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Single-phase product obtaining via crude glycerine depolymerisation of polyurethane elastomer: Structure characterisation and rheological behaviour.

Patrycja Kopczyńska[a], **Janusz Datta**[a*]

Abstract

Polyurethane recycling is a topic of growing interest due to the increasing amount of polyurethane waste. The main purpose of polyurethane feedstock recycling is to recover the starting polyol, a valuable material. In this work, a method of polyurethane thermo-chemical recycling, glycerolysis by means of crude glycerine is proposed. The main effort of this paper is focused on the employment of crude glycerine without purification from the biodiesel production, as decomposing agent for polyurethane recycling. The influence of polyurethane to glycerine mass ratio (PU/GL) on chemical structure analysed by FTIR, ^{1}H NMR and GPC, glass transition (T_g) and thermal properties by DSC and TGA and rheology were examined. FTIR and ^{1}H NMR analysis of the glycerolysates showed peaks similar to virgin polyol. From GPC chromatograms was concluded that glycerolysates are a mixture of compounds with different molecular weight such as recovered polyol, urethane oligomers or carbamates. Glycerolysates indicated T_g in the range from -65 to -60 ^{o}C and for high PU/GL ratio, second T_g appeared. Thermal stability of glycerolysates increases with higher PU/GL ratio. The molecular weight of glycerolysates was ranging from 700 to 1020 g mol^{-1} depending on PU/GL mass ratio. The semi-products were defined as non-Newtonian fluids, where viscosity depended on the shear rate. Crude glycerine, derived from biodiesel production, was successfully used in polyurethane decomposition process and resulted valuable semi-products.

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[*] Correspondence to: jandatta@pg.gda.pl

[a] Department of Polymer Technology, Faculty of Chemistry, Gdańsk University of Technology
G. Narutowicza Str. 11/12, 80-233 Gdańsk, Poland

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INTRODCUTION

Polyurethanes (PUs) are a group of plastics, which has a very large range of applications due to their variable structure depending on used substrates and reaction mechanisms. Pus can be obtained in the form of foams (rigid, elastic, viscoelastic), elastomers, adhesives, coatings etc. They are used as upholstery and mattresses sponges in the furniture industry, automotive industry, as insulating materials, adhesives and glues, in refrigeration, as packaging product, shoe soles and in many other industries and articles of daily use.[1, 2] PUs are placed sixth in the global market for plastic production, which corresponds to about 14 million tonnes produced PUs, thus representing ca. 6% of all plastic waste (Plastemart (http://www.plastemart.com/)). With such huge quantities, the storage of generated PU waste, both post-production and post-use, it is burdensome and should not be practiced in the future. The situation takes place because PUs occupy a very large area due to their low density (in a case of PU foams app. 0-100 kg m^{-3}),[3] poor biodegradability and it pose a threat to the environment. Additionally, polyurethanes are quite expensive materials (compared to polyethylene) so preferably would be to reuse post-consumer and waste materials during processing. Moreover, in recent years the quantitative limits of waste destined for disposal are implemented, in accordance with international regulations (Eur-LeX, European Directive 1999/31/WE (http://eur-lex.europa.eu/)). For this reason, management and reprocessing of polyurethane waste becomes nowadays a necessity. Recycling is an alternative approach to the landfilling of waste. In addition to reducing the amount of waste itself, giving it the prospect of saving natural resources because polymer materials are made mostly from oil and gas.[4, 5] The most common methods are mechanical recycling, chemical recycling and incineration (energy recovery).

Chemical recycling of plastics is based on the decomposition of polymer by means of heat, chemical or catalytic agent, to yield products ranging from the chemical monomers to a mixtures of compounds, which can be a source of chemicals or fuels. Feedstock recycling processes can be classified into three main areas: recycling to fuels (gasoline, liquefied petroleum gas (LPG) and diesel oils), recycling to monomers and recycling to industrial chemicals (Ylä-Mella J (http://www.oulu.fi/resopt/PlastRec.pdf)). In feedstock recycling of PUs the urethane, urea and biuret groups are treated through chemical reaction with a special decomposing agent. The most well-known chemical recycling methods include: hydrolysis (chemical agent: water),[6] glycolysis (glycols),[7] alcoholysis (alcohol), acidolysis (organic acids) and aminolysis (amines).[8, 9] Glycerine has been also proposed as decomposing agent with promising results.[10]

Obtained from PU decomposition intermediates, often named re-polyols can differ between each other due to the used decomposition agent,[11, 12] catalyst,[13] reaction temperatures and parameters[14] and different waste material to reaction agent ratios.[15] The waste to agent ratio influences on physical properties (change in OH number, density, viscosity) and chemical structure of obtained decomposition semi-products. The semi-products indicate very often properties close to commercial substrates, so many researchers prepared new polyurethane material e.g. elastomers,[15, 16] or foams[17] contained re-polyols as a component replacing partially or completely commercial polyol. Polyurethane system are manufactured in different types of polyurethanes (flexible and rigid foams, elastomers, adhesives, varnishes).[18] The main ingredient of such system is mostly oligomer or polyol (60-70%), mostly this component is from petrochemical source. Nowadays, the idea is to introduce renewable (i.e. vegetable oils[19] or recycled components to reduce the share of substrates derived from fossil fuels. Therefore introducing the obtained chemical recycling semi-products seems to be a promising way. In addition, another advantage can be lowering the cost of production, due to using re-polyol obtained from recycling process i.e. glycolysis can be several times cheaper than commercial polyols. Nikje et al. used recycled polyol in synthesis of integral skin foam, where re-polyol obtained from glycolysis of polyurethane waste was mixed with the virgin polyol in amounts of 30, 40, 50 and 60%.[20] They found that the glycolysis method and its product has an approximately similarity with foam formulated by virgin polyol. Simon et al.[21] prepared flexible and rigid polyurethanes foams products of polyurethane glycolysis, from the upper and bottom phase, respectively.

However, the preparation of polyurethane system depends on the number of chemical (OH number, water content, molecular weight) and mechanical factors as well. The viscosity of the used components and final system is very important factor for polyurethane processing. The knowledge about rheological behaviour be important during the production where stirring, dispensing and pumping of the product will subject it to a variety of shear rates. Rheology studies can be very helpful in the selection of the temperature and pressure programs used in the processing of polymer materials, including reactive polyurethane mixtures.

In the following years, the biodiesel production become a matter of interest, as is predicted the European Directive 2003/30 / EC of 2003, which implies that the share of bio-components in the transport fuel market should be at 2% in 2005, 5.75% in 2010 and 20% in 2020 (Eur-LeX, European Directive 2003/30 / EC (http://eur-lex.europa.eu/)). Biodiesel is produced in the transesterification reaction of vegetable oil or animal fat with an alcohol (e.g. methanol) in the presence of alkaline catalyst (Figure 1).

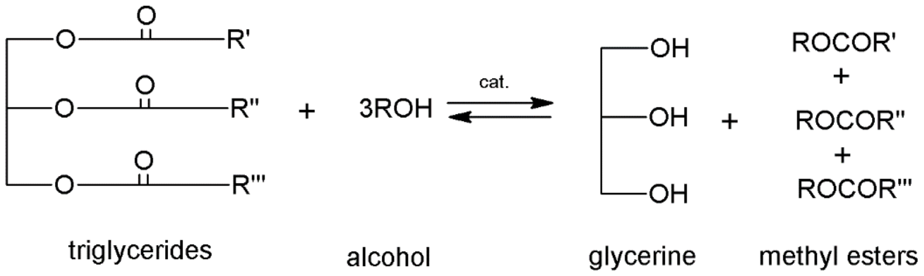

Figure 1. A schematic representation of the transesterification of triglycerides (vegetable oil or animal fat) with alcohol to produce fatty acid methyl esters (biodiesel). R’, R’’ and R’’’ are long hydrocarbon chains, sometimes called fatty acid chains.

Glycerine is obtained as by-product from biodiesel production. For every 1 L of biodiesel are obtained 200-250 g of waste glycerine phase. After the transesterification, a settling is carried out to separate product on two phase: ester and glycerine phase. Depending on the installation and the process conditions, the glycerol content in by-products ranges between 30% -80%. Such crude glycerine can be further purified and refined. Most of the glycerine potential applications require complex and costly refining processes in order to obtain pure glycerol for further processing. Therefore, finding the right application and development of crude glycerine is problematic, but advantageous for economic and environmental reasons. The refined glycerine can be used in pharmaceutical, chemical industry and also in alkyd resins, cellulose coatings, but the cost of purification and refining are high.[22, 23]

In the current work, we study the glycerolysis of elastomeric polyurethane waste using crude glycerine with 60% purity as decomposing agent. Hereby we propose a rout for treating polyurethane waste and crude glycerine from biodiesel production.[23] The obtained semi-products are characterised by gel permeation chromatography, Fourier transform infrared spectroscopy, proton nuclear magnetic resonance, differential scanning calorimetry thermogravimetric analysis, analytical analysis and rheological measurements, in order to check chemical structure, thermal properties and to examine the effect of polyurethane to glycerine mass ratio on quality of glycerolysates.

EXPERIMENTAL

Materials and glycerolysis reaction

PU elastomer waste based on polyester polyol (M_n=2000 g mol^{-1}, OH_{number}=58 mg KOH g^{-1}, acidity 0.05 mg KOH g^{-1}) and 4,4’-methyldiphenyl diisocyanate (MDI, Borsodchem, Hungary) was reacted in various mass ratios with crude glycerine with purity 60% (Euroservice, Poland). DABCO (1,4-diazabicyclo[2.2.2]octane, Sigma Aldrich, Poland) was used in the amount of 0.5% on polyurethanes, as catalyst in order to accelerate reaction.

Glycerolysis reactions were carried out at following PU to glycerine (PU/GL) mass ratios: 1:1, 4:1 and 10:1. The reactions were carried out during 25 – 90 min depending on the PU/GL ratio, in a 2 L steel reactor equipped with a mechanical stirrer and reflux condenser in the temperature 225 – 230 °C.[24] Temperature was maintained constant during the feeding and the reaction. Glycerine was not separated from the product after the process of glycerolysis. No purification and filtration process were provided in order to keep minimum as needed process operation to be more likely useful for industry. Table 1 presents codes of prepared samples.

Characterisations of obtained semi-products

Spectroscopic analysis of glycerolysates was carried out by means of Fourier transform infrared spectroscopy 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. Spectra were registered at room temperature for wavenumbers ranging from 700 to 4000 cm^{-1} at 2 cm^{-1} nominal resolution with 32 scans.

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

Glass transition temperature of glycerolysates was determined by DSC using a Mettler Toledo DSC822e equipment, provided with a robotic arm and an electric intracooler as a refrigeration unit. Temperature program: heating from -75 to 200 °C at a heating rate of 20 °C min^{-1}, using N_2 as a purge gas (20 mL min^{-1}), cooling from 200 to -75 ^oC at a heating rate of 5 ^oC min^{-1} and second heating run from -75 to 200 °C at a heating rate of 20 °C min^{-1}.

Thermogravimetric analysis (TGA) was performed on a NETZSCH TG 209 apparatus using 5 mg samples at a temperature range of 35–600 ^{o}C and under nitrogen atmosphere at a heating rate of 20 ^{o}C min^{-1}.

Density was determined using pycnometer by a standard method (PN-EN ISO 1675).

Hydroxyl number of the recovered polyol was determined by a standard titration method (PN-EN ISO 2554:2001).

Based on hydroxyl value, number average molecular weight (M_n) was calculated from Eq. 1:

$$M_n = \frac{56100 \cdot f}{OH_{number}} \tag{1}$$

where f represents the functionality of the compound, assumed f= 3,[17] 56100 is the molecular weight of KOH in mg·mol^{-1}.

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 certain value for 180 s; constant shear rate of certain value for 180 s; and decreasing shear rate from certain to 1 s^{-1} for 180 s. The certain value of shear rate is in correspondence to shear rate ranges in some industrial processes e.g. mixing 10–500 s^{-1}or pumping 10–300 s^{-1} .[25] 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.

RESULTS AND DISSCUSION

In glycerolysis process, crude glycerine with three OH would replaces by interchange the ester or ether group of the urethane (Figure 2) providing to obtain re-polyol, similar to virgin polyol used to produce PU and by-products such as low weight carbamates and diamines.

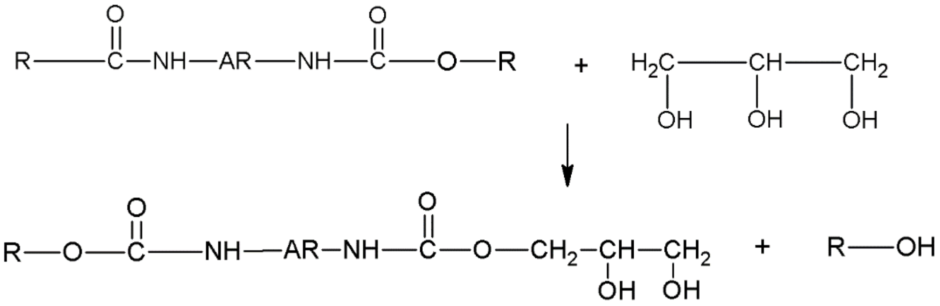

Figure 2. Scheme of polyurethane decomposition by means of glycerine. For described polyurethane, where AR is a rest of MDI, R- rest of polyester polyol.

The reaction products can be compounds ending in hydroxyl and/or amine groups. Schematic reactions in polyurethane decomposition by means of glycerine are shown in Figure 3.

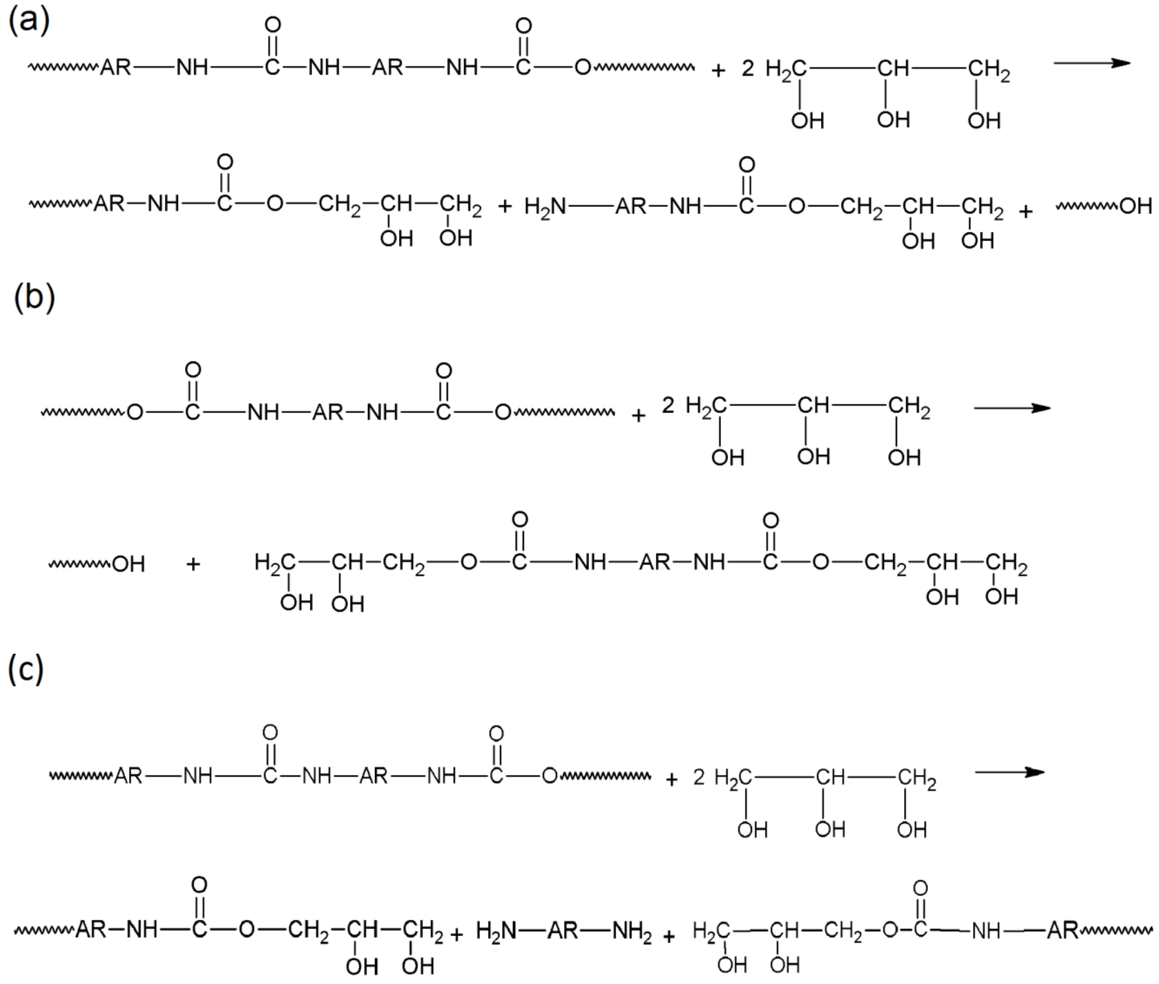

Figure 3. Probable reactions in the degradation of polyurethanes during glycerolsis. Schematic reaction of forming mono- (a), dicarbamates (b) and diamines (c).

The chemical structures of obtained glycerolysates were confirmed and compared with commercial polyol by FTIR spectroscopy (Figure 4). The characteristic band, coming from hydroxyl group in the range 3500-3300 cm^{-1} is overlapped with characteristic stretching vibrations of -NH bond, which occurs at 3363 cm^{-1} for GL 10/1 sample coming from urethane bond (from poly(ester-urethane) which is shown in smaller graph in Figure 4). With higher polyurethane to glycerine mass ratio, the band from OH is less intense, but peak from -NH group is becoming more intense. The higher content of hydroxyl groups in the recovered polyol is due to the partial solubility of glycerine in the glycerolysate. The peak is more intense due to high OH number of the glycerine in comparison to the OH number of polyol (58 mg KOH g^{-1}). Intensive absorption bands at wavenumber 2950 - 2870 cm^{-1} correspond to symmetric bending oscillation of $–CH_2$ and $–CH_3$ groups.

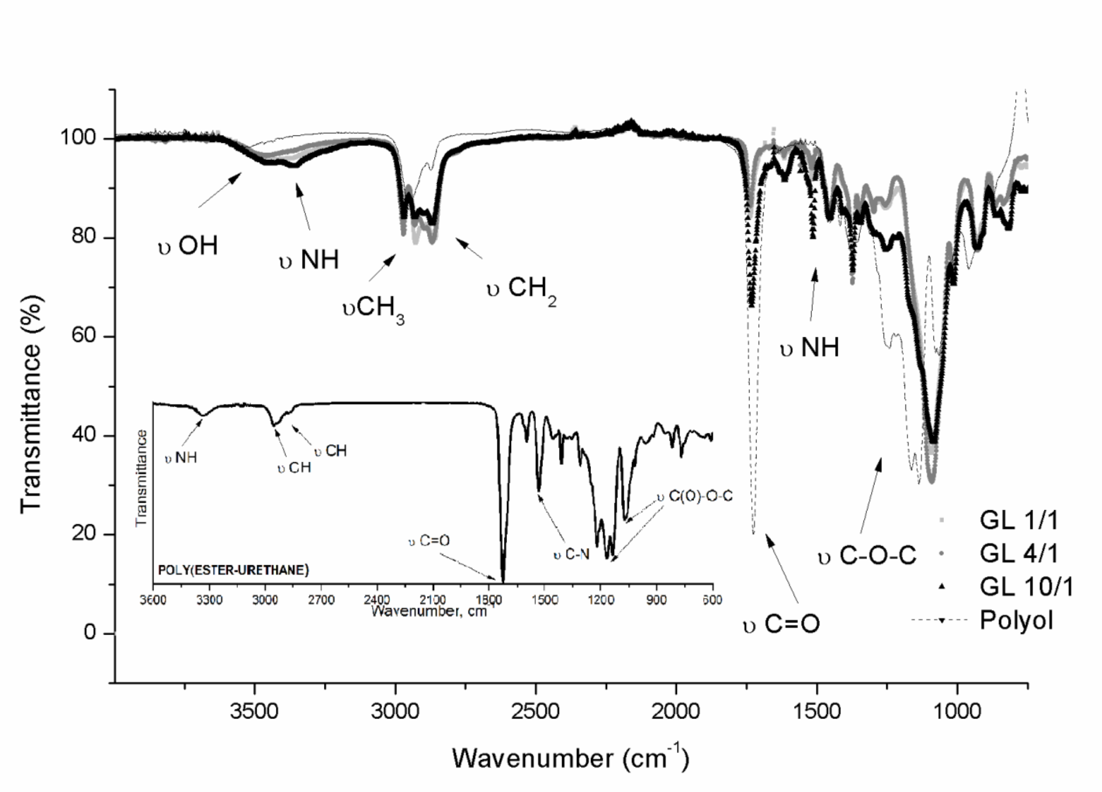

Figure 4. FTIR spectra of resulting semi-products obtained using crude glycerine as decomposing agent, polyol and poly(ester-urethane).

The FTIR spectra differences between the glycerolysates are shown in Figure 5. The peak at wavenumber 1722 cm^{-1} is characteristic for ether group C=O occurs only for semi-products from single-phase reaction.[14] This peak can corresponds to transesterification products, carbamates (glycerolysis by-product) and by urethane groups of the original foam.[20] The schematic process of forming carbamates during glycerolysis is shown in Figure 3. The absorption bands at 1610 and 1590 cm^{-1} correspond to bending vibrations of –NH and indicates that nearby the glycerolysis process decarboxylation takes place therefore glycerolysates contains carbamates.

The region ca. 1530 cm^{-1} corresponds to the stretching vibrations of –NH in primary amines. Therefore absorption bands at 1610, 1590 and 1530cm^{-1} are related to the bending vibrations of amine groups derived from MDI, which has been dissolved within the products. These bands are more intense for GL 10/1 sample due to higher content of polyurethane used in the process and likely higher content of by-products.

Bands visible at 1520-1350 cm^{-1} are attributed to deformational oscillation of –CH_3 groups and other oscillation from the bonds between carbon atmos. The absorption bands in the spectral region in 1465 and 1388 cm^{-1} characteristic of bending vibrations of methylene and methyl groups in the polyol chain.[10] The C–O (urethane) band of urethane bonds at 1220 cm^{-1} appears for glycerolysates it can be assumed that those samples are more contaminated with carbamates. The C–O band at 1008 cm^{-1} from hydroxyl compounds present in glycerolysates and is assigned to C-O in the polyol chain because of transesterification. In the region between 1140 and 1050 cm^{-1} one double peak was observed that marks the presence of C-O-C and –CH_2-OH bonds for polyol. In the same region one single peak for glycerolysates is present which can be attributed to the stretching vibrations of C-O-C bond.[19] This bending vibrations are characteristic for ether group in ether polyol.

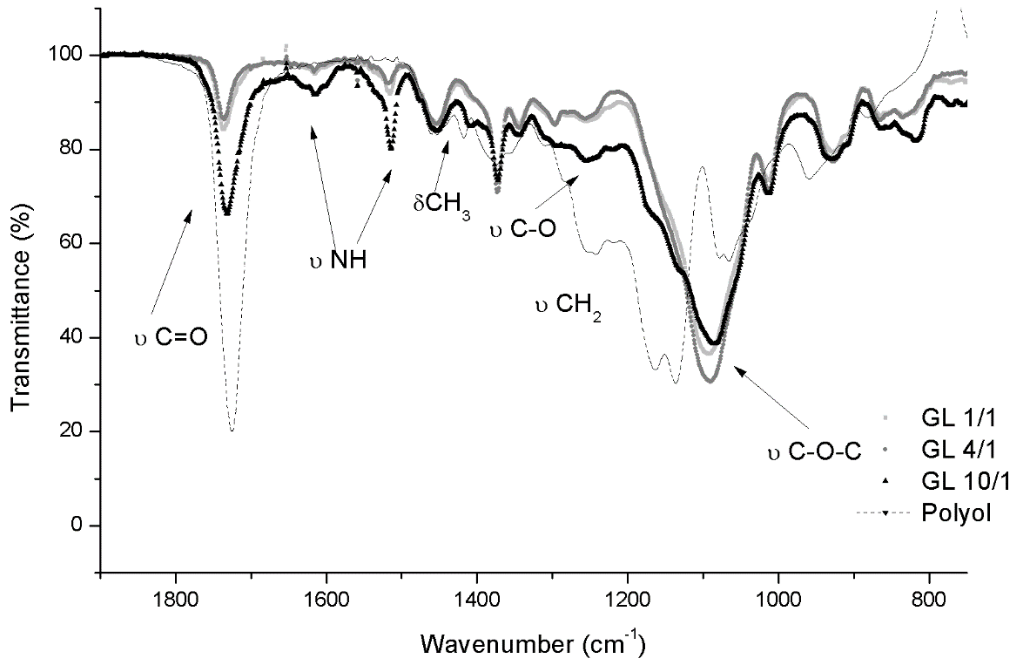

Figure 5. The differences between FTIR spectra of glycerolysates obtained using crude glycerine as decomposing agent and original polyester polyol.

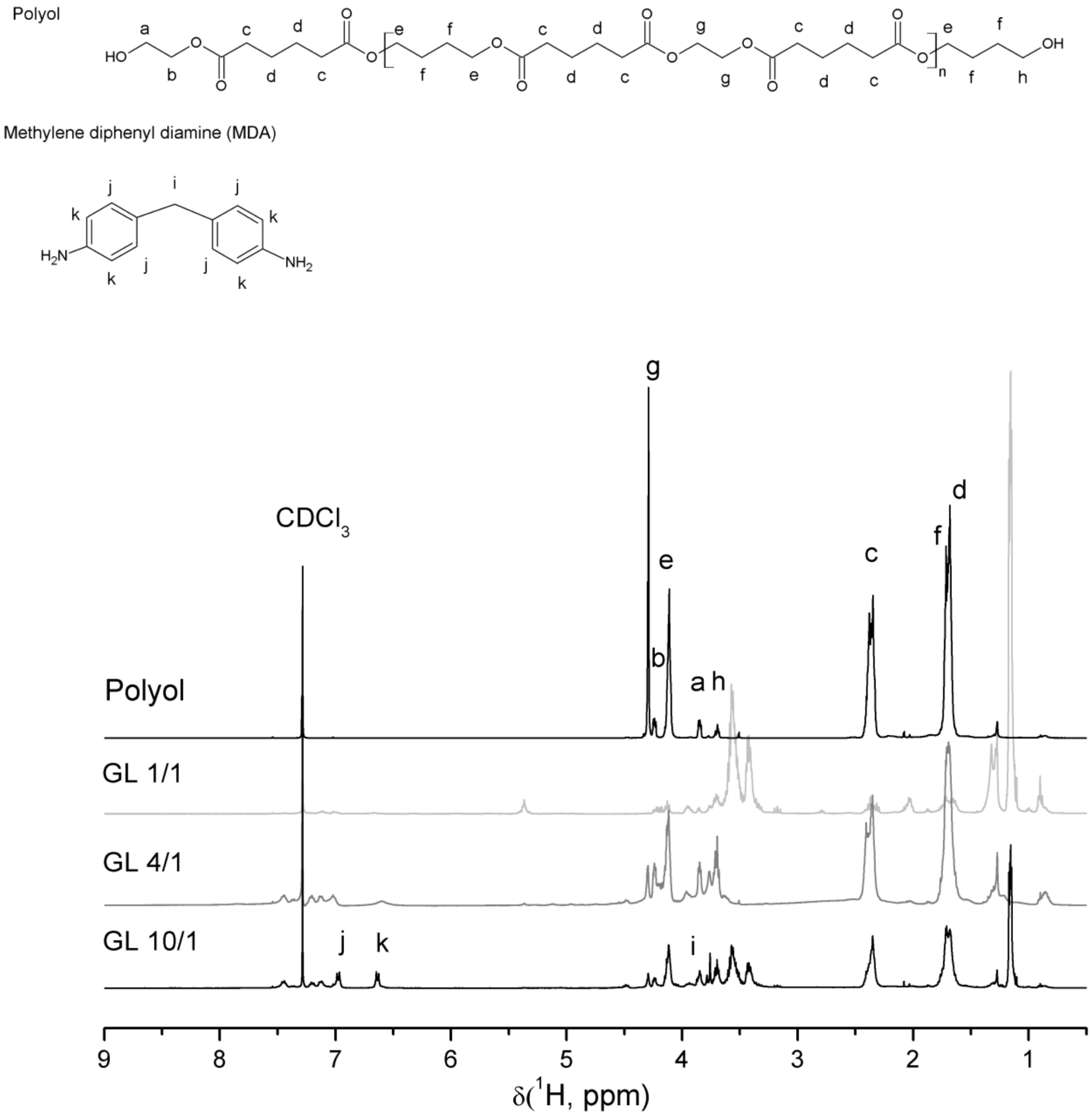

Figure 6. ^{1}H NMR spectra of glycerolysates GL 1/1, GL 4/1, GL 10/1 and polyol.

Figure 6 shows ^{1}H NMR spectra of glycerolysates in comparison with virgin polyol, which was polyester polyol. The structure of polyol and methylene diphenyl diamine (MDA) are shown in Figure 6 and the main protons in these compounds are marked by letters and assigned to peaks in the spectra. There are few characteristic peaks at 1.7 ($-CH_2-$), 2.3 (ester $-CH_2-C(O)-O-$), 3.8-4.2 ($-CH_2-O-$) ppm in ^{1}H NMR spectra of glycerolysates and virgin polyols that indicates their structural similarity.[10] But due to the excess of polyurethane and partial solubility of aromatic amine (i.e.MDA) and carbamates (the rest resulting from urethane bond disintegration) causes the glycerolysates contamination in comparison with virgin polyol and the additional peaks at 3.9 ($-CH_2-$ between two aromatic rings) and 6.6 and 6.9 ($-CH-$ coming from aromatic rings) appear. For GL 1/1 in the range 3.3-3.6 (CH_2-O-, $-CH-O-$) appear peaks from crude glycerine. At δ 1.1 peak corresponds to methyl equivalent hydrogen's. Comparing obtained glycerolysates spectra, the semi-product GL 4/1 seems to be most similar to virgin polyol which can be deducted from the high intensity of peak appearing in the same chemical shifts as for virgin polyol and because GL 1/1 has still glycerine and GL 10/1 is too contaminated.

GPC chromatograms of obtained glycerolysates are presented in Figure 7. Polyurethane is degraded by the glycerine and converted into smaller fragments (urethane oligomers), releasing polyol into reaction media. In the Figure 7 can be observed few different peaks. The polyol is released from the first stages of degradation, this means that there is a wide distribution of molecular weights.[13] The first high intensity peak, appearing ca. 32 min retention time for all samples, is assigned to recovered polyol. The peak for glycerolysates is narrower than the one from neat polyol due to the presence of other compounds like urethane oligomers (peak 2) in glycerolysate.

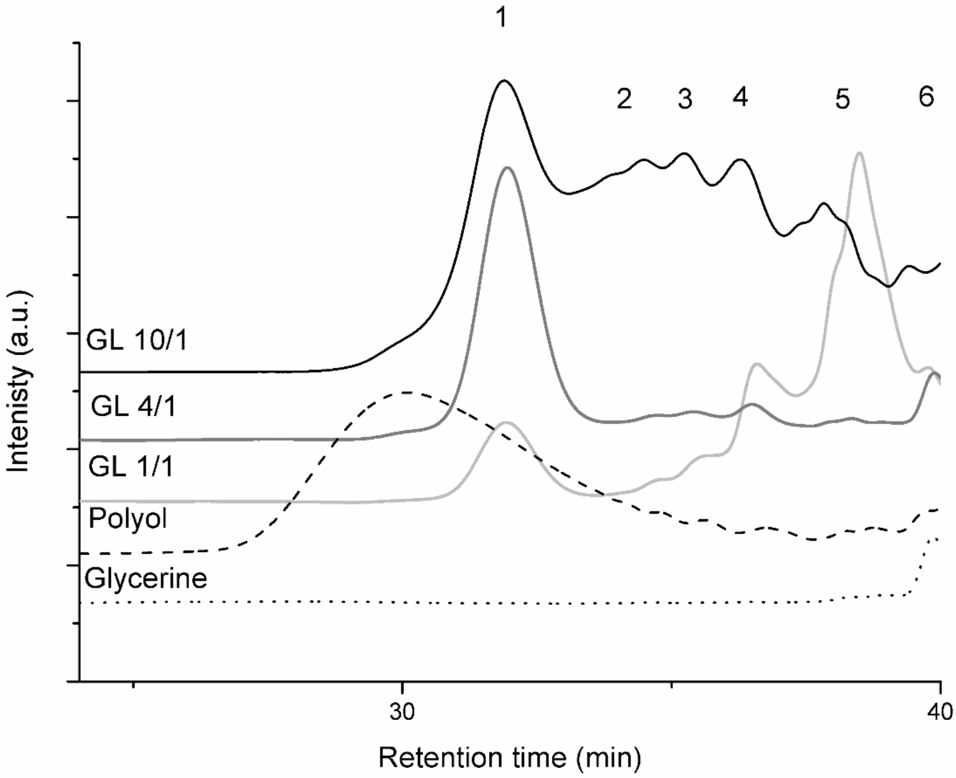

Figure 7. GPC chromatograms of the glycerolysates (GL 1/1, GL 4/1 and GL 10/1) obtained with crude glycerine and DABCO and comparison with the industrial polyol (M_n≈2000 (data sheet), $M_{n\ \mathrm{PS\ standard}}$ ≈4000) and glycerine.

In the Table 2 are presented number-average molecular weight of each peak. These values are overstated due to the standard was polystyrene, true M_n of Poles is approx. 2000 g mol^{-1} and the one obtained from GPC is ca. 4000 g mol^{-1}, so we can assume that all values should be two times lower. The first peak becomes broader for glycerolysates which represents higher polyurethane to glycerine ratio, probably due to higher concentration of urethane oligomers. This indicates that the applied glycerolysis conditions allowed polyurethane degradation to obtain the glycerolysates, but not pure virgin polyol which molecular weight is higher. The following peaks 2-5 are assigned to by-products and correspond to the low weight carbamates (mono- and dicarbamates) and aromatic amines derived from the glycerine substitution in the urethane bond.[12] The peaks 6 are assigned to the reactant – glycerine (M_n above 100 g mol^{-1}). Samples GL 1/1 has a very intensive peak 5 likely caused by the presence of low molecular weight compounds dissolved in glycerine. It can be noticed that in a case of sample GL 10/1, which has the large excess of polyurethane the chromatogram has more peaks, probably consisted with different compounds with different length of chains.

The differential scanning calorimetry behaviour of the glycerolysates was compared to the behaviour of the commercial polyol (Figure 8 and Table 3). Recorded thermograms identify that the glass transition (T_g) is similar for all glycerolysates and it is in the range from -65 to -60 ^{o}C. It is characteristic low value for polyurethane polyol (Poles 55/20 $T_g \approx$ -60 ^{o}C) which was used for polyurethane synthesis.[11] Glycerolysates did not show, as polyol, melting peak. It can be noticed that with higher polyurethane to glycerine ratio (GL 10/1), the second glass transition temperature appears (-34 ^{o}C). This situation takes place due to high concentration of urethane oligomers in sample (confirmed by GPC), it is associated with polyurethane T_g.

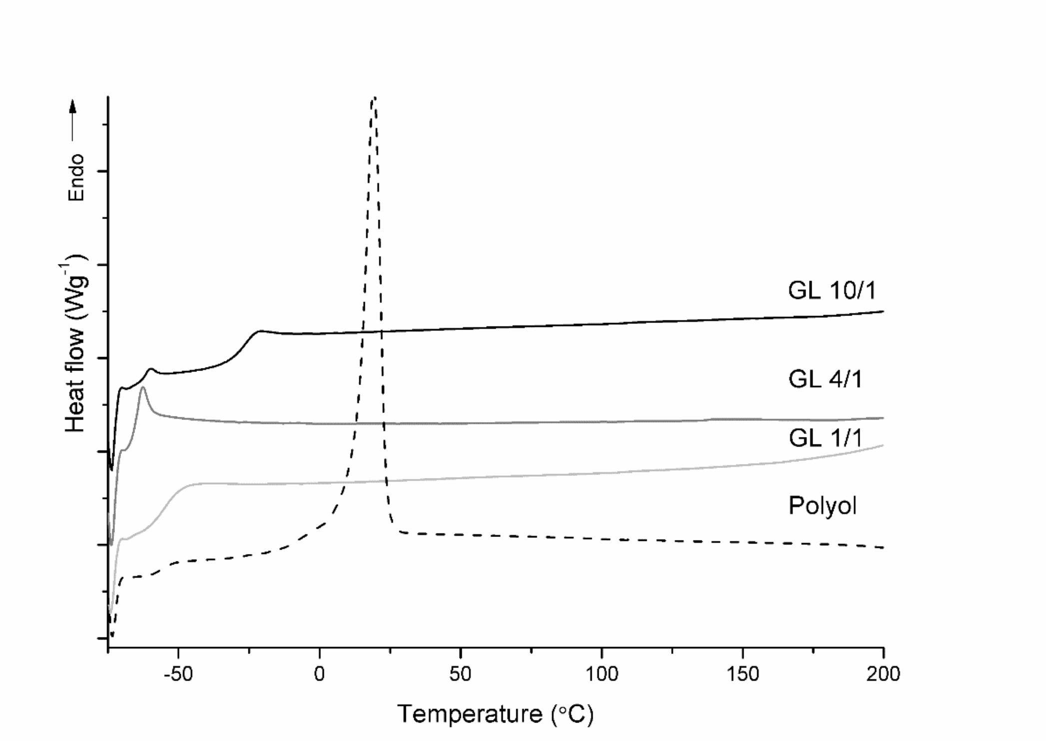

Figure 8.DSC thermograph of the glycerolysates and virgin polyol.

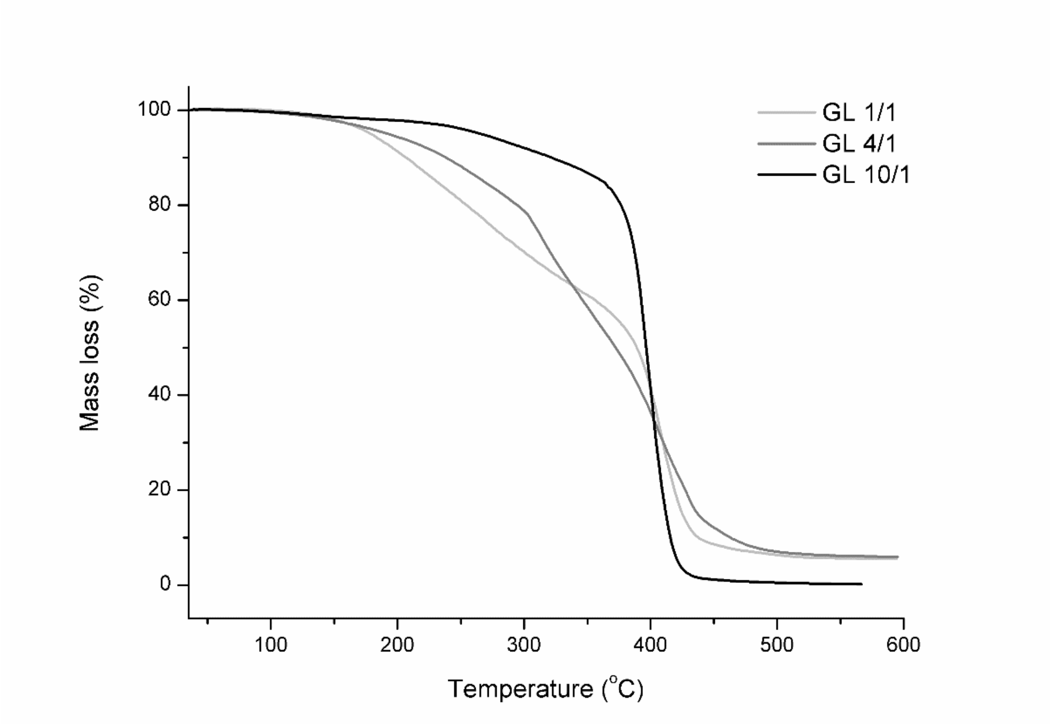

Figure 9. Mass loss as a function of temperature for glycerolysates under nitrogen at 20 ^{o}C/min.

The thermal behaviour of the glycerolysate is shown in Figure 9 and Table 4. The results shows the presence of unreacted glycerine in glycerolysates. An inflection is present for the GL 1/1 TGA curves between 180 and 220 ^{o}C which can be explained by the glycerine evaporation. Similar inflection observed Colomines et al. in glycolysate obtained from PET glycolysis.[26] Values of $T_{5\%}$ and $T_{10\%}$ are increasing with higher PU/GL ratio due to lower mass loss resulted from lower content go glycerine. Glycerolysates GL 1/1 and GL 4/1 indicate two stages of the fastest mass loss, where first (T_{Stage1}), as mentioned before, is related with crude glycerine evaporation. The second fastest mass loss (T_{Stage2}) is in the range 401-409 ^{o}C. This mass loss is caused by degradation of oligomers chains.[11] It can be assumed, that glycerolysates have thermal behaviour between glycerine and commercial polyol, depending on the PU/GL ratio.

The variation in the density, hydroxyl number and molecular weight with different PU/GL mass ratio are presented in Table 5. The obtained glycerolysates have density ranging from 1.2302 to 1.1616 g cm^{-3}. It can be stated after analysing the density results, that density decreases with higher PU/GL ratio. It can be explained by low content of crude glycerine, which has density 1.26 g cm^{-3} (Euroservice, Crude glycerine data sheet).

The obtained values of hydroxyl number are in the range from 240 to 163 mg KOH g^{-1}. It is noticeable that with higher amount of polyurethane waste introduced to reaction media, the values of OH_{number} decreasing. This dependence is due to with quite high amount of glycerine (as in a case of GL 1/1) relative to polyurethane, the higher OH_{number} values are obtained which can be caused by partly not reacted glycerine in the reaction medium.[27] However, the properties of the final semi-product are not in the range of a neat polyol, which is ca. 58 mg KOH g^{-1}. These high OH values can be also observed in the Figure 4 (peak at 3470 cm^{-1} associated with OH groups hydroxyl compounds). Moreover, on the GPC chromatogram of GL 1/1 sample we could see more intense peak at low molecular weight than for other samples.

It is favourable, because obtained semi-products will indicate higher molecular weight and that's create possibility to direct use in prepolymer urethane synthesis. Molecular weight was calculated from Equation 1. Furthermore, the range of the glycerolysate obtained (700-1028 g mol^{-1}) is also out of range of virgin polyether polyol (approx. 2000 g mol^{-1}).

The Figure 10 shows the rheograms of obtained in single-phase glycerolysis at 50, 60 and 70 ^{o}C. The maximum values of shear stress in the temperature 50 ^{o}C is 340, 310 and 900 for GL 1/1, GL 4/1 and GL 10/1, respectively. In the flow curves of glycerolysates a large reduce of shear stress (ca. three times) with rising the temperature from 50 to 70 ^{o}C can be noticed. With 10 ^{o}C higher temperature, shear stress reduces two times. The small hysteresis loop are formed, so those samples tend to be non-Newtonian fluids, where viscosity increases or decreases under an imposed shearing action.[28] The occurrence of hysteresis can be explained by existence of different molecules, with short and long chains, the longer chains starts to moving with higher temperature. It can be estimated that shear stress values, as well as the reaction, depend on the polyurethane to glycerine mass ratio. Higher PU/GL ratio resulted in decreased thixotropic behaviour, and the area between the curves is smaller probably due to higher concentration of urethane oligomers and by-products with longer chains in comparison GL 1/1.

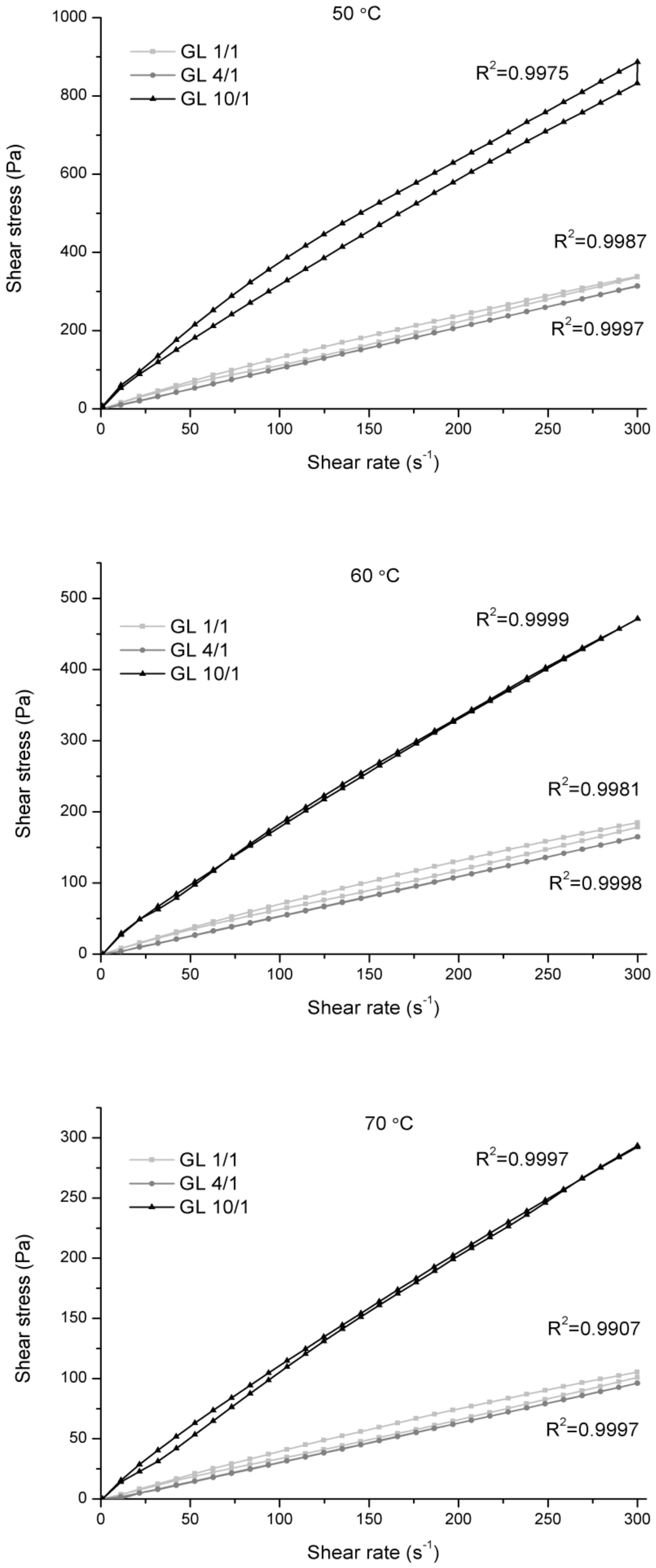

Figure 10. Flow curves of glycerolysates at 50, 60 and 70 ^{o}C.

In Table 6, the parameters from rheological models: Ostwald and Herschel Bulkely are presented. The results were calculated and obtained from Rheo3000 program. Optimal model, to describe flow curves Ostwald and Herschel-Bulkley (Figure 10), was chosen due to the highest determination coefficient (R^2). Those models are described by following equations:

$$\tau = \tau_0 + m \cdot \gamma^n \qquad \text{(HB)} \qquad (2)$$

$$\tau = m \cdot \gamma^n \qquad \text{(Ostwald)} \qquad (3)$$

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}).

The results show that the glycerolysates shows different types of fluid, they are non-Newtonian fluids: dilatant and pseudoplastic, which can be described by Herschel-Bulkley and Ostwald model. [29, 30]

Obtained in applied conditions re-polyols GL 1/1 and GL 10/1 have the flow index lower than 1, so they tend to be pseudoplastic fluid and their behaviour under stress is shear thinning. Pseudoplastic fluids become thinner when the shear rate increases, until the viscosity reaches a plateau of limit viscosity. This behaviour is caused by increasing the shear rate and the elements suspended in the fluid will follow the direction of the current. There will be a deformation of fluid structures involving a breaking of aggregates at a certain shear rate and this will cause a limit in viscosity. For pseudoplastic fluids the viscosity is not affected by the amount of time the shear stress is applied as these fluids are non-memory materials i.e. once the force is applied and the structure is affected, the material will not recover its previous structure. As the shearing stress is increased, disarranged molecules orient themselves to the direction of flow. This orientation reduces internal friction and resistance of the molecules and allows a greater rate of shear at each shear stress.[28,

[29] Sample GL 4/1 act as dilatant fluid, which becomes thicker when agitated, i.e. the viscosity increases proportionally with the increase of the shear rate. When stress is removed, a dilatant system returns to its original state of fluidity. The consistency index (*m*) gives an idea about the viscosity of the fluid, the higher it is, the higher viscosity exhibits the material.

In the Figure 11 the viscosity curves are presented. The viscosity arises from the interaction among the particles in substance. It can be notice that the curves indicate such character as it is described by mathematical models. Also, like we can see in Table 5, with higher temperature, the consistency index (*m*) decrease, the same does viscosity. The GL 4/1 re-polyols exhibit shear thickening in all temperatures where with higher shear rate, the viscosity is increasing.[18] The glycerolysates GL 1/1 and GL 10/1 indicate a shear thinning behaviour in all temperatures. The observed shear thinning behaviour can be explained by changes in the orientation of molecules caused by flow field. The molecules passing in the flow field change their direction by rotation, to become parallel to the flow direction. This configuration results in lower frictional resistance as well as lower viscosity.[31] In relations to presented changes, it can be concluded that glycerolysates, under shear rate, are not resistant to shear under given conditions.[18] Comparing the curves, it can be seen that for GL 10/1 sample, the viscosity is much larger than for other samples. This situation could be expected after GPC chromatogram where sample GL 10/1 demonstrated higher intensity of urethane oligomers and by-products in glycerolysate (Figure 7). Also calculated from Eq.1 average molecular mass is higher than for other glycerolysates therefore it can be assumed that GL 10/1 sample has more extended structure.

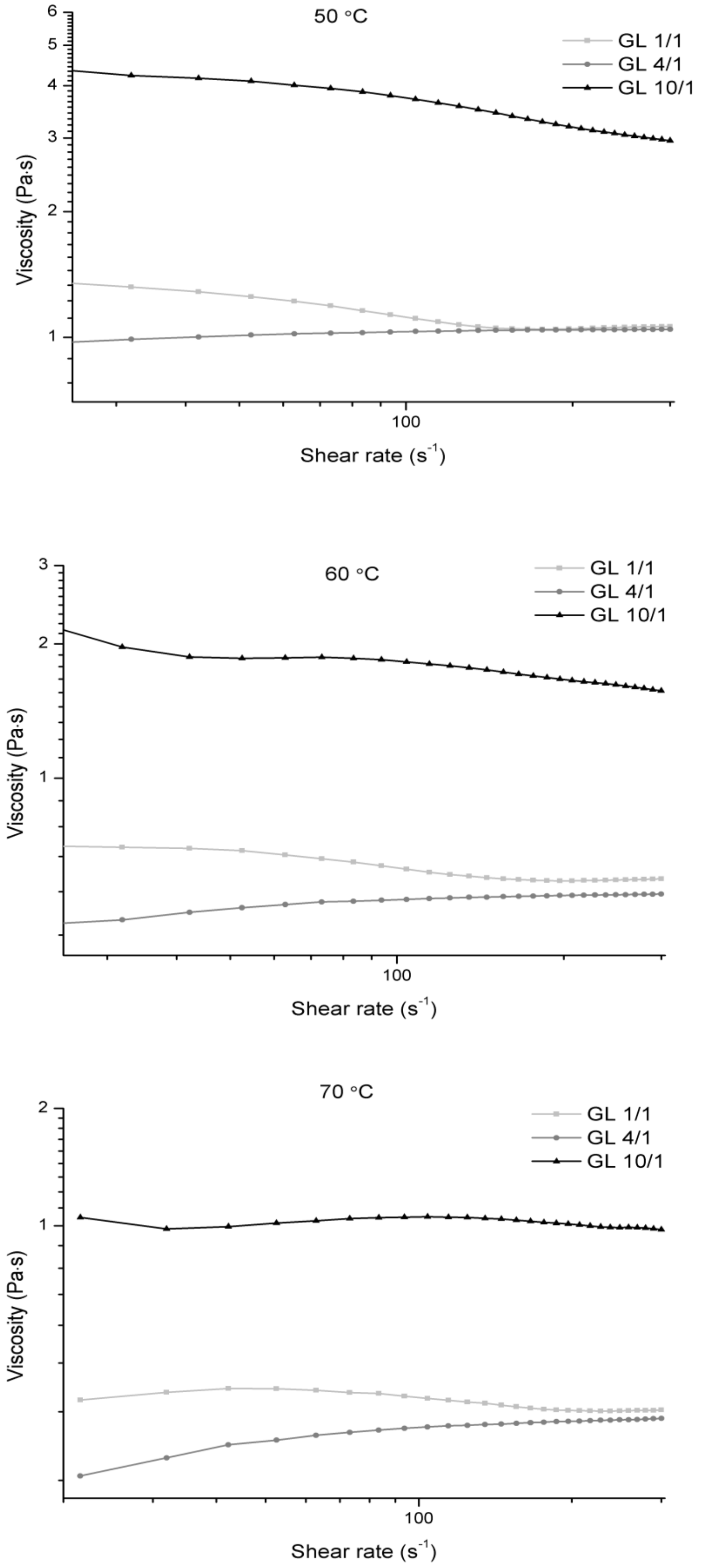

Figure 11. Viscosity curves of glycerolysates at 50, 60 and 70 ^{o}C.

CONCLUSIONS

In the research, the employment of crude glycerine from the biodiesel production, as decomposing agent for polyurethane recycling was investigated. Glycerolysis process has many advantages because it combines management of two waste components in one process, namely polyurethane waste and crude glycerine. The influence of PU/GL mass ratio on glycerolysates properties were examined. The FTIR spectra confirmed that PU/GL mass ratio has insignificant influence on chemical composition of glycerolysates. Generally, the chemical structure of glycerolysates are quite similar to virgin polyol. That was also confirmed by ^{1}H NMR spectroscopy, because the same peaks were found as for polyol. Additional peaks occurred in spectra due to glycerolysate contamination by amines and the rest of urethane bonds. Glycerolysates chromatograms showed that those semi-products do not contain only recovered polyol, but as well other compounds, by-products such as urethane oligomers, carbamates and small amount of unreacted glycerine, which is in compliance with FTIR and ^{1}H NMR spectra. The glass transition of obtained semi-products is similar for all glycerolysates in the range -65 to -60 ^{o}C and it is characteristic low value for polyols which are used in polyurethane synthesis. Glycerolysate, GL 10/1, shows second T_g derived from urethane oligomers. Thermal stability of glycerolysates increases with higher PU/GL ratio. It can be assumed that incorporating such glycerolysate into new polyurethane system would not worsen thermal properties. Polyurethane decomposition resulted in glycerolysates with molecular weight ranging from 700 to 1020 g mol^{-1}. Semi-products with similar OH$_{number}$ and molecular weight were successful applied as component in polyurethane elastomer synthesis by Datta and Rohn.[31] Rheological measurements were performed in order to find appropriate conditions of processing polyol and polyurethane system in production. The glycerolysates behave as non-Newtonian fluids under shear rate. To conclude, the most similar to virgin polyol and at the same time allowing the use of quite high amount of polyurethane waste seems to be glycerolysate GL 4/1.

It was established that glycerolysis process is suitable for polyurethane recycling. Using a large excess of polyurethane waste to glycerine will benefit in faster polyurethane waste reduction. Additional advantages are management of waste glycerine form biodiesel production and the possibility of glycerolysates usage in polyurethane synthesis, replacing a part of petrochemical polyol.

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CAPTIONS OF TABLES

Table 1. Code of samples

Table 2. GPC results of the glycerolysates, where M_{p1} represents M_n of first peak etc.

Table 3. DSC results of glycerolysates and commercial polyol

Table 4. Thermogravimetric analysis of the glycerolysates

Table 5. Characteristic of obtained glycerolysates

Table 6. The model functions based on the rheological data glycerolysates samples

Table 1. Code of samples

Code of sample	PU/GL mass ratio	Reaction time (min)
GL 1/1	1:1	25
GL 4/1	4:1	60
GL 10/1	10:1	90

Table 2. GPC results of the glycerolysates, where M_{p1} represents M_n of first peak etc.

Sample	M_{p1}	M_{p2}	M_{p3}	M_{p4}	M_{p5}	M_{p6}
GL 1/1	3125	-	820	542	253	111
GL 4/1	2986	-	830	560	282	125
GL 10/1	3074	1216	894	599	320	111
Poyol	4037	-	-	-	-	-
Glycerine	-	-	-	-	-	117

Table 3. DSC results of glycerolysates and commercial polyol

Samples	T_g (^oC)	ΔCp (J $^oC^{-1}$ g^{-1})	Tm (^oC)	ΔHm (J g^{-1})
GL 1/1	-60	0.732	-	-
GL 4/1	-64	0.737	-	-
GL 10/1	-65 and -34	0.305 and 0.630	-	-
Polyol	-60	0.223	19	7.954

Table 4. Thermogravimetric analysis of the glycerolysates

Samples	$T_{5\%}$	$T_{10\%}$	$T_{90\%}$	T_{Stage1}	T_{Stage2}
GL 1/1	179.1	206.6	436.6	231.3	408.9
GL 4/1	192.7	237.7	462.7	315.5	408.9
GL 10/1	263.9	321.5	416.5	-	401.4

Table 5. Characteristic of obtained glycerolysates

Samples	Density (g cm^{-3})	OH$_{number}$ (mg KOH g^{-1})	Mn (g mol^{-1})
GL 1/1	1.2302	239.2	≈704
GL 4/1	1.1852	240.4	≈700
GL 10/1	1.1616	163.6	≈1028

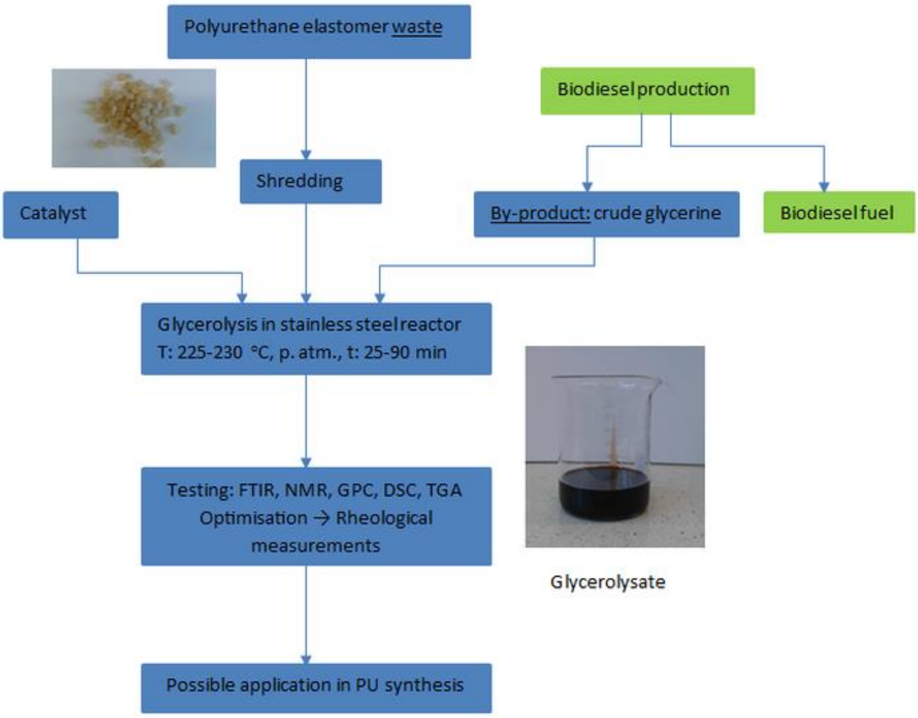
Table 6. The model functions based on the rheological data glycerolysates samples

Sample	T (^{o}C)	Equation	m (Pa s^{n})	n	Model	S^2	R^2
GL 1/1	50	$\tau = 1.7911 * \gamma^{0.9169}$	1.7911	0.9169	Ostwald	7.4148	0.9987
	60	$\tau = 1 * \gamma^{0.9104}$	1	0.9104	Ostwald	4.9296	0.9980
	70	$\tau = 1 * \gamma^{0.7931}$	1	0.7931	Ostwald	6.1034	0.9907
GL 4/1	50	$\tau = 1 * \gamma^{1.0027}$	1	1.0027	Ostwald	2.6620	0.9997
	60	$\tau = 0.4476 * \gamma^{1.0361}$	0.4476	1.0361	Herschel-Bulkely	0.5735	0.9998
	70	$\tau = 0.2254 * \gamma^{1.0623}$	0.2254	1.0623	Herschel-Bulkely	0.4411	0.9997
GL 10/1	50	$\tau = 6.0816 * \gamma^{0.8725}$	6.0816	0.8725	Ostwald	26.6744	0.9975
	60	$\tau = 3.235 * \gamma^{0.8733}$	3.235	0.8733	Ostwald	2.2506	0.9999
	70	$\tau = 1.4934 * \gamma^{0.9271}$	1.4934	0.9271	Ostwald	2.8005	0.9997

Single-phase product obtaining via crude glycerine depolymerisation of polyurethane elastomer. Structure characterization and rheological behaviour.

Patrycja Kopczyńska, Janusz Datta*
*Correspondence to: jandatta@pg.gda.pl

Crude glycerine was used as decomposing agent in polyurethane recycling. It was found that resulted semi-products are valuable and can be used in polyurethane synthesis as replacement of polyols.


Polyurethane elastomer waste
Biodiesel production
Shredding
Catalyst
By-product: crude glycerine
Biodiesel fuel
Glycerolysis in stainless steel reactor
T: 225-230 °C, p. atm., t: 25-90 min
Testing: FTIR, NMR, GPC, DSC, TGA
Optimisation → Rheological measurements
Glycerolysate
Possible application in PU synthesis