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The influence of different glycerine purities on chemical recycling process of polyurethane waste and resulting semi-products.

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Abstract

Chemical recycling is the most favourable recycling method due to the possibility of polyol recovery. This work is dedicated to the utilisation of crude glycerine and polyurethanes waste. It aims at determining the impact of the use of glycerine from the production of biodiesel with various purity degrees as a cleavage agent on the decomposition process of polyurethane foam. The influence of glycerine purity on the chemical structure of recycling products was analysed by FTIR, ¹H NMR and GPC. Hydroxyl and amine values were determined, and rheological measurements were performed. Glycerolysates showed minor structural differences due to the presence of amine groups and exhibited heterogeneous structure compared to original polyols. The ones obtained in decomposition using 84, and 99.5% glycerine had a lower viscosity below 0.45 Pa·s at 50 °C and higher hydroxyl number 183 and 220 mg KOH g⁻¹, respectively compared to the ones obtained with glycerine purity of 40 and 62% due to a different chemical structure. All of the products of decomposition were defined as non-Newtonian fluids, where viscosity depended on the shear rate. Selected, glycerolysates were used in the production of cast polyurethanes with satisfactory mechanical properties.

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Keywords: chemical recycling, polyurethanes, crude glycerine, chemical structure, rheology

1. INTRODUCTION

Glycerine is mainly obtained from vegetable oil or animal fat, during the reaction of hydrolysis, transesterification or saponification. Transesterification reaction is also used for biodiesel production ¹. During the process of biodiesel production, triglycerides from vegetable oil or animal fat are transformed using an excess of alcohol (methanol or ethanol) with the alkaline catalyst in addition to methyl ester, with glycerine as a by-product. Therefore, for each ton of biodiesel produced, approximately 100 kg of crude glycerol is made ². Having in mind the scale of annual biodiesel production which was about 11 million tonnes in the European Union in 2014, and is forecasted to be about 14 mln as reported by United States Department of Agriculture, Foreign Agricultural Service, the approximate amount of glycerine by-product is 1.4 tone ³ and due to Directive 2009/28/EC of the European Parliament, which assumes that the share of bio-components in the transport fuels market should be at the level of 10% in 2020 this amount is going to increase ⁴. To reduce the overall cost of biodiesel production, possible applications of non-refined glycerine are sought. The effect of using crude glycerine on the properties of polyols and then polyurethane foams were also investigated ⁵. Promising results were presented by us in another work where glycerine from biodiesel as a decomposition agent of polyurethane elastomer was applied ⁶.

Depending on the type of oil used in the reaction, the technology used and the parameters of the process, crude glycerine, apart from glycerol contains impurities. In particular, they can be potassium soaps, fatty acids, esters, methanol, catalyst, but also



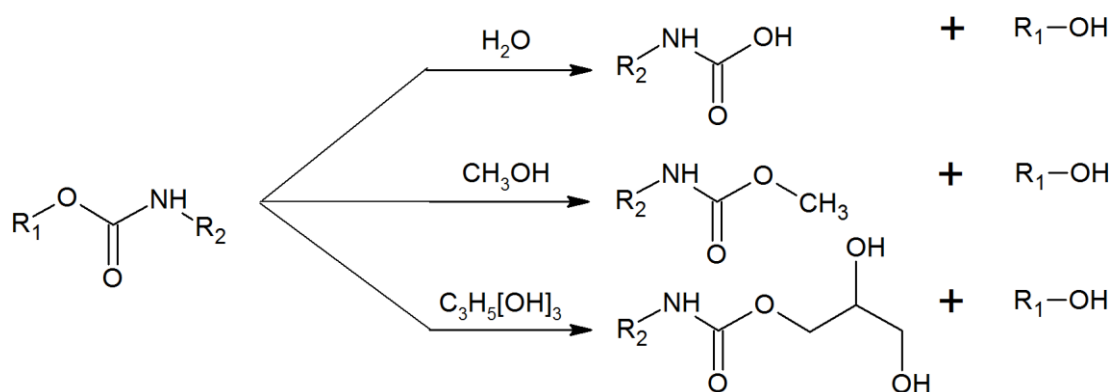
can contain lecithin, proteins, peptides and phospholipid residues and natural dyes such as chlorophyll, anthocyanin. In minimal quantities also many other natural organic compounds can be found. Due to complex composition of crude glycerine, the process of purification is costly and requires using filtration, chemical and fractional vacuum distillation, obtaining glycerin of high purity. Pharmaceutical glycerine with purity rate of more than 99.5%, can be obtained using physicochemical methods such as coagulation and filtration, ion exclusion, ion exchange, adsorption of activated carbon. New methods of crude glycerin purification include for example anaerobic fermentation of glycerol ⁷.

According to plastic Europe, in 2015 the demand for plastic materials was 49 million tons, including about 3.5 million tons of polyurethane ⁸ which translates on the big amount of plastic waste generated. Applying to the principles of sustainable development imposes the need for management of the exploited wares, post-production scraps and post-consumers items. There are companies, i.e. Du Point, which buy consumed wares and manage them by their technology. The easiest way of waste management is landfilling, however from an environmental point of view, it is the least-profitable option. Apart from that, landfilling of plastic is now banned in many European countries for example in Sweden, Norway, Germany or Denmark. To other ways of plastic waste management can be included energy recovery by incineration ⁹ and recycling (mechanical and chemical) ¹⁰⁻¹² which corresponds respectively to 41.6 and 31.1% of post-consumer plastic management in Europe in 2016 ¹³. In addition biodegradation can be included as an opportunity for waste elimination or reuse in a sustainable way, however, it is only suitable for some types of polymers ^{14,15}. Mechanical recycling focuses on the reprocessing of the polymer and usage in the new product



while improving or not affecting the final properties ^{16,17} while in chemical recycling the chemical substance and heat are used to obtain monomer or raw chemicals ^{18–20}.

The emphasis on chemical recycling of PUs is even more desirable due to alternative thermal methods such as pyrolysis and combustion produce a number of toxic gases, among them carbon monoxide, hydrogen cyanide and nitrogen oxides ²¹. Interest in the thermo-chemical decomposition of PUs has been growing steadily since the 1970s due to the possibility of process control through the use of various decomposition agents, temperature and catalysts ^{22,23}. The most frequently used decompositions agents of PUs are water, glycols, alcohols, amines and organic acids, then the process is called respectively, hydrolysis, glycolysis, alcoholysis, aminolysis, acidolysis ^{24–27}. During the decomposition reaction, the urethane bonds are torn resulting with releasing semi-products which can be a mixture of compounds with hydroxyl and/or amine groups ending. The simplified reaction schemes of PU decomposition by various cleavage agents are shown in **Scheme 1**.

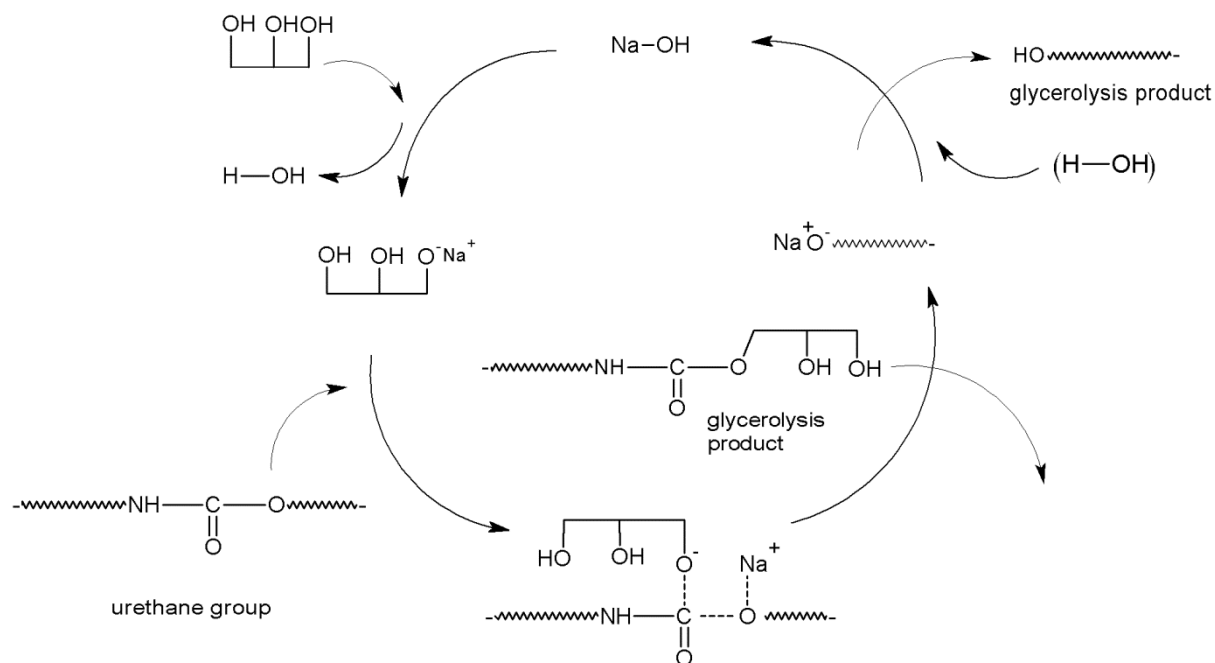


Scheme 1. Simplified polyurethane decomposition with water, methanol and glycerine as a cleavage agent.



Pure glycerin has also been proposed as a decomposing agent with promising results ²⁸. Nikje and Mohammadi used sorbitol/glycerine/water mixture as glycolysis agent in flexible polyurethane recycling ²⁹. Performing the decomposition using glycol, decomposition product can be obtained in split-phase or one phase. In split-phase the upper phase consists mostly of polyol, making the process of glycol purification easier, while bottom phase contains unreacted glycol and by-products ³⁰. The mechanism of PU decomposition with glycerine and sodium hydroxide as a cleavage agent and catalyst respectively can be as follows based on the literature ^{31,32}. NaOH allows for a nucleophilic attack of an oxygen atom from the hydroxyl group of NaOH on the urethane bond $-N(H)C(O)O-$. Because this catalyst is not selective, beside glycerolysis also hydrolysis can take place and therefore it forms hydroxyl salt and water. Next, hydroxyl salt forms as a four-membered group with the urethane bond, in which there are two bonds C–O and Na–O. Na–O bond breaks and the reaction retreats with glycerol hydroxyl salt reconstruction or the reaction proceeds to obtain the degradation products. The presence of water allows for reconstruction NaOH and resulting with the hydroxyl terminated compounds (i.e. polyols) into the medium. The second reaction product is degraded polyurethane with a lower molecular weight (carbamates), terminated with the glycerol rest.





Scheme 2. Proposed mechanism for PU decomposition catalysed by NaOH. Adapted from ³¹.

In the current work, we study the glycerolysis of polyurethane foam waste using glycerine from biodiesel production with different purity rate of 40, 62, and 84% as a decomposing agent. Glycerine with 99.5 % purity was used, to determinate the influence of impurities on chemical recycling process. Hereby we propose a route for treating polyurethane waste and crude glycerine from biodiesel production. The obtained semi-products are characterised by gel permeation chromatography, Fourier transforms infrared spectroscopy, proton nuclear magnetic resonance, analytical analysis, and rheological measurements, to examine the effect of glycerine grade and properties of obtained glycerolysates. The chosen recovered polyols were used to produce cast polyurethanes in order to determine their suitability for use in industry.

2. MATERIAL AND METHODS

2.1. Materials and glycerolysis reaction

Flexible polyurethane foam waste based on polyether polyol (Rokopol F 3600 purchased from PCC Rokita, Poland, $M_n=3600 \text{ g mol}^{-1}$, $\text{OH}_{\text{number}}=45-50 \text{ mg KOH g}^{-1}$, acidity $0.1 \text{ mg KOH g}^{-1}$) and polymeric diphenylmethane-4,4-diisocyanate (pMDI, Borsodchem, Hungary) was reacted in a decomposition reaction with glycerine in weight ratio 3:1. The used glycerine had different purity grade, namely 40% (Lotos, Poland), 62% (Euroservice, Poland), 84% and 99.5% (Rafinieria Trzebinia S.A., Poland) and was used as a decomposing agent. The sodium hydroxide (POCH Avantor, Poland) was used as a catalyst, in the amount of 0.5% in relation to polymer amount. The reaction was carried out in a 1 L stainless steel reactor with a mechanical stirrer and reflux condenser. The reaction temperature varied depending on the purity of glycerine, and for 40, 62, 84 and 99.5% of purity grade was 150, 210, 220 and 220 °C, respectively. Polyurethane scraps were fed by portions with the speed 5 g min^{-1} , and after dosing the last portion, the reaction was carried out 30 min. Samples after the glycerolysis process were collected from the reactor at a temperature of about 80 °C (still liquid form) and poured into glass storage bottles. After cooling down from split-phase samples (GL40, GL84, GL99.5), the upper phase was decanted to another storage bottle. The use of GL62 for decomposition resulted in a single-phase product. No purification and filtration processes were provided to keep minimum as needed process operation to be more likely useful for industry ³³.



Sample designations will correspond to the degree of glycerine purity, a sample of glycerine with purity, 40%, 62%, 84% and 99.5% will be referred to as GL40, GL62, GL84 and GL 99.5 respectively.

2.2. Cast polyurethane synthesis

In order to evaluate the possibility of usage obtained glycerolysates, the cast polyurethanes were obtained. PUs was synthesised by prepolymer method, broader described in our previous article ³⁴. Prepolymer was synthesised from a polyol (poly(tetramethylene ether)glycol) (PTMG, BASF PolyTHF®, 2000, Germany), chosen glycerolysate (GL40 or GL84) and 4,4'-diphenylmethane diisocyanate (MDI, Interchemol S. A., Poland). Phosphoric (V) acid (H_3PO_4 85% wt. in water, POCH Avantor, Poland) 0.5% on the glycerolysate amount was added as side reactions inhibitor. The percentage of free NCO groups in prepolymer was equal to 6.5%. In the second step, the prepolymer chains were extended by using 1,4-butanediol (BD, Brenntag, Poland). DABCO, 1,4-diazabicyclo[2.2.2] octane (Sigma-Aldrich), was used as the catalyst only for the reference sample. The designation of samples named as PU-X-Y, where X denotes the type of glycerolysate and Y wt. % of glycerolysate concerning the total weight of the polyol.

2.3. Characterisations of obtained semi-products

Spectroscopic analysis of glycerolysates was carried out using an FTIR Nicolet 8700 spectrophotometer (Thermo Electron Corporation) and the ATR technique. The Specac Heated Golden Gate single reflection diamond ATR accessory was used, and it operated up to 200 °C. Spectra were registered at room temperature for wavenumbers ranging from 500 to 4,500 cm^{-1} at 4 cm^{-1} nominal resolution with 64 scans.



From the FTIR spectra, the range of PU glycerolysis can also be observed from the conversion (X) of the $-NCOO-$ functional group in the urethane. It can be calculated because the methyl C-H group in PU and polyol chain is more stable than is the $-NCOO-$ functional group and is not destroyed in the decomposition temperature range and is used as a base for calculation of conversion. The conversion of the $-NCOO-$ functional group in PU can be estimated by the relative absorption intensity of the $-NCOO-$ (at about 1727 cm^{-1}) to that of the methyl C-H (at about 1373 cm^{-1}). The conversion is calculated by the relative comparison of the absorption intensity of mentioned bands of glycerolysate and the PU foam ³⁵. The conversion rate (X) is calculated from following equations (1,2):

$$[-NCOO-]_r = \frac{[-NCOO-]}{[-CH-]} \quad (1)$$

$$X\% = 1 - \left(\frac{[-NCOO-]_{r\ of\ GL}}{[-NCOO-]_{r\ of\ PU}} \right) \times 100\% \quad (2),$$

where

$[-NCOO-]_r$ - relative absorbance

$[-NCOO-]$ - the intensity of the absorption band of $-NCOO-$,

$[-CH-]$ - the intensity of the absorption band of methyl C-H

Proton nuclear magnetic resonance (^1H NMR) spectra of glycerolysate were recorded on Bruker AV400 MHz spectrometers in a CDCl_3 solvent at ambient temperature. The simulation and iteration of spectra were made using Bruker software.

Gel permeation chromatography (GPC) was used to determine the molecular weight distribution. 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 $30\text{ }^\circ\text{C}$



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 an 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 obtained glycerolysate in DMF and THF (fraction DMF to THF was 1:5) at 1.6 wt.% and filtering using nylon filters with 2 μm pore size. M_n was reported as weight average polystyrene standards.

Hydroxyl value of the recovered polyol was determined by a standard titration method (PN-EN ISO 2554:2001). Each experimental analysis was repeated at least twice, and the average value has been given. All chemicals used in this analyse were of the quality required in the standards.

Amine value of glycerolysate was determined by a standard titration method (BN-69 6110-29) with hydrochloric acid. Each experimental analysis was repeated at least twice, and the average value has been given. All chemicals used in this analyse were of the quality required in the standards.

Rheological measurements were performed by using rotary rheometer R/S-CPS+ (Brookfield, USA). Measurement system cone/plate has been applied for rheological testing. The rheological parameters were calculated by using Rheo3000 program. Measurements were conducted with controlled shear rate (CSR). The following program was applied: increasing shear rate from 1 s⁻¹ to 300 s⁻¹ for 180 s; the constant shear rate of 300 s⁻¹ for 180 s; and decreasing shear rate from 300 s⁻¹ to 1 s⁻¹ for 180 s. Based on the rheological measurements, the viscosity and flow curves of glycerolysates at different temperatures were plotted. The rheological models and parameters were defined by using Rheo3000 program.



The mechanical analysis in static condition was conducted with a tensile test (tensile strength (TS), elongation at break (ϵ)) and performed using Zwick Z020 tensile testing machine. Dumbbell shaped samples with normalised dimensions by PN-ISO 37:1998 were tested. The cross-section of samples was 6.8×2.8 mm. The tests were executed at 200 mm min⁻¹ rate. Measurements of the mechanical properties were carried out at the room temperature. The obtained results are reported as average values calculated from four samples.

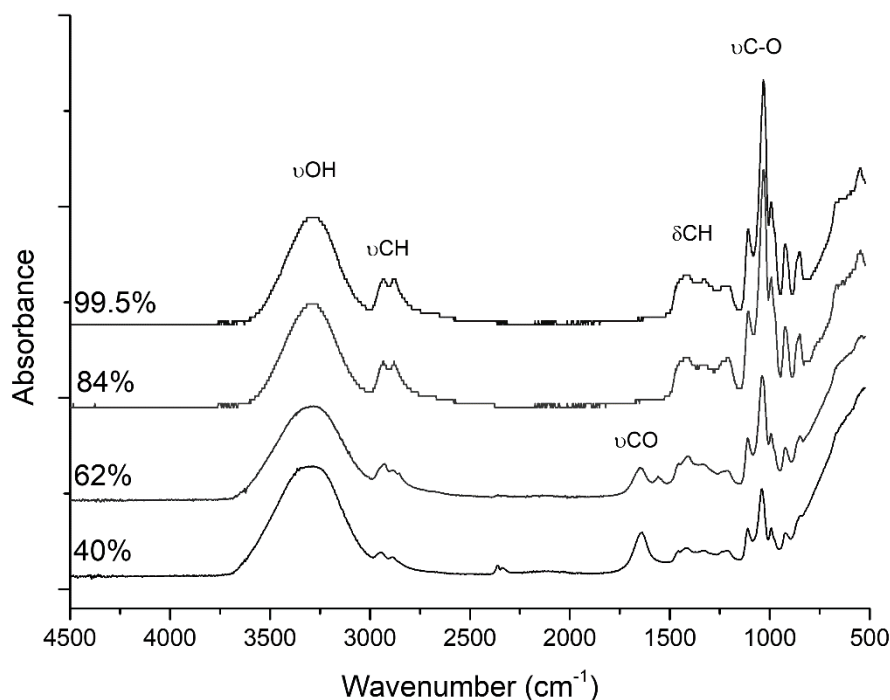
Hardness was determined according to PN-EN ISO 868:2005 standard using an electronic durometer type A Zwick/Roell. Shore A durometer perpendicularly applied for 3 s.

3. RESULTS AND DISCUSSION

3.1. Crude and refined glycerine

A comparison of the chemical structures of glycerine used for the decomposition is shown in **Figure 1**. The obtained spectrum for a GL84 sample is practically identical to the spectrum of the sample with pharmaceutical purity represented by GL99.5. All visible absorption bands of these samples correspond to the absorption band of pure glycerine. However, they may have differed in intensity or width, caused by some minor impurities³⁶. The absorption band in range 3600 – 3000 cm⁻¹ is associated with stretching vibration of the hydroxyl group of glycerol and methanol. For sample GL62, the intensity of the peak is the smallest, which is consistent with the information presented in **Table 1**. Other glycerine-specific peaks occur at wavelengths in the range of 2990 – 2700 cm⁻¹ and 1520 – 1150 cm⁻¹ and are caused by stretching and bending vibrations of C-H group, respectively³⁶. The absorption bands around 1150 – 950 cm⁻¹ is associated with

stretching vibration of C–O bond present in primary or secondary hydroxyl groups current in glycerine. All of the absorption mentioned above bands also occur in samples GL62 and GL40, but their intensity is lower, which confirms the increased presence of impurities, which are visible in the form of additional absorption bands at wavenumbers 16370 and 1559 cm^{-1} . The absorption band at 1580 cm^{-1} present in sample GL62 corresponds with the absorption of the carbonyl group of an ester or carboxyl acid from matter organic non-glycerol (MONG) impurities ³⁷. Also, peak at 1638 cm^{-1} wavelength visible for sample GL40 and GL 62 is also attributed to MONG pollution ^{38,39}. The relatively high absorption intensity for the wavenumber 1202 cm^{-1} in the case of the GL84 sample compared to sample 99.5, may be associated with the stretching vibration of the saturated aliphatic esters derived from the MONG ³⁸.



(Single column fitting image) Figure 1. FTIR spectra of crude and refined glycerine.

Table 1 presents the composition of glycerine used for the decomposition process. In the case of glycerine with a glycerol content of 40%, an approximate composition was given, which depends on the batch of material. The apparent decrease in the density of glycerine with the lowering of the glycerol content is caused by the increased amount of impurities. In addition, the presence of impurities significantly affects the colour of glycerol, glycerine with a high degree of purity are transparent, while those with low purity are brown. All samples of glycerol with the exception of GL62 are liquid at room temperature, a different state of sample GL62 could be the reason for obtaining single-phase glycerolysate. In Table 1 a possible number of active hydroxyl groups per glycerine are also presented. The number of moles OH were calculated from glycerol, methanol and water amount. Therefore, there is evident indication that the lowest reactivity during glycerolysis will reveal glycerine purity 62%. Nevertheless, this calculation is shown only to present the possibilities of other reaction during the decomposition with crude glycerine such as alcoholysis (here methanolysis) and hydrolysis. However, these two reactions run less effectively under normal conditions (only elevated temperature) without higher pressures or even supercritical conditions 40,41.

3.2. Chemical structure of recovered polyols

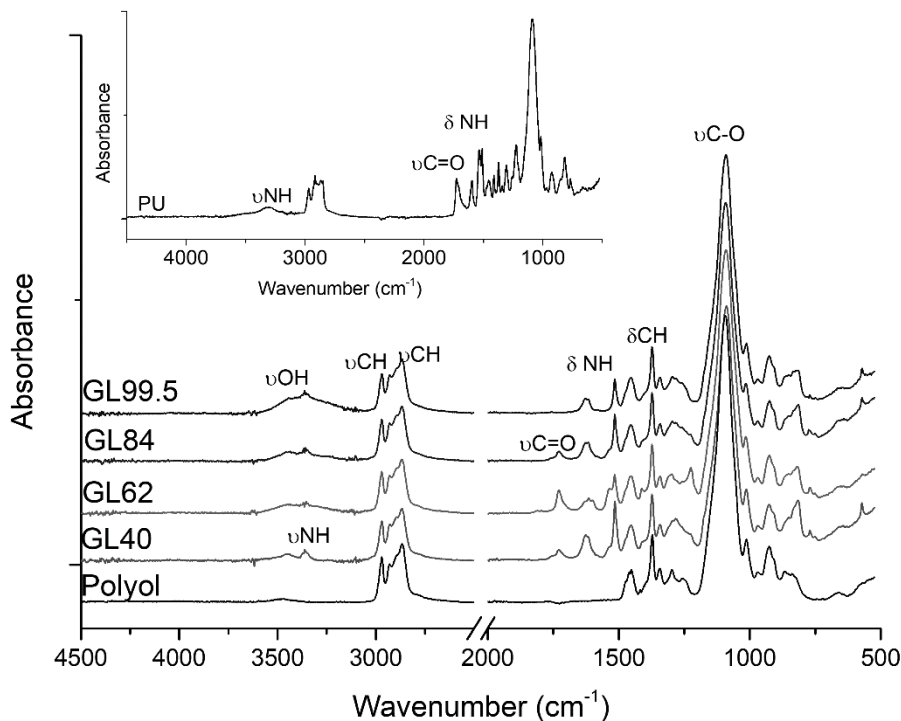
The chemical structure of described recovered polyols, confirmed by FTIR spectroscopy is presented in **Figure 2**. In general view, the spectra of all glycerolysates exhibit similar absorbance bands, what suggest a similar to some extent chemical structure. In the range of $3600 - 3200 \text{ cm}^{-1}$ wavenumber occurs the characteristic stretching vibration of the hydroxyl group. It can be the result of the presence of unreacted glycerol during the



reaction. The intensity of this band increases with a higher purity of glycerine used for the decomposition, as probably more glycerine stayed in the reaction medium. It also correlates with hydroxyl values of glycerolysates. However, for the glycerolysates, that band is also overlapped with the peak corresponding to the stretching vibration of –NH group at 3362 cm^{-1} , derived from the broken urethane bond. The absorption bands at wavenumber in the range $2950 - 2870\text{ cm}^{-1}$ are ascribed to symmetric oscillation of –CH₂ and –CH₃ groups ⁴². Whereas, peak at wavenumber 1727 cm^{-1} is characteristic for carbonyl group C=O and occurs with the highest intensity for the GL62 sample. This peak corresponds to the urethane linkage, and when the band exhibits lower intensity absorbance, the complete decomposition of PU was achieved. This region can also be associated to carbamates which were formed during the transesterification. For GL99.5 sample this peak almost disappeared, and it can be suggested that the conversion of PU was high. The absorption band at 1624 cm^{-1} is associated with bending vibration –NH group assigned to amines similar to methylene diphenyl diamine which can be reaction by-product ⁴³. Bands at 1540 and 1514 cm^{-1} correspond to the stretching vibration of –NH in amines and vibrations of C=C, respectively. The absorption bands in the region of $1450 - 1300\text{ cm}^{-1}$ can be ascribed to the bending deformation of the methylene group in the polymer chain. For GL62 sample an additional peak occurs at 1220 cm^{-1} which is associated with the C–O (urethane) band of urethane bonds it can be assumed that those samples are more contaminated with carbamates ⁴⁴. That is another difference from other glycerolysates, as that sample was homogenous, not split into two phase and therefore this sample is more contaminated with the degradation by-products. The characteristic intense band at 1090 cm^{-1} is derived from stretching vibration of the C–O–



C of ether group in the polyol. Peaks recorded at 914 and 809 cm^{-1} are presumably derived from the C-H bond vibration ⁴².



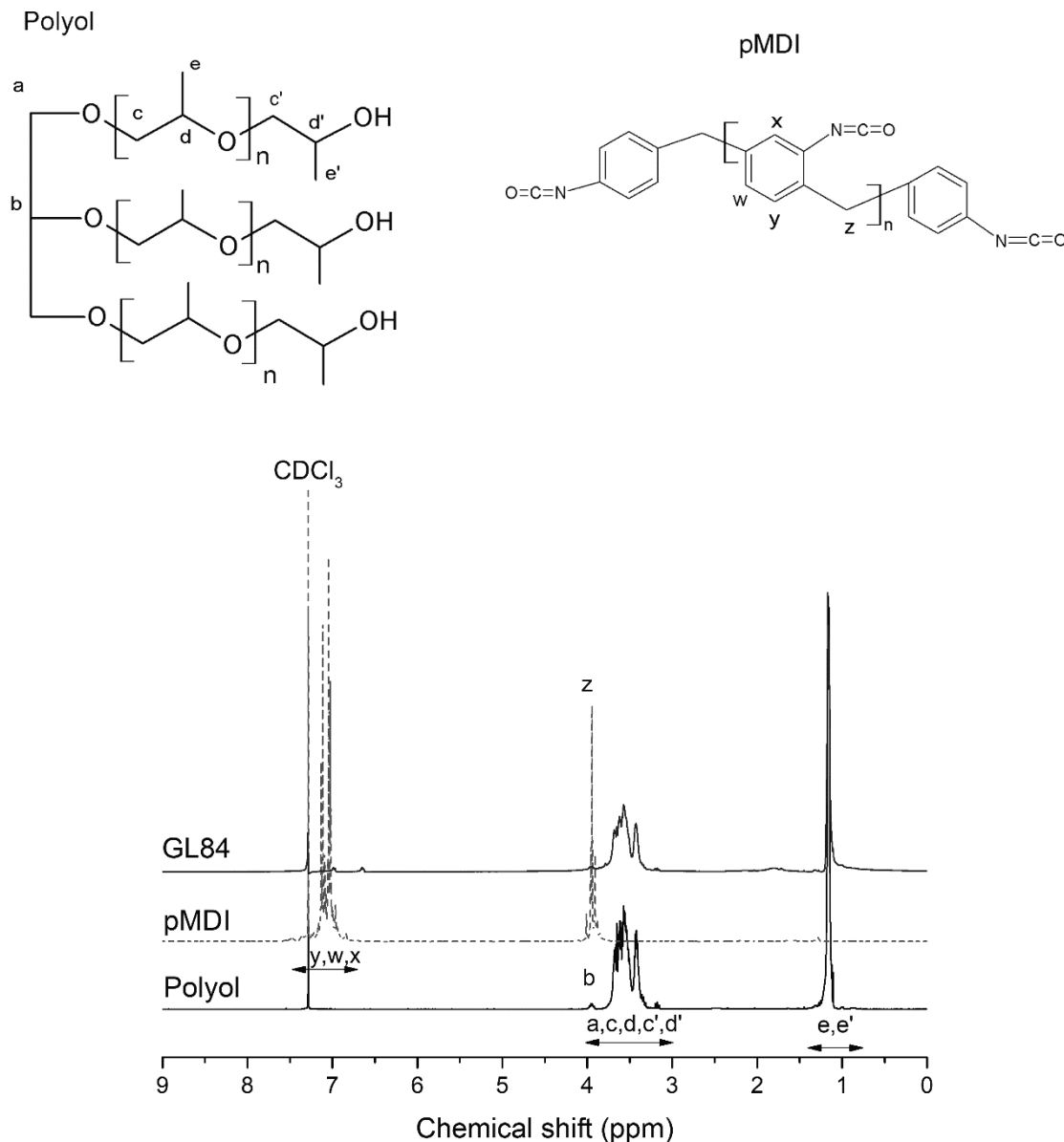
(Single column fitting image) Figure 2. FTIR spectra of resulting recovered polyols obtained with glycerine of various purity.

The conversion rate calculated from FTIR spectra according to the Eq. 1 and 2 are 76.5, 51.8, 78.4 and 95.9% for GL40, GL62, GL84 and GL99.5, respectively. The decomposition reactions were conducted at the same time, 30 min. The influence of the glycerine type is noticeable. The highest conversion exhibits GL99.5, the lowest GL62 sample. It is probably related to the higher possibility of breaking urethane linkage by the more pure glycerol. Moreover, it can be connected with a lower number of effective hydroxyl groups in the crude glycerine compared to others of purity 62% (**Table 1**). The low conversion for GL62 can also be associated with forming more low molecular weight

carbamates, as it was shown in GPC results (**Table 2**). However, the conversion rate probably could be increased by the longer conducting the reaction as it was reported in the literature work ⁴⁵.

The differences between the structure of virgin polyol and chosen recovered polyol (GL84) were analysed by ¹H NMR (**Figure 3**). For more precise structure description of glycerolysate, the chemical structures of original polyol and pMDI are presented. The main protons in these compounds are marked by letters in their chemical formula, and they are assigned to the corresponding peaks in the spectra. The peak located at 7.23 ppm in spectra was attributed to the solvent CDCl₃ used for sample preparation. The polyol spectrum exhibits multiple peaks in the range of 3.4 – 4.0 ppm which are related to methylene hydrogen's (-CH₂) and hydrogen's which their carbons are directly connected to the oxygen (-CH₂O). The intense peak at 1.15 ppm is ascribed to methyl equivalent hydrogen's (-CH₃) and represents a side chain of the polyol. Concerning the spectrum of GL84 the same peaks corresponding to the same chemical shifts as for polyol spectrum was observed. Apart from these, the presence of some new peaks was noticed. Considering the impurities, the peak at around 3.95 ppm was assigned to CH₂ protons, which are associated with the pMDI units (z protons). The new peaks observed in the range of 6.7–7.1 ppm evidenced the presence of aromatic structures derived from the isocyanate ^{31,46} suggesting that some by-products from the decomposition reaction remained.





(Single column fitting image) Figure 3. ¹H NMR spectra of GL84, neat polyol and pMDI.

GPC chromatograms of recovered and virgin polyols are presented in **Figure 4**. Glycerolysates are more heterogeneous than the neat polyol as there can be featured additional peaks coming from the by-products present in glycerolysate such as carbamates and diamines (as it was confirmed by FTIR analysis). During the

decomposition reaction, polyurethane is converted into smaller molecules by cleavage agent (glycerine) and the polyol is released into reaction media. The first peak is assigned to the oligomers, which poses higher molecular weight than polyol. The second peak and third peaks correspond to recovered polyol and reaction by-products such as carbamates and amines, respectively ⁴³.

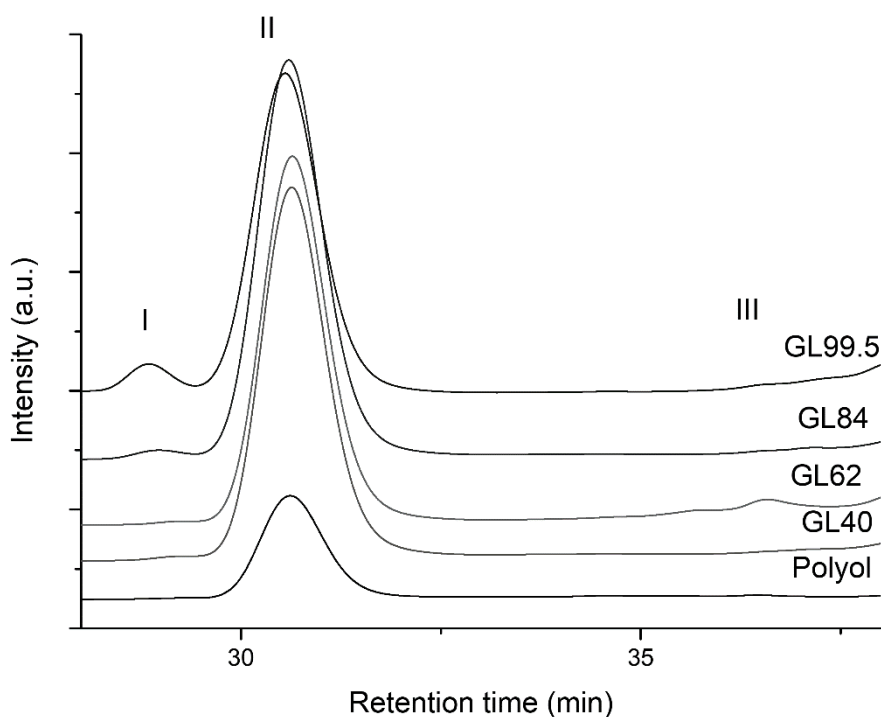


Figure 4. GPC curves of virgin and recovered polyols.

The integration of the chromatogram peaks allowed for estimating the percentage by weight (**Table 2**). The significant share has polyol. However, the molecular weight of glycerolysates is different from the virgin polyol due to the presence of higher molecular weight oligomers and lower molecular weight by-products. The difference between each of recovered polyols is noticeable. The highest contamination with by-products was observed for a GL62 sample which was by the FTIR analysis, where bands associated

with amine groups showed high absorbance intensity. It can be a result of a lesser number of moles of OH groups. The presence of oligomers for GL84 and GL99.5 can be a result of forming possibility higher molecules because these two types glycerine were less contaminated with compounds such as water and methanol in the case of glycerine with 40 and 62% of the purity grade. That could cause simultaneous reaction of glycerolysis and hydrolysis of what could result in obtaining lower molecular weight semi-products. Moreover, the metal hydroxide catalyst can influence the formation water during the decomposition ³¹. Overall, the recovered polyols can be described as quite similar to the original polyol (over 90% of polyol recovery) therefore the functionality of these compounds can be estimated approximately 3.

The hydroxyl value for the recovered polyols using GL40, GL62, GL84 and GL99,5 was 155, 164, 183 and 220 mg KOH g⁻¹, respectively. The hydroxyl value is an essential parameter in planning the synthesis of new polyurethane materials. It determines the content of hydroxyl groups which, in combination with multifunctional isocyanates, are capable of forming a urethane moiety [-OCONH-] ⁴⁷. The determination of the hydroxyl number thus serves to assess the degree of polymerisation of the glycerolysates. The lowest hydroxyl value exhibits sample GL40, the highest GL99.5. It can be concluded that with higher purity degree of the glycerine, the higher hydroxyl value is achieved. It is connected with the composition of the glycerine itself, as they contain a higher amount of the glycerol. It is possible that because of it the reaction is slower when higher purity grade glycerine is applied, as the decomposition undergoes only with glycerolysis, not combined with hydrolysis or alcoholysis as it is in the case of low purity crude glycerine.



The amine value expressed in mg KOH g⁻¹ was 1 for GL40, 5 for GL62, and 0 for samples GL82 and GL99.5. The presence of the high amount of amine group is an undesirable option, as it can further influence on the polyurethane synthesis for example by the higher crosslinking of newly produced materials. The highest value indicates sample GL62 which is in accordance with FITR and GPC analyses. However, the lack of amine value for GL84 and GL99.5 may mean that during the decomposition were formed carbamates than amines rather, as by-products formed during transesterification reaction.

3.3. Rheology

The rheology measurements were performed to have an insight into the possible industrial processing of these recovered polyols for example during polyurethane synthesis. The results will show the best processing temperatures and speed when used agitation.

The viscosity at 50 °C was estimated during constant shear rate mode at 300 s⁻¹. It was found that the use of more pure glycerine in the decomposition caused a decrease in viscosity. Therefore the effect of present impurities in crude glycerine it noticeable.

The flow curves represent a graphical dependence of the shear stress recorded during the flow as a function of the shear rate. The flow curves were plotted at 50 and 70 °C (**Figure 5a**). The shear stress increases with the increasing shear rate. The shear stress is decreasing with raising the temperature about 20 °C twice times. The highest shear rate was recorded for the GL40 (250 Pa), the lowest for GL99.5 (102 Pa). The relationship between the glycerine used and the shear stress is visible. The more

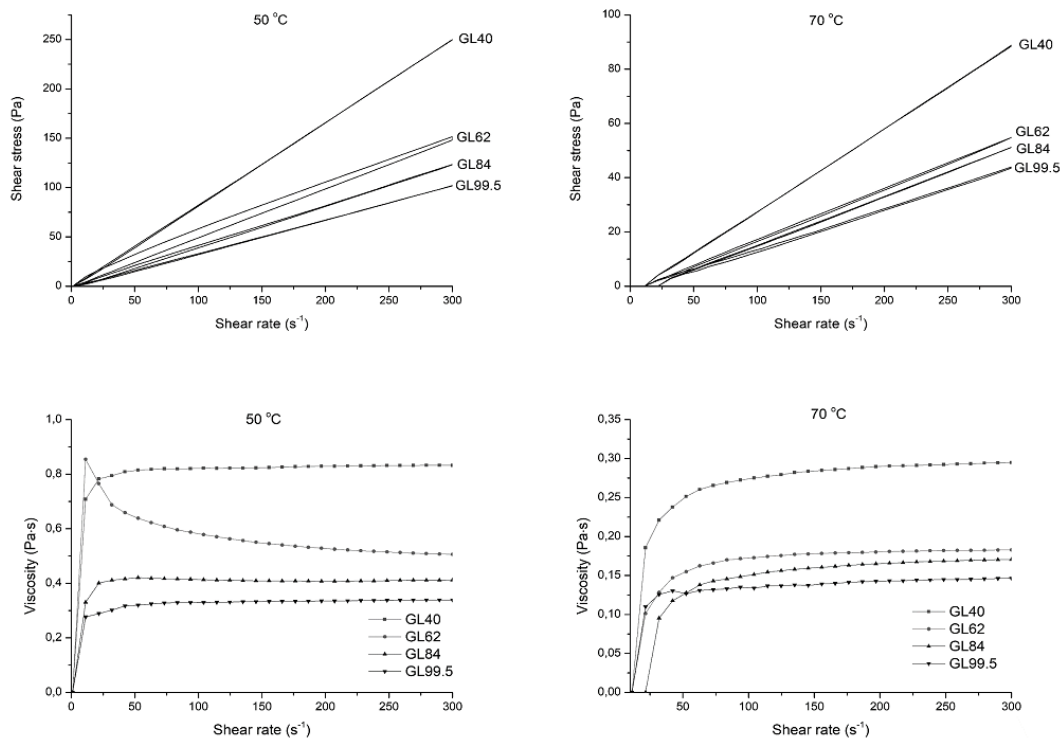


contaminated glycerol used for PU decomposition, the higher shear stress. It may be due to the presence of impurities resulting from the saponification of fats in the applied glycerine. The trend is that with higher purity grade of glycerine, the lower shear stress is evident for all chosen temperatures. However, the composition of glycerolysate itself can indicate the changes as for sample with higher molecular weight hence longer chains are present in the sample. Moreover, for samples with more complex structure, hysteresis loops are present. Mainly it is visible for a GL62 sample which presents the most heterogeneous structure with the presence of small molecular weight by-products which can shear under stress. The obtained flow curves show almost linear behaviour, especially at high shear rates. The return of the curves to the initial point allows to state that the glycerolysates have properties of non-Newtonian fluids that return to their original viscosity with the disappearance of shear forces ³¹.

The viscosity curves show the graphical dependence of the dynamic viscosity changes of the liquids studied on the shear rate. These characteristics were developed based on the results of rheological tests at temperatures of 50 and 70 °C for each of the glycerolysates (**Figure 5b**). The obtained viscosity curves show that as the shear rate increases, changes in viscosity can be observed and from a shear rate about 100 s⁻¹ it stabilises and the plateau is reached. Similar curves exhibit glycerolysates GL40, GL84 and GL99.5. For these samples, there is the tendency of fast increasing viscosity with increasing shear rate up to constant value, in both chosen temperatures which can be ascribed as dilatant liquids. For sample GL62 the viscosity curve at 50 °C exhibit different course. At first, it reaches high viscosity peak and with increasing the shear rate it values decreases. A sharp drop in viscosity with an increase in shear rate may be the effect of disrupting bonds in the tested samples or a change in the orientation of



molecules in the direction parallel to the flow (shear thinning). However, the curve for GL62 at 70 °C looks differently and presents a dilatant behaviour.



(2-column fitting image) Figure 5. a) Flow curves of glycerolysates at 50 (left) and 70 °C (right) and **b)** Viscosity curves of glycerolysates at 50 (left) and 70 °C (right).

The viscosity provides information about the behaviour of the material and determines the measure of resistance it puts when flowing ⁴⁸. **Table 3** presents the differences in the achieved average viscosity values of glycerolysates at various temperatures. It is noticeable that the viscosity of the polymers decreases with increasing temperature, which can be explained by the increase in the mobility of the macromolecules and the free volume between them. It was found that the use of more pure glycerine for PU decomposition caused a decrease in viscosity. The highest value of medium viscosity at 50 °C is achieved by GL40. On the other hand, the lowest



average viscosity values can be attributed to glycerolysates GL99.5 in the whole temperature range. It can be a distinguished correlation between viscosity and hydroxyl number as with higher hydroxyl number of glycerolysates, the lower viscosity.

Table 3 also presents the parameters derived from rheological models: Herschel-Bulkley (HB) and Ostwald. The results were calculated using the Rheo3000 program. The chosen optimal model was by matching the highest determination coefficient (R^2) for the tested sample. Those models are described by following equations:

$$\tau = \tau_0 + m \cdot \gamma^n \text{(HB)} \quad (1)$$

$$\tau = m \cdot \gamma^n \text{(Ostwald)} \quad (2)$$

Where τ is shear stress (Pa), τ_0 is yield stress (Pa), m the consistency index (Pa·s) and n flow index, γ shear rate (s^{-1}). These parameters allows for describing the different behaviour of fluids. These glycerolysates are included to the non-Newtonian fluids as they tend to exhibit dilatant or pseudoplastic behaviour, therefore Herschel-Bulkley or Ostwald models are chosen ⁴⁹.

Almost for all recovered polyols in applied temperatures, the most suitable model was Herschel-Bulkely. The exception is sample GL62, for which at 50 °C the best matching model would be Ostwald. It is probably due to its more viscous nature in comparison to other recovered polyols, which is confirmed by the consistency index (high $m=1$). Moreover, only for that sample, the flow index is $n=0.869 < 1$. Therefore this fluid exhibit the pseudoplastic behaviour and this sample can be characterised as shear thinning fluid. This correlated with the viscosity curves **Figure 5b**. For glycerolysates described by Herschel–Bulkley model, samples in the whole temperature range have flow index higher than 1 hence can be described as dilatant fluid, which means they

become thicker as the higher shear stress is applied. In addition, it can be noticed that all samples with higher applied temperature become more dilatant and their consistency index is decreasing. Therefore these samples at high temperatures will be characterised by low viscosity, but with higher speed rotation they will become thicker ⁴⁹.

3.4. Valorisation of the glycerolysates in polyurethane synthesis (preliminary study)

The presented and described glycerolysates were used as a component in cast polyurethane synthesis to evaluate their usefulness in this application. Although that the decomposition was carried out on the foam, obtained glycerolysates could be applied in solid polyurethanes (not foams).

The composition of each polyurethane differed with the glycerolysate, GL40 or GL84, and the amount of used glycerolysate instead of neat polyol, which supposed to act as a polyol in prepolymer mixture due to the presence of active hydroxyl groups in the end of the polymer chain that can react with isocyanate groups. For the produced polyurethanes, the ratio of NCO to OH groups was 1.0, while glycerolysates accounted for 5 or 10% with respect to the polyol. However, due to the higher hydroxyl value of glycerolysates than neat polyol (56 mg KOH g⁻¹), the amount of MDI was higher to keep a constant percentage of unreacted isocyanate group in the prepolymer. The glycerolysates were much more active than neat polyol due to their composition (a mixture of various compounds) therefore, to stabilise prepolymerisation reaction more inhibitor was used in accordance with the amount of used recovered polyol. The role of phosphoric acid was to inhibit secondary reaction such as the reaction of isocyanate with carbamates or amines instead of polyol (recovered and neat). Moreover, because



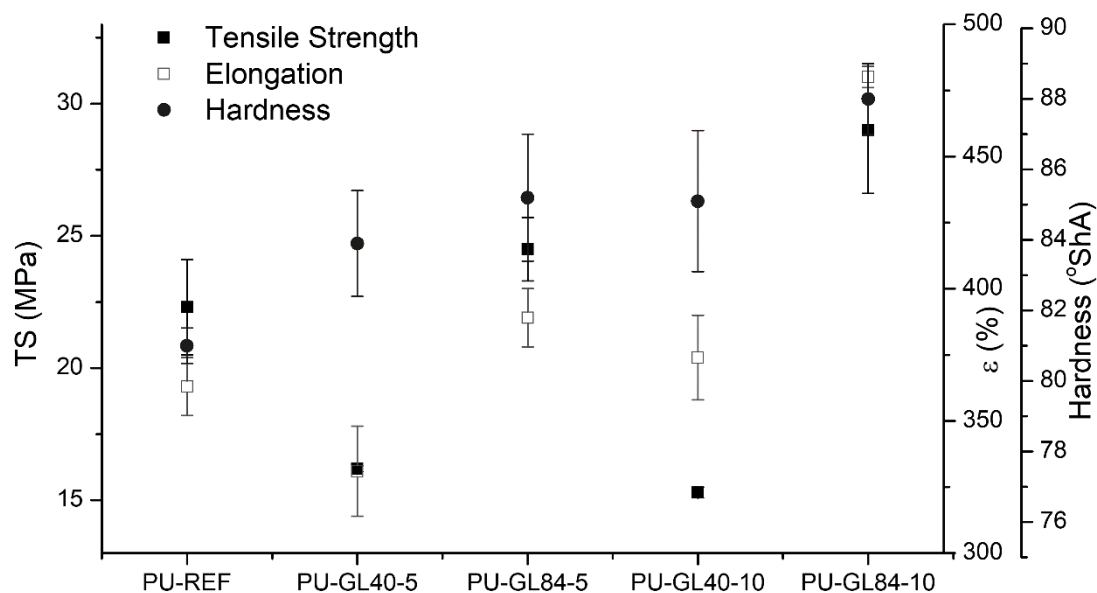
of the reactivity of glycerolysates for these samples, the catalyst was not used, as in the case of the reference sample.

The obtained polyurethanes were tested by tensile strength test, and hardness was checked to provide a view of mechanical properties in this preliminary study (**Figure 6**). The sample PU-GL84-10 reveal even better properties than the reference sample, as the usage of this glycerolysate in a small amount of virgin polyol can provide more stiff yet elastic structure. This can be due to reinforcement provided by a possible linkage during the reaction. It can be noticed that the GL40, though the quite pure chemical structure causes lowering mechanical properties in comparison with PU-REF. It could be associated not only with its composition but also with the higher viscosity of the glycerolysate that could cause the trouble during degassing, mixing and casting the polyurethane into the mould.

Addition of glycerolysates caused an increase in hardness in comparison to the reference material. Also, the higher the proportion of glycerolysate, the higher the hardness values are observed. It could be caused by the probable branching or crosslinking of these samples, as used glycerolysates in contrast to the neat polyol, were not linear and functionality was approx. 3 as the polyol used for foam production was trifunctional (**Figure 3**).

Further studies on this topic are planned. The main aim will be incorporate more than 10% of glycerolysate instead of neat polyol. Moreover, the full characteristic of these materials including thermal, structural, thermo-mechanical properties will be investigated.





(Single column fitting image) Figure 6. Variation of tensile strength (TS), elongation at break (ϵ) and hardness depending on the type and amount of glycerolysates.

4. CONCLUSIONS

In this work, the research topic aims to utilise both types of waste (polyurethane and glycerine) in one reaction to obtain valuable raw materials. The use of crude glycerine instead of pure results in a successful decomposition process at a reduced cost. The recovery of a polyol, as well as the management of crude glycerine, is in line with the principles of sustainable development.

In the study, the glycerolysis reactions of flexible foam waste using glycerine with different purity grade: 40, 62, 84 and 99.5% were conducted. Obtained raw materials were characterised adequately to justify their properties acting as a polyol. The influence

of glycerine purity grade on the recovered polyols was tested. Spectroscopic analyses revealed similarity of the chemical structure of glycerolysates to the virgin polyol. However, in recovered polyols spectra new bands are visible, related to the presence of transesterification reaction by-products, namely amines and carbamates and the unreacted glycerine. The highest contamination indicated sample obtained with glycerine of 62% purity as a cleavage agent. Amines affect the increase of the amine number, which is 1 and 5 mg KOH g⁻¹ for GL40 and GL62, respectively. The degree of glycerine purity affects the rate of the decomposition process, as well as mechanism because, with lower purity of glycerine, hydrolysis and glycolysis reactions can occur due to the contamination. Glycerolysates also exhibited more heterogeneous structure in comparison to the polyols confirmed by GPC. The chromatogram of recovered polyols revealed two to three peaks corresponding to oligomers, polyols and by-products (carbamates and amines). The hydroxyl value of glycerolysates was lower for glycerolysates obtained with less pure glycerine and was 155 and 164 mg KOH g⁻¹ for GL40 and GL62, respectively. All obtained glycerolysates can be described as non-Newtonian fluids, and almost all of them exhibited dilatant behaviour, except for sample GL62 at 50 °C which acted as shear-thinning fluid. The purity of applied in decomposition glycerine also influenced the viscosity of obtained recovered polyols and resulted in higher viscosity with used lower purity grade glycerine for decomposition. The various properties of the lower grades of glycerine are caused by the occurrence of side reactions in the form of hydrolysis and alcoholysis, as well as lower reaction efficiency.

Two chosen glycerolysates were applied as a part of polyol for cast polyurethane synthesis, containing 5 and 10% of glycerolysates instead of neat polyol. The addition of



PU-GL84 caused an increase in hardness, tensile strength and elongation, in the case of PU-GL40, the hardness increased.

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Compliance with Ethical Standards

Conflict of interest. Declarations of interest: none.

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REFERENCES

- 1 Fangrui M and Milford HA *Bioresour Techno* **70**, 1–15 (1999).
- 2 Choi WJ *Recent Pat Biotechnol* **2**, 173–180 (2008).
- 3 Flach B, Lieberz S, Rondon M, Williams B and Wilson C, *Biofuels Annual: EU Annual Biofuels 2016* (2016).
- 4 European Parliament. Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009.
- 5 Hejna A, Kosmela P, Formela K, Piszczyk Ł and Haponiuk JT, *Renew Sustain Energy Rev* **66**, 449–475 (2016).
- 6 Datta J, Kopczyńska P, Simón D and Rodríguez JF, *J Polym Environ* **26**, 166-174 (2018).



- 7 Yazdani SS and Gonzalez R, *Curr Opin Biotechnol* **18**, 213–219 (2007).
- 8 PlasticsEurope. *Plastics – the Facts 2016: An analysis of European plastics production, demand and waste data*. PlasticsEurope (2016).
- 9 Park SW *et al.*, *Procedia Environ Sci* **35**, 498–505 (2016).
- 10 Singh N *et al.*, *Compos Part B* **115**, 409–422 (2017).
- 11 Djeki P, Milutinovi B and Tomi M, *A CTA Tech CORVINIENSIS – Bull Eng* **11**, 51–54 (2018).
- 12 Ragaert K, Delva L and Van Geem K, *Waste Manag* **69**, 24–58 (2017).
- 13 PlasticsEurope. *Plastics – the Facts 2017: An analysis of European plastics production, demand and waste data*. (2017).
- 14 Howard GT, *Int Biodeterior Biodegrad* **49**, 245–252 (2002).
- 15 Khan S *et al.*, *Environ Pollut* **225**, 469–480 (2017).
- 16 Grause G, Buekens A, Sakata Y, Okuwaki A and Yoshioka T, *J Mater Cycles Waste Manag* **13**, 265–282 (2011).
- 17 Al-Salem SM, Lettieri P and Baeyens J, *Waste Manag* **29**, 2625–2643 (2009).
- 18 Datta J and Kopczyńska P, *Crit Rev Environ Sci Technol* **46**, 905–946 (2016).
- 19 Rahimi A and García JM, *Nat Rev Chem* **1**, 1–11 (2017).
- 20 Schneiderman DK *et al.*, *ACS Macro Lett* **5**, 515–518 (2016).
- 21 Paabo M and Levin BC, *Fire Mater* **11**, 1–29 (1987).
- 22 Oblinger FG, Hydrolytic decomposition method. US 4 281 197 (1981).
- 23 Pizzini LC, PattorT and Patton JT, Process for recovery of polyether polyols from polyurethane reaction products. US 3 441 616. (1969).
- 24 Zia KM, Bhatti HN and Bhatti AI, *React Funct Polym* **67**, 675–692 (2007).
- 25 Yang W *et al.*, *Procedia Environ Sci* **16**, 167–175 (2012).



- 26 Nikje MMA, in *Recycling of Polyurethane Wastes*. 13–48 (Smithers Rapra Technology, 2016).
- 27 Simón D, Borreguero AM, de Lucas A and Rodríguez JF, *Waste Manag* (2018).
doi:10.1016/j.wasman.2018.03.041
- 28 Nikje MMA and Nikrah M, *Polym Bull* **58**, 411–423 (2007).
- 29 Nikje MMA and Mohammadi FHA, *Polimery* **54**, 541–545 (2009).
- 30 Simón D, García MT, De Lucas A, Borreguero AM and Rodríguez JF, *Polym Degrad Stab* **98**, 144–149 (2013).
- 31 Kopczyńska P and Datta J, *Polym Eng Sci* **57**, 891–900 (2017).
- 32 Murai M, Sanou M, Fujimoto T and Baba F, *J Cell Plast* **39**, 15–27 (2003).
- 33 Datta J and Kopczyńska P, Method of glycerolysis of polyurethane waste product and glycerolysates obtained by the method. EP 3 098 257 A1. (2015).
- 34 Jutrzenka Trzebiatowska P, Deuter I and Datta J, *React Funct Polym* **119**, 20–25 (2017).
- 35 Wu C-H, Chang C-Y and Li J-KG, *Polym Degrad Stab* **75**, 413–421 (2002).
- 36 Carriço CS, Fraga T, Carvalho VE and Pasa VMD, *Molecules* **22**, (2017).
- 37 Nanda M, Yuan Z and Qin W, *Austin J Chem Eng* **1**, 1–7 (2014).
- 38 Maru BT, López F, Kengen SWM, Constantí M and Medina F, *Fuel* **186**, 375–384 (2016).
- 39 Yong KC, Yunus W, Ooi T, Dzulkefly K and Hazimah AJ, *Oil Palm Res.* **13**, 39–44 (2001).
- 40 Liu L, Tang L, Wu Y, Ni Y and Zhu Z, *Polym Degrad Stab* **98**, 2520–2528 (2013).
- 41 Nemade AM, Mishra S and Zope VS, *Polym Plast Technol Eng.* 37–41 (2009).
- 42 Coates J, *Interpretation of Infrared Spectra, A Practical Approach. Encyclopedia of*



Analytical Chemistry (John Wiley & Sons Ltd, 2000).

- 43 Simón D, Borreguero AM, de Lucas A and Rodríguez JF, *Polym. Degrad. Stab.* **121**, 126–136 (2015).
- 44 Kopczynska P and Datta J, *Polym. Int.* **65**, 946–954 (2016).
- 45 Hekmatjoo N *et al.*, *Polym. Int.* **64**, 1111–1120 (2015).
- 46 Nikje MMA, Nikrah M and Mohammadi FHA, *J Cell Plast* **44**, 367–380 (2008).
- 47 Prociak A, Rokicki G and Ryszkowska J, *Materiały poliuretanowe*. (PWN, 2014).
- 48 Sunthar P, in *Rheology of Complex Fluids* (eds. Deshpande AP, Krishnan JM and Kumar S) 171–191 (Springer-Verlag, 2010).
- 49 Wilczyński K, *Reologia w przetwórstwie tworzyw sztucznych*. (WNT, 2001).



Table 1. Physical and chemical properties of used glycerine.

Purity grade of glycerine	99.5%	84.5%	62%	40%
Density (g cm⁻¹)	1.261 (at 20 °C)	1.262 (at 25 °C)	1.231(at 40 °C)	1.176 (at 25 °C)
Form	Liquid	Liquid	Paste	Liquid
Colour	Transparent	Pale brown	Brown	Brown
Odour	Characteristic	Characteristic	Characteristic	Characteristic
Other	-	-	T _m =37 °C	-
The content of individual compounds and impurities in glycerine				
Glycerol (%)	99.54	85.40	62.0	40
Ashes (%)	<0.01	3.14	2.2	2–5
Water (%)	0.17	10.20	2	10–12
Methanol (%)	0.26	0.26	8	42–44
MONG (%)	-	1.8	21.0	2-5
Number of moles of OH group*	3.26	3.9	2.49	3.86

*Calcuated per 100 g of glycerine

Table 2. GPC results where M_{p1} represents M_n of the first peak etc. and the concentration of the product in the recovered polyols.

Sample	Peak 1		Peak 2		Peak 3		ΣM_n *% by weight
	M_{pI}	% by weight	M_{pII}	% by weight	M_{pIII}	% by weight	
	(g mol ⁻¹)		(g mol ⁻¹)		(g mol ⁻¹)		(g mol ⁻¹)
GL40	-	-	3586	99.3	201	0.7	3562
GL62	-	-	3584	98.1	206	1.9	3490
GL84	8228	0.8	3653	99.0	200	0.2	3683
GL99.5	8598	4.2	3724	93.8	202	2.0	3858
Poyol	-	-	3600	100	-	-	

Table 3. The model functions based on the rheological data glycerolysates samples and their viscosity

Sample	T (°C)	η (Pa·s)	Model	τ_0 (Pa)	n	m (Pa·s ⁿ)	S	R ²
GL40	50	0.83	Herschel–Bulkley	0	1.022	0.733	0.59	0.9999
	60	0.47	Herschel–Bulkley	0	1.045	0.367	0.59	0.9998
	70	0.29	Herschel–Bulkley	0	1.077	0.191	0.49	0.9996
GL62	50	0.50	Ostwald	-	0.869	1	4.88	0.9972
	60	0.29	Herschel–Bulkley	0	1.028	0.248	0.81	0.9998
	70	0.18	Herschel–Bulkley	0	1.084	0.114	0.50	0.9990
GL84	50	0.41	Herschel–Bulkley	0	1.028	0.349	0.99	0.9992
	60	0.26	Herschel–Bulkley	0	1.087	0.158	0.48	0.9995
	70	0.17	Herschel–Bulkley	0	1.132	0.081	0.40	0.9992
GL99.5	50	0.34	Herschel–Bulkley	0	1.045	0.262	0.47	0.9997
	60	0.22	Herschel–Bulkley	0	1.092	0.129	0.45	0.9994
	70	0.15	Herschel–Bulkley	0	1.104	0.081	0.41	0.9989

The influence of different glycerine purities on chemical recycling process of polyurethane waste and resulting semi-products

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Research has been carried out on the effect of glycerine purity on chemical decomposition products of polyurethanes. Glycerolysates have been used to obtain cast polyurethanes.

