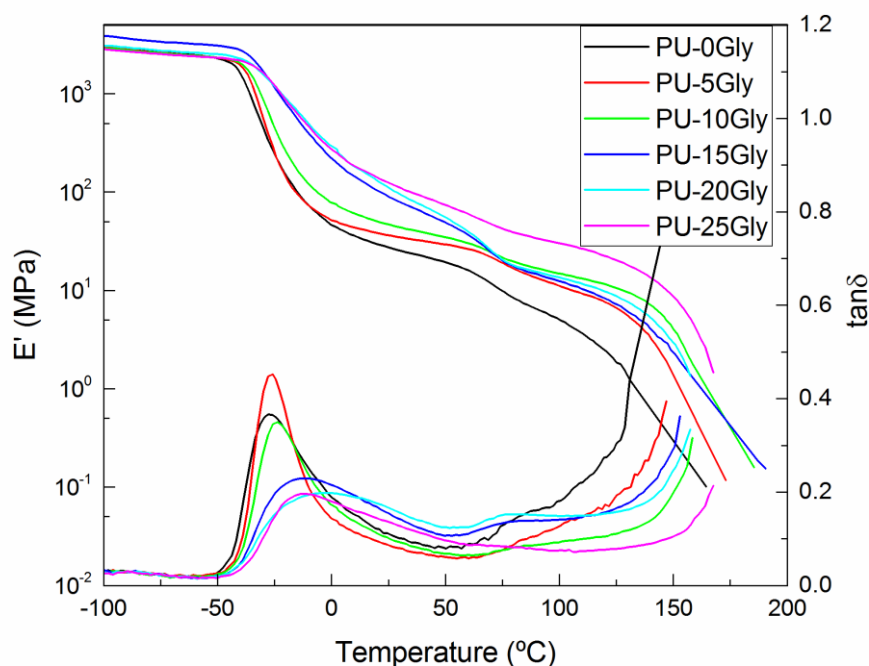
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Figure 8. Evolution of storage modulus (E') and loss factor (tanδ) with temperature for synthesized thermoplastic polyurethanes.

Figure 9 presents stress-strain curves, and the results from the static mechanical test as well as shore D hardness values are shown in Table 4. The results of the mechanical properties test showed that all the samples which contain Gly polyol, improve their mechanical properties with regard to the reference PU-0Gly. As can be seen in Figure 9, Young's modulus increases as the concentration of Gly polyol increases, probably due to increase of interactions between hard segments. On the other hand, the tensile strength increased as the amount of Gly polyol do, reaching the maximum value in the sample PU-15Gly, and then gradually decreased. This could be due to the decrease in phase separation observed in polyurethanes with high Gly polyol contents which could result in a decrease of reinforcing effect of the hard segments in the strain direction. Concerning elongation at break values, the incorporation of low Gly polyol contents enhanced the deformability of the sample presumably due to the increase in hydrogen bond interactions between hard segments. Again, at high Gly polyol contents, elongation at break values diminished suggesting a decrease of purity of flexible soft domains though values can be considered still high for this type of materials. In general, all the samples showed a significant improvement in mechanical properties over the reference sample PU-0Gly. Concerning hardness values, it was observed that they followed the same tendency of the Young's modulus, in good agreement with the increase of Gly polyol and hard segment content and the interactions between urethane groups.
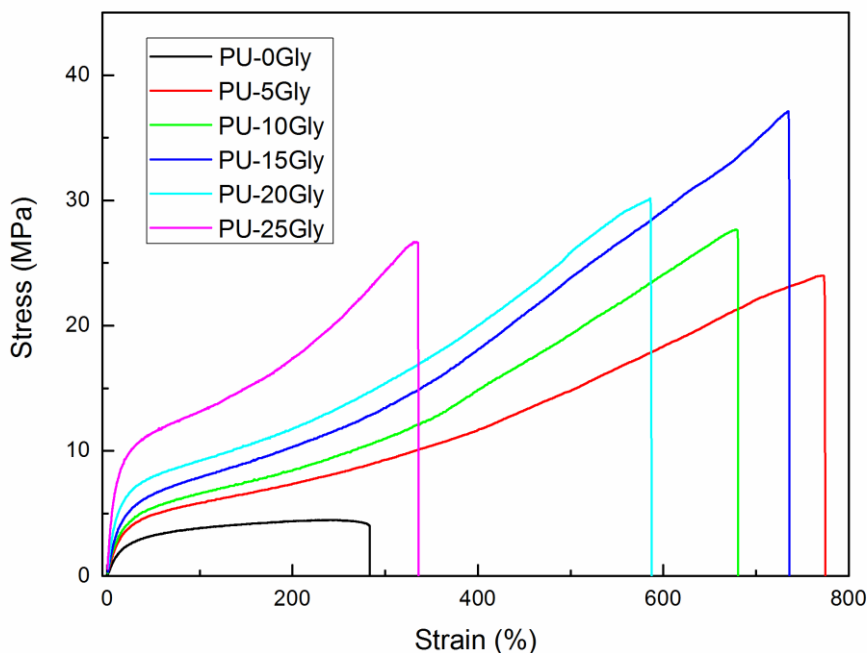
Figure 9. Stress-strain curves of synthesized thermoplastic polyurethanes

Table 4. Mechanical properties of synthesized polyurethanes: Young modulus (E), tensile strength (σ_t), elongation at break (ε_b) and Shore D hardness.

Sample	E (MPa)	σ_t (MPa)	ε_b (%)	Shore D
PU-0Gly	19.8 ± 2.0	4.5 ± 0.2	269.3 ± 7.1	32.2 ± 0.5
PU-5Gly	28.7 ± 1.0	24.3 ± 1.9	774.5 ± 45.4	39.6 ± 0.9
PU-10Gly	40.1 ± 5.5	27.7 ± 0.8	678.4 ± 23.4	44.6 ± 0.9
PU-15Gly	40.7 ± 1.9	37.1 ± 0.9	735.0 ± 15.0	51.2 ± 0.9
PU-20Gly	65.0 ± 4.50	30.2 ± 5.9	586.7 ± 80.7	54.3 ± 0.5
PU-25Gly	113.3 ± 11.0	19.9 ± 5.9	275.0 ± 56.3	56.3 ± 1.5

CONCLUSIONS

Thermoplastic polyurethanes were successfully synthesized with glycolysate polyol from recycled waste. Elastomers were obtained with replacing PEBA macrodiol with recycled one up to 25 wt% over the whole polyol mass. It showed that glycolysate polyol could be a valuable component in polyurethane production and at the same time it allowed for the management of polyurethane waste. FTIR spectra confirmed the total polymerization reaction for all samples and their chemical structures were similar to each other. Higher content of glycolysate resulted in Tg_{SS} shifted to higher temperatures and Tg_{HS} to lower temperatures if compared to polyol and MDI-BD segments, denoting there was some degree of phase mixing. Moreover, Tm shifted to lower temperatures if compared to PEBA macrodiol and MDI-BD system. Nevertheless, a higher

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concentration of glycolysate polyol caused a slight decrease in thermal stability because glycolysate itself exhibited poor stability as it started to degrade at 210 °C. The thermomechanical stability was higher as glycolysate polyol content increased. Moreover, the storage moduli of polyurethanes with glycolysate is higher in all temperature range than for reference PU. Static mechanical properties of polyurethanes indicated that with the addition of glycolysate polyol the Young modulus and the tensile strength were improved. All polyurethanes containing Gly polyol showed higher percentages of elongation at break than the reference.

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