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# Cast polyurethanes obtained from reactive recovered polyol intermediates via crude glycerine decomposition process

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## ABSTRACT

In this work, the possibility of applying intermediates from polyurethane waste recycling in polyurethane synthesis was presented. Polyurethanes were synthesised in a two-step method using a mixture of petrochemical polyol and glycerolysate, used as a reactive component, 4,4-diphenylmethane diisocyanate (MDI) and 1,4-butanediol (BD). Glycerolysates were produced during decomposition of polyurethane elastomer by crude glycerine from biodiesel production. The glycerolysates were incorporated into polyurethane structure and co-created a soft segment with their functional groups. Chemical structure and properties of the cast polyurethanes were characterised by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA) and mechanical tests. Results showed that higher incorporation of glycerolysates shifts the glass transition to higher temperatures and the mechanical properties indicates that material exhibits more stiff structure. Prepared polyurethanes which contained glycerolysates have good and similar (in a small amount of glycerolysate) properties to the reference polyurethane which indicates the possibility of glycerolysate application as a polyol in the polyurethane synthesis.

## 1. Introduction

Polyurethanes (PUs) are a group of plastics that can be produced from the wide spectrum of substrates, and that can be submitted on obtaining a various structure with different structure and ipso facto on the final application of these materials. Hence PUs found many uses in almost every branch of industry. One of the main components in polyurethane synthesis are polyols, which play a significant role in building the certain structure of polymer [1,2]. In the recent years, there is a noticeable increase in research where compounds from chemical recycling or renewable resources such as vegetable oils and animal fats are applied [3–5]. The interests in such components is a result of European Union directives [6,7] related to limiting and recycling of waste and searching for new alternative raw materials. This is the step into the development of clean technologies so-called green chemistry that are using natural resources in cost effective manner and manufacture of these products will be held in order to minimise the amount of created waste.

During chemical recycling of polymer waste, the intermediates with the possibility of reuse are obtained but also the amount of landfilled waste is decreased [8,9]. Many researchers are applying obtained recycled polyols in polyurethane foam synthesis [10–13]. Polyol obtained from polyethylene terephthalate decomposition was used with 4,4-diphenylmethane diisocyanate to produce polyurethane foam [14]. Molero et al. applied, recovered polyol from glycolysis of polyurethane, up to 50% could be applied without relevant changes in rising profiles and the physical properties of the foams [15].

In our earlier work [16] glycolysates, obtained during polyurethane glycolysis by using difunctional hydroxyl compounds (1,4-buthanediol and polyethylene glycol), were applied in polyurethane synthesis as a chain extender. DMA results showed the higher content of glycolysate in chain extender mixture, the better polyurethane properties. In another our work [17] also the glycerolysate was applied into new polyurethanes as a part of the polyol component. Nonetheless, in the contrast to this paper, only the upper phase of glycerolysate was used and furthermore the glycerolysate was obtained from flexible polyurethane foam decomposition, while in this paper the used glycerolysates were obtained during polyurethane elastomer decomposition and moreover, the applied glycerolysates were single-phase.

In general, the satisfactory mechanical properties of PUs fall above 80 °C, and the thermal degradation starts above 200 °C. Thermal stability of material is affected by the crosslinking which can occur in the subsequent stages due to the reaction of isocyanate groups with urethane or urea bonds and allophanate or biuret groups are formed. Increasing the concentration of polymer crosslinking can be achieved by increasing the functionality of the polyol, isocyanates and chain

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extender, ($f > 2$) or the use of a higher molar ratio [NCO]:[OH]. It is caused because more energy is needed to break additional bonds resulting from increased crosslinking density, before the disintegration of the entire network [18,19]. Therefore addition or replacement of commercial polyol with the one from recycling can result in the higher thermal stability of new material [17].

The aim of this study was to investigate the possible use of intermediates obtained by glycerolysis, which was detailed described in our previous paper [20]. Glycerolysis of polyurethane elastomer waste was carried out using crude glycerine with 60% of purity derived from the biodiesel production. Obtained intermediates – called glycerolysates were used in the synthesis of polyurethanes, as a part of the polyol component. The glycerolysates were applied in similar polyurethane system which was used to produce the polyurethane elastomer, that was later recycled. Due to their reactivity, the phosphoric acid was added as an inhibitor of side reactions. The obtained materials products were tested to determine the effect of glycerolysate on the structure and properties of polyurethane.

## 2. Experimental

### 2.1. Materials and polyurethane synthesis

Intermediates obtained from glycerolysis of polyurethane elastomer were used in this study as a reactive polyol component, replacing part of commercial polyol. Glycerolysates used in this study were widely characterised in our paper [20]. The hydroxyl value of glycerolysate GL 4/1 and GL 10/1 is 240 and 163 mg KOH g$^{-1}$, respectively.

Recycled polyurethane elastomers based on a mixture of glycerolysate (GL) – reactive recovered intermediate and poly(ethylene-butylene)adipate diol as polyol component was synthesised by the prepolymer method under pressure in 0.5 dm$^3$ glass reactor. The dried polyol (Polios 55/20, Purinova, $OH_{number} = 58$ mg KOH g$^{-1}$) and glycerolysate (GL 4/1 and GL10/1 described in a paper [20]) were first premixed for 30 min in different polyol/glycerolysate ratios (up to 20% replacement of commercial polyol) and phosphoric (V) acid ($H_3PO_4$ 85% wt. in water, POCH Avantor, Poland) 0.5% on glycerolysate amount was added as side reactions inhibitor. After that, the 4,4′-diphenylmethane diisocyanate (MDI, Interchemol, Poland) was added. The prepolymerisation step was carried out at 80 °C for 1,5 h under the vacuum. The percentage of the free NCO groups in prepolymer was equaled to 8 according to standard PN-EN 1242:2013-06 with a change of solvent from toluene to acetone. In the second stage, the 1,4-butanediol (BD, Brenntag, Poland) was added to the prepolymer as a chain extender and stirred for 30 s. DABCO, 1,4-diazabicyklo[2.2.2] octane (Sigma-Aldrich), was used as the catalyst only for the reference sample. The molar ratio of [NCO]:[OH] was kept constant for all samples 1:1. All samples were moulded by gravity casting to the forms and then cured at 100 °C for 24 h. For comparison, a reference polyurethane without glycerolysate was synthesised.

The scheme of two steps synthesis of polyurethane obtained with a commercial polyol, glycerolysate, MDI and BD is shown in Scheme 1. The codes of polyurethane samples used in the study, hard segment (HS) content and degree of phase separation (DPS) are given in Table 1.

### 2.2. Characterisation techniques

*Spectroscopic analysis* of polyurethane elastomers was carried out using an FTIR Nicolet 8700 spectrophotometer (Thermo Electron Corporation) and 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 4500 cm$^{-1}$ at 4 cm$^{-1}$ nominal resolution with 64 scans.

Based on FTIR analysis, the degrees of phase separation (DPS) were calculated using the following equations [21]:

$$R = \frac{A_b}{A_f} \tag{1}$$

$$DPS = \frac{R}{R+1} \tag{2}$$

where $R$—carbonyl hydrogen bonding index; $A_b$— absorption intensity of hydrogen-bonded carbonyl; $A_f$—absorption intensity of free carbonyl. These values were taken from the bands in the wavenumber range of 1640–1770 cm$^{-1}$, corresponding to the stretching vibration of the C=O group, by analysing the intensities of the carbonyl stretching vibrations of free and hydrogen-bonded groups whose overlapping bands were located at 1728 and 1702 cm$^{-1}$.

*Differential scanning calorimetry* (*DSC*) measurements were performed on a Perkin-Elmer DSC-7 equipment. PU samples with a weight between 5 and 10 mg were encapsulated in aluminium pans and were heated from − 75 to 200 °C at a scanning rate of 20 °C min$^{-1}$ under a constant nitrogen flow. The inflexion point of heat capacity change observed was chosen as glass transition temperature ($T_g$). Melting temperature ($T_m$) was settled as the maximum of endothermic peak taking the area under the peak as melting enthalpy ($\Delta H_m$).

*Thermogravimetric analysis* (*TGA*) was performed with a Netzsch TG209 apparatus using 8 mg samples in the temperature range 35–600 °C and under a nitrogen atmosphere at a heating rate of 20 °C min$^{-1}$.

*Dynamic mechanical analysis* (*DMA*) of polyurethane elastomers was performed using DMA Q800 Analyzer (TA Instruments) according to ASTM D6045. Measurements were taken in a temperature range of − 70 °C to + 150 °C at an operating frequency of 10 Hz and a heating rate of 4 °C min$^{-1}$. Approximate dimensions of samples were 40 mm × 10 mm × 4 mm (length × width × thickness).

*Mechanical analysis* in static condition was conducted with a tensile test (tensile strength (TS), elongation at break ($\varepsilon_b$), permanent elongation after break ($\varepsilon_p$) and performer 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. Structure characterisation

In Fig. 1 infrared spectra of chosen polyurethanes synthesised with glycerolysates and polyol mixture: Polios 100%, GL 4/1 (20%) + Polios 80%), GL 10/1 (20%) + Polios (80%) are shown. It is possible to observe two main vibration regions. At 3330 cm$^{-1}$ appears −NH groups stretching vibration, which increased as glycerolysates were incorporated. The other one is associated with carbonyl stretching vibrations $\nu$C=O at wavenumber region 1727–1700 cm$^{-1}$. Double peak of C=O is related with the absorbance of H-bonded carbonyl groups which appears at lower wavenumbers than of free urethane carbonyls [4]. The position of the hydrogen-bonded C=O groups was assigned to the 1701 cm$^{-1}$ wavenumber and that of non-hydrogen-bonded C=O groups to the 1727 cm$^{-1}$ wavenumber. The intensity ratio of the hydrogen-bonded to the non-hydrogen-bonded peaks is slightly higher for polyurethane synthesised with glycerolysate than for reference PU. Peaks appearing at 2966 and 2880 cm$^{-1}$ are associated with stretching vibrations of methyl and methylene groups, whereas the deformation stretching of $\delta_C$-H can be found at 1415 cm$^{-1}$. Vibration bands at 1530 and 1309 cm$^{-1}$ correspond to the $\nu$NH amine group in urethane bond