Postprint of: Jutrzenka Trzebiatowska P., Beneš H., Datta J., Evaluation of the glycerolysis process and valorisation of recovered polyol in polyurethane synthesis, Reactive and Functional Polymers, Vol. 139 (2019), 25-33, DOI: https://doi.org/10.1016/j.reactfunctpolym.2019.03.012

Evaluation of the glycerolysis process and valorisation of recovered polyol in polyurethane synthesis

Patrycja Jutrzenka Trzebiatowska [a1], Hynek Beneš [b], Janusz Datta [a]

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

[b] *Department of Polymer Processing, Institute of Macromolecular Chemistry, CAS, Heyrovského nám. 2, 162 06 Prague, 6, Czech Republic*

Abstract

In this study, the glycerolysis of polyurethane (PU) foam and the applicability of obtained glycerolysate (GLY) for cast PUs were investigated. It was found that crude glycerine with purity grade of 84% might be successfully used for the glycerolysis. The optimal conditions were determined as follows: reaction time of 60 min at 220°C using dibutyltin dilaurate catalyst (0.5%). Moreover, the purification of GLY by means of liquid-liquid extraction and distillation was also adapted.

Cast PU based on GLY were prepared using a two-step method, during which a prepolymer was first synthesized from a mixture of virgin polyol, GLY and 4,4'-diphenylmethane diisocyanate (MDI). The prepolymer was then extended with a chain extender, 1,4-butanediol or 1,3-propanediol. The effect of virgin polyol replacement by GLY (up to 75%) on thermal and mechanical properties of the cast PU was determined. The PU based on GLY exhibited slightly lower thermal stability, higher storage modulus and higher glass transition temperature than the neat PU. The tensile strength of all prepared PU was beneficially high (12 – 15 MPa), while the elongation at break decreased with the increasing GLY content probable due to the branching of PU chains.

Keywords: chemical recycling; polyurethanes; recovered polyol; crude glycerine; glycerolysis

---

[1] Corresponding author. Tel.: +48 58 347 14 47.
E-mail address: patrycja.kopczynska@pg.edu.pl (P. Jutrzenka Trzebiatowska)

1. Introduction

Nowadays the chemical industry shifts their interest to pro-ecological activities. At present, most of the polyols used in the production of polyurethanes (PU) are of petrochemical origin. However, crude oil resources are limited and therefore the European Union [1–3] has introduced legislation that addresses the need to develop reusable products, high-quality recycling processes and to reduce waste disposal. In 2018, the European Commission presented “A European Strategy for Plastics in a Circular Economy” (COM/2018/028), that aims to transform the ways how plastics and plastic products are designed, produced, used and recycled [4]. Therefore, novel processes of chemical recycling and the use of renewable resources such as vegetable oils and animal fats instead of petrochemical polyols have been developed for PU materials [5–7]. A lot of papers report the synthesis of bio-sourced monomers for polyurethanes [8–10] aiming to reduce the dependence on foreign oil suppliers as well as on fossil fuels.

Chemical recycling is considered one of the most sustainable way of PU waste treatment among other methods such as mechanical recycling or incineration. During the chemical recycling, the PU waste converts into valuable semi-products which usually consist of a mixture of various compounds bearing hydroxyl or amine end-groups. They exhibit similar properties as commercial (virgin) polyols and therefore they can be used as raw materials to fabricate new PUs. Their most suitable final application depends on their properties, typically hydroxyl value, viscosity, molecular weight and a chemical structure [11,12]. All these parameters are affected by the used depolymerisation agent, temperature, reaction time, type of catalyst and PU / reagent ratio [11].

A lot of papers concerns the synthesis of new PU based on the recycled component. Recycled polyol (in the case of glycolysis known as glycolysate, GLY) can be introduced into the PU systems to obtain rigid [13] or flexible [14] foams, elastomers [15] and adhesive [16]. They can also be used as a plasticiser for poly(vinyl chloride) or rubber [17,18]. **Table 1** summarises the influence of recovered intermediates (GLY) on the properties of various PU materials. The content of GLY affects the properties of the obtained material. Usually, the best properties are held up to 20–25% of polyol replacement.

Table 1.

In this paper, we studied the glycerolysis process of flexible PU foam using glycerine as a cleavage agent. Glycerolysis process has many advantages because it combines the management of two waste components in one process, namely PU waste and crude glycerine, a by-product from the biodiesel fabrication. Type and concentration of catalyst and the purity of glycerine (refined vs. crude) were investigated with the aim to obtain (recovered) semi-product (GLY) applicable for the synthesis of cast PU. The decomposition process was monitored using infrared (FTIR) spectroscopy, size exclusion chromatography (SEC) and hydroxyl number determination. In the next step, the obtained GLY was applied to prepare the cast PU with a high content of GLY (up to 75% of commercial polyol replacement). The usage of bio-sourced chain extender (CE), 1,3-propanediol (bio-PD), as an alternative to the petrochemical one 1,4-butanediol (BD) was also tested. The synthesised PU were characterised in details.

2. Materials and methods

2.1. Materials and glycerolysis reaction

The ground flexible polyurethane foam based on polyether polyol (Rokopol® F3600 purchased from PCC Rokita, Poland, M_n=3600 g mol^{-1}, I_{OH}=45-50 mgKOHg^{-1}, acidity 0.1 mgKOHg^{-1}) and polymeric diphenylmethane-4,4-diisocyanate (pMDI, Borsodchem, Hungary) was subject of the reaction with crude glycerine (purity grades: 84%, Rafinferia Trzebinia S.A. and 62%, Euroservice, Poland) or a refined glycerine (purity grade 99.5% Rafinferia Trzebinia S.A.). The used weight PU / glycerine ratio was 3 / 1. The following catalysts were used in the amount of 0.5% in relation to the PU amount: 1,4-diazabicyclo[2.2.2]octane (DABCO, Sigma Aldrich, Poland), dibutyltin dilaurate (DBTDL, Merck Millipore, Poland), potassium acetate (KAc, POCH, Poland), sodium hydroxide (NaOH, POCH, Poland), tin(II) 2-ethylhexanoate (StOc, Sigma Aldrich, Poland) and triethylamine (TEA, Sigma Aldrich, Poland). The chosen catalyst was used in an amount of 0.5–2 % in relation to the PU amount. The reaction was carried out in a 1 L stainless steel reactor with a mechanical stirrer under reflux. PU scrap was fed by portions with the speed 5 g min^{-1} for 30 min. After finishing the foam feeding process, the reaction time was started to be recorded. The reaction took place at 220 °C and at atmospheric pressure until complete dissolution of PU. Glycerine was not separated from the product after the glycerolysis. The product was split into two phases; the upper liquid phase of glycerolysate GLY was decanted and separated from the bottom solid phase. The upper phase was further characterised and then used for PU synthesis. The weight ratio of the upper/bottom phase was approx. of 2 / 1.

2.2. Glycerolysate purification

To obtain high quality recovered polyol, purification was applied to the chosen GLY prepared under optimised conditions: DBTDL catalyst in the amount of 0.5% on the PU weight, the reaction time of 60 min at 220 ^{o}C. The upper phase of GLY was subjected to the liquid-liquid extraction to remove the residual amines. The extraction was carried out using a distilled water acidified with phosphoric acid (85%, from POCH Avantor, Poland) to obtain a solution with pH in the range of 4-5. After the extraction, the mixture was separated into two phases: the bottom purified polyol phase and the upper water phase. Finally, vacuum distillation of the bottom phase was carried out at 190 °C with the aim to remove by-products from the intermediate and to reduce the hydroxyl number.

2.3. Characterisations of glycerolysates

Infrared (FTIR) analysis of GLY was carried out using a FTIR Nicolet 8700 spectrophotometer (Thermo Electron Corporation) and the ATR technique (the Specac Heated Golden Gate single reflection diamond ATR accessory). FTIR 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.

The conversion (X) of the –NCOO– functional group of PU was calculated according to [24].

SEC was performed on a Modular GPC System equipped with a refractive index detector RIDK-102 (Laboratorni pristroje Praha, Czech Republic) and an UV-vis photometric detector LCD 2084 (ECOM, Czech Republic) operated at λ= 254 nm, and a set of two columns PLgel 10E3 Å and 50 Å, 10 μm particle size, 300 mm x 7.5 mm (Polymer Laboratories, UK). Chromatographic data were collected and treated using Clarity software (Data-Apex, Czech Republic). Tetrahydrofuran and toluene are used as a mobile phase and a flow marker (retention time of toluene was ca 17.72 min) at a flow rate of 1 $mLmin^{-1}$, respectively. SEC was used to determine the molecular weight distribution (MWD) as well as the amount of recovered polyol in the products.

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

2.4. Cast polyurethane synthesis

Cast PU based on GLY were prepared using a two-stage synthesis. In the first step, a PU prepolymer was synthesised and in the second step, CE was added to the prepolymer to increase its molecular weight. The reaction took place in a 0.5 dm^3 glass reactor. In the first step, a dried polypropylene glycol (PPG, Rokopol® D2002, PCC Rokita, Poland, M_n~2000 g mol^{-1}, I_{OH}= 53-66 $mgKOHg^{-1}$, f=2, information given by the company) and GLY (M_n~3141 g mol^{-1} as calculated from SEC, I_{OH}= 135 $mgKOHg^{-1}$, f~2.41 calculated from critical conversion at gel point which was performed according to procedure previously described in the literature [25,26]) were first premixed for 30 min using different PPG / GLY ratios (100/0, 75/25, 50/50, 25/75). Phosphoric (V) acid (POCH Avantor, Poland), 0.5% on the GLY amount, was added as side reactions inhibitor. After that, the melted and filtrated 4,4′-diphenylmethane diisocyanate (MDI, Ongronat® 3000, BorsodChem, Hungary) was added. The prepolymerisation step was carried out at 80 °C for 1.5 h under vacuum. The percentage of the unreacted NCO groups in prepolymer was equalled to approx. 8.7% validated according to standard PN-EN 1242:2013-06 with a change of solvent from toluene to acetone.

In the second stage, a dried BD (Brenntag, Poland) or bioPD (Susterra®, DuPont Tate & Lyle, USA) obtained from an organic maize production, was added to the prepolymer as a CE and stirred for 30 s. DBTDL (Merck Millipore) in the amount of 0.3% on CE was used as the catalyst only for the reference samples (PU-0-BD and PU-0-bioPD). The PU syntheses took place without the addition of any catalyst due to the high reactivity of GLY (residual DBTDL was present in GLY from the PU decomposition). The molar NCO / OH ratio equal to 1.05 was kept constant for all samples. The samples were cast into a pre-heated (80 °C) steel mould and cured at 100 °C for 24 h.

2.5. Characterisation of cast polyurethanes

FTIR analysis of PU elastomers was carried out using the same equipment and conditions as for the GLY characterisation.

Thermogravimetric analysis (TGA) was performed on a Pyris 1 TGA analyser (PerkinElmer) in the temperature range of 35 – 650 ^{o}C at a heating rate of 20 ^{o}C min^{-1} under a nitrogen atmosphere.

Dynamic mechanical analysis (DMA) was performed using DMA Q800 Analyzer (TA Instruments) in three-point bending mode according to ASTM D6045. Measurements were taken in a temperature range from −100 ^{o}C to +180 ^{o}C at an operating frequency of 10 Hz and a heating rate of 4 ^{o}C min^{-1}. Approximate dimensions of samples were 40×10×3 mm^3 (length ×width ×thickness).

The mechanical analysis in static condition was conducted with a tensile test (tensile strength (TS), elongation at break (ε_b), permanent elongation after break (ε_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^2. 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. Glycerolysis of polyurethane foam

This section describes the evolution of the decomposition process of flexible polyurethane foam by using glycerine. In the glycerolysis process, we obtained two-phase glycerolysate. The bottom dark phase (solid at room temperature) was removed and the amber-coloured upper phase (the recovered polyol) with a polyol-like viscosity was further analysed (see below).

3.1.1. Influence of the catalyst type

The catalyst influence on the glycerolysis was examined by FTIR and SEC. **Figure 1a** shows FTIR spectra of GLY in the range of 1900–1200 cm^{-1} obtained in the presence of various catalysts. The peak at 1727 cm^{-1}, characteristic for C=O bonds of urethane groups corresponds to carbamates, the by-products of transesterification [27]. The absorption bands at 1610, 1590, 1511 and 1530 cm^{-1}

corresponding to both deformation of the aromatic ring and the bending vibration –NH indicate aromatic carbamates presence in GLY. These bands have higher intensity for NaOH catalyst indicating higher contamination of this glycerolysate with the aromatic by-products. The bands at 1450 and 1371 cm^{-1} associated to bending vibrations of methylene and methyl groups and the band at 1008 cm^{-1} assigned to the stretching vibrations of C–O prove the presence of aliphatic recovered polyol in GLY [6,28]. The C–O band of urethane groups at 1220 cm^{-1} appeared only for GLY when TEA, DABCO, KAc were used as catalysts. The reason may be that these catalysts did not lead to full foam dissolution and the rest of urethane oligomers and carbamates contaminate these glycerolysates. Contrary to that, GLY obtained in the presence of DBTDL catalyst is the least polluted sample, since its FTIR spectrum is similar to that of the neat polyol (**Figure 1a**).

This may be due to the selectivity of the DBTDL, which directs the glycerolysis reaction and simultaneously can limit hydrolysis reaction during the decomposition, as shown in **Scheme 1**. The mechanism of the catalysis is done with the formation of a metal coordination complex, which consists of DBTDL, polyurethane linkage (urethane group) and glycerine. The tin atom forms a complex with the oxygen atom of the glycerol. The opposite side of the tin atom is complexed with carbon of carbonyl from the urethane group. This is due to the hydrogen bonds from the urethane group and from glycerine. In the next step, they form O-Sn-C and H-O-C-O groups, where the transformation of the proton from glycerine to the urethane chain happens. Then, the breakdown between O-C atoms of urethane linkage and the bonding of oxygen from glycerine with urethane chain occur. The hydrogen bonds interactions are weakened and the catalyst is detached [29].

Scheme 1.

The progress of glycerolysis was monitored using FTIR and the PU conversion (X) was calculated (**Figure 1b)**. The highest conversion is obtained in the presence of DBTDL catalyst in a relatively short time (45 min up to over 90% of conversion), the second one is NaOH. In general, the metal-organic compounds and hydroxides allow accelerating of the reaction. Unfortunately, NaOH also promotes secondary reactions [24], and thus produced GLY is contaminated with by-products. According to the literature [31], the slowest reaction occurred when amine catalysts were applied and therefore the reaction must be carried out for a longer time to obtain a much higher conversion rate.

Figure 1. a), b).

Glycerolysates are usually mixtures of oligomers, recovered polyol, by-products (di- and mono-carbamates, amines) and the rest of glycerine [32]. From the SEC chromatograms, the relative percentage by weight (% by weight) of each compound was obtained by integration of the area under the peaks of GLY. **Table 2** shows the correlation between the catalyst type versus the hydroxyl value and the products' concentration by weight. It can be observed that KAc, TEA and DABCO glycerolysates are significantly more contaminated with oligomers than StOc, NaOH or DBTDL ones. The high concentration of oligomers may indicate too short reaction time and hence incomplete urethane bonds disruption. The NaOH sample exhibits the highest contamination with the by-products, which is in accordance with the FTIR spectra (**Figure 1a**). The highest polyol recovery allowed DBTDL (82%), then DABCO and StOc (ca. 76%). The catalyst type influences also the hydroxyl number of GLY. Hydroxyl numbers of GLY are in the range of 120 – 140 mgKOHg^{-1}, i.e. the higher than that of neat polyol. GLY with the lower hydroxyl number is difficult to obtain due to a partial solubility of the reaction by-products.

Table 2.

3.1.2. Influence of the catalyst concentration

The DBTDL catalyst was chosen as the most appropriate since it allowed obtaining the highest conversion rate of PU (**Figure 1b**). This subsection aims to determine the influence of catalyst amount on the glycerolysis rate and the quality of formed semi-products.

The FTIR spectra of GLY obtained using different DBTDL concentrations (**Figure SI 1**) revealed no significant structural differences showing the similar bands that were described in the section above. An additional band at ca. 1800 cm^{-1} can correspond to C=O group of a carboxylic acid.

The PU conversion was quite high (77–94%) for all used catalyst concentrations (**Figure 2**). The higher catalyst concentration accelerates the glycerolysis especially in the initial phase; e.g. X = 50% at 0 min for the GLY sample with 2% DBTDL. Once the recovered polyol is formed, the reaction slows down.

However, the short reaction time in the case of 2% sample could be the reason for the relatively low conversion of C=O groups in PU.

Figure 2.

For all samples, the SEC chromatograms (**Figure SI 2**) revealed no presence of oligomers. Additionally, with the higher DBTDL concentration, the peak of recovered polyol was narrower indicating a more pure product. **Table 3** presents polyol concentration and hydroxyl numbers of the final GLY. For samples with 0.25 and 0.5% DBTDL, the highest amount of the recovered polyol was observed. However, due to too short reaction for 2% concentration, less polyol was recovered, and the higher amount of the carbamates and amines was found in the product upper phase. This higher GLY pollution with by-products can also be a result of mutual enhancement of phase (upper and lower) solubility supported by the higher catalyst concentration [12]. Nevertheless, the lower catalyst amount results in the slower PU decomposition. Hydroxyl values of GLY range from 139 to 182 mgKOHg^{-1} and decreased with the decreasing DBTDL concentration. The reason may be too short reaction time of glycerolysis at high catalyst concentrations and the enhanced phase miscibility, which increased the glycerine content in GLY (as also indicated by SEC).

Table 3.

3.1.3. Influence of the glycerine purity

The FTIR results (**Figure 3a)** did not show any differences between the GLY samples prepared using the refined glycerine (99.5%) and the crude glycerine 84%. Contrary to that, using the crude glycerine 62% for the PU glycerolysis leads to a GLY sample exhibiting the highly intensive FTIR band at 1514 cm^{-1} associated with aromatic ring vibrations of amines. In addition, the peak at 1622 cm^{-1} attributed to the carbonyl group of an ester or carboxyl acid from the matter organic non-glycerol (MONG) impurities [33] originating from the used crude glycerine 62% [34,35] was clearly visible in the FTIR spectrum of the sample 62%.

Figure 3b shows the PU conversion during the PU decomposition by means of glycerine with different purity grade. The high conversion rate of PU, over 90%, is achieved for all tested glycerine purity grades when sufficiently long reaction time is applied. However, the usage of glycerine with 62% purity allowed fast decomposition from the beginning which could be directly related to the water, methanol and MONG contents present in the crude glycerine. These impurities might cause the simultaneous methanolysis, hydrolysis and acidolysis beside the main reaction path – the glycerolysis of PU foam [24]. Moreover, these side reactions might take place at a lower temperature than the glycerolysis proceeds. As consequence, the initial PU conversions (at zero time) of the crude glycerine samples are higher than that of the sample prepared from the refined glycerol.

Figure 3. a), b)

In **Table 4**, the relative products' concentrations and hydroxyl values of GLY are given. The highest contamination with by-products was observed for the 62% sample (ca. 32%) as consistent with the FTIR results (see **Figure 3a**). The high MONG concentration (21%) in the 62% glycerine can also reduce polyol recovery due to side reactions increasing the amount of by-products. Contrary to that, the high level of polyol recovery was achieved when the 84 or 99.5% glycerine was used. It suggests that the purity and also the composition of crude glycerine influence the efficiency of the whole glycerolysis process. The highest hydroxyl value exhibits the GLY sample prepared using the 62% glycerine.

Table 4.

3.1.4. Influence of the reaction time

The results mentioned above showed the optimal DBTDL concentration equal to 0.5% and the sufficient glycerine purity of 84% to reach a high PU conversion during the glycerolysis. The produced GLY contained a high percentage of the recovered polyol and had a similar structure to the original polyol. The FTIR spectra of GLY samples at different reaction times (0–60 min) are displayed in **Figure 4.** The intensity of the urethane C=O band at ca. 1727 cm^{-1} significantly decreases with extending decomposition time and the reaction reaches higher conversion (Figure 3b). However, a new small band appears at ca. 1805 cm^{-1} which can be associated with the carbonyl group from derivatives of carboxylic acid. The aromatic ring peaks at 1600 and 1510 cm^{-1} and the amines' peak at 1530 cm^{-1} indicate the presence of by-products. From these peaks' evolution it can be concluded that with the longer reaction time, the purer recovered polyol is obtained.

Figure 4.

The SEC chromatograms of GLY sampled in different reaction time showed the progress of PU glycerolysis (**Figure 5**). At the beginning of the reaction (0 min), even six different peaks are observed. The peak no. 1 corresponds to high molecular weight oligomers bearing urethane groups, as also proved by the FTIR analysis (the C=O band at ca. 1727 cm^{-1}). The other peaks correspond to the recovered polyol (the peak no. 2), carbamates (the peaks no. 3 and 4), aromatic amines (the peak no. 5) and the rest of glycerine (the peak no. 6). With the increasing reaction time, the peak no. 1, associated with oligomers, decreases. The longer decomposition time caused a higher recovery of polyol (from 35 to 86%, **Table 5**). The obtained results are in accordance with the FTIR spectra, which showed the lowering intensity of the following bands: C=O carbonyl group from urethane bond (oligomers), N-H group associated with amines (by-products, peak 3 – 5) and hydroxyl group associated with the unreacted glycerine. These results are also in agreement with the hydroxyl numbers of the GLY samples, which decreased with the increasing reaction time up to the value of ca. 135 mgKOHg^{-1} at the end of the reaction (**Table 5**). The higher hydroxyl number of GLY compared to the virgin polyol was expected due to the residual content of glycerine (as observed from the FTIR spectra and the SEC).

Table 5.

Figure 5.

3.1.5. Purification of the glycerolysate

The produced GLY contains not only the recovered polyol but also a group of by-products (carbamates, amines) and unreacted glycerine. These impurities might increase GLY reactivity and pH (due to the basicity of amines). Hence, the purification steps involving extraction and distillation are proposed. The efficiency of purification was monitored using the FTIR spectroscopy (**Figure 6),** SEC and the hydroxyl number determination (**Table 6**).

After the extraction process, the band derived from OH groups at 3600–3200 cm^{-1} is more intense, probably due to the residual water in the polyol fraction. However, it is already noticeable that the intensity of the C=O band at 1722 cm^{-1} is reduced. After the vacuum distillation process, the OH group band almost disappeared and the C=O band is no longer present. In addition, the band intensity of the aromatic ring of amines at 1619 cm^{-1} decreased.

Figure 6.

Table 6 summarises the hydroxyl numbers and products' compositions of GLY before after the purification. During the extraction, the amines present in GLY react with phosphoric acid producing phosphates as by-products. After the extraction, the hydroxyl number of GLY slightly increases due to the presence of residual water. The hydroxyl number of GLY after the distillation is significantly lowered as free glycerine was removed (as in accordance with the FTIR spectrum). Similar results were mentioned in the literature, where such easy operations can be applied for purification of reaction products [27]. Repeating of the purification steps might further decrease the hydroxyl number of GLY reaching the value of original polyol, but then a substantial loss of the product yield could occur.

Table 6.

3.2. Characterisation of polyurethanes containing glycerolysate

In this section, the properties of PU elastomers with different amount of GLY (up to ca. 75% commercial polyol replacement) are described The obtained samples were more beige with a higher amount of GLY in the system.

The results of tensile tests and hardness measurements are summarised in **Table 7**. The highest tensile strength (TS) was observed for PU-0-BD and the TS value slightly dropped (by 2 - 3 MPa) with the polyol replacement by GLY. The further increase of GLY content (up to 75%) caused only insignificant changes in TS. For the PU-bioPD series, the TS value of PU-25-bioPD is even higher than that of the reference sample. With the increasing content of GLY in PU, the elongation at break (ε_b) and the permanent elongation (ε_p) decreased while the hardness increased (**Table 7**). These results, which correlate well with the storage moduli, indicate probable branching of PU materials (**Figure 8**). Permanent elongation is a significant parameter which characterises returning of the material to its original state. With the increasing GLY content, the ε_p value of PU materials significantly decreased, which is a favourable phenomenon. From this point of view, the prepared cast PUs with high

GLY content are comparable or even better than similar materials described in the literature [36]. Moreover, the usage of CE from the renewable resources instead of petrochemical one can contribute to a more sustainable approach in the synthesis of polyurethanes without significant worsening the material properties.

Table 7.

All prepared PU containing GLY were analysed by FTIR spectroscopy (**Figure SI 3**) to check the complete isocyanate – hydroxyl groups' reaction (no presence of the isocyanate peak at 2270 cm^{-1}).

Thermal stability of the prepared PU materials was studied using TGA. The thermogravimetric (TG) and derivative (DTG) curves are shown in **Figure 7**, and the detailed results are listed in **Table 8**. Thermal decomposition of PU is a complex multi-stage process consisted of few steps, especially in the case of multicomponent PU [37]. The temperature corresponding to a mass loss of 5% is connected with the release of easily volatilised products. For all prepared materials the mass loss starts above 318 ^{o}C ($T_{5\%}$) and their thermal stability is thus considered as a good one. Generally, the PU-BD series exhibit slightly better thermal stability than the PU-bioPD samples, as the beginning of mass loss starts at higher temperatures (difference of ca. 10 ^{o}C). However, the incorporation of GLY influences much more the thermal stability of PU. It can be noticed that together with replacement of polyol by GLY, the mass loss starts at lower temperatures (**Table 8**). This decrease can be associated with disruption of the PU structure due to the presence of low molecular weight carbamates and aromatic amines in GLY. The amount of solid residue is in the range of approx. 7.7–9.9% and 5.0-7.9% for PU-BD and PU-bioPD series, respectively. The slightly higher content of solid residue for PU with GLY results from the presence of the by-products in GLY [38].

The DTG curves (**Figure 7a**) show three stepped mass loss of PU samples. The first stage connected with the decomposition of hard segments starts at ca. 360 ^{o}C for PU-BD while for PU-bioPD at ca. 340 ^{o}C [39]. The second and third steps are connected to the degradation of the polyol rich phase. The second mass loss is associated with the beginning of soft segment degradation[40] as it appears at ca. 380 and 390 ^{o}C for PU-bioPD and PU-BD, respectively and the third step at approx. 416 ^{o}C, at a degradation temperature close to that of the original polyol (PPG) [41].

An additional step at 530 ^{o}C appears that might correspond to degradation of aromatic rings and carbon chains [42]. Furthermore, the first and the second decomposition stages of the PU-bioPD series start at lower temperatures than of the PU-BD samples, which probably results from the lower hard segment content in the cases of the PU-bioPD series. These results confirm that a higher crystallinity degree (higher hard segment content) enhances the thermal stability of PU materials [43].

Figure 7.

Table 8.

Figure 8 shows the temperature dependence of the storage modulus (E') and damping factor (tanδ) of PUs. The E' values at the glassy state of the PU-bioPD series (4.3 – 4.9 GPa) are slightly lower than those of the PU-BD series (4.4 – 5.4 GPa). The sharp drop in the E' value occurs at the temperature range from -35 to 20 ^{o}C due to the α relaxation of the soft segment, associated with the glass transition temperature (T_g) [37] which can be determined from the tanδ peak. Above T_g, the rubbery E' increases with the increasing GLY content, i.e. with the higher content of hard segments. Additionally, the higher functionality of GLY (*f*~2.4) compared to the neat polyol (*f*~2.0) promotes branching of PU chains resulting in the increased E' and T_g values and the broadening of the tanδ peak. The mobility of soft segments is restricted, probably due to the enhanced hydrogen bonding promoted by the urethane groups of GLY [44] and the increased chain rigidity originating from the carbamates structures in GLY [45]. The height of the tanδ peak is in the range of 0.28–0.51 showing materials ability for vibration damping (absorption) [46]. The values drop with the higher GLY content which is connected with a smaller proportion of soft segment participating in the glass transition [22]

Figure 8.

4. Conclusions

In this research, the use of crude glycerine from the biodiesel production, as a cleavage agent for the recycling of flexible PU foam was studied. The effect of different catalysts (DBTDL, StOc, NaOH, KAc, DABCO and TEA) on the progress of

PU glycerolysis was investigated. While KAc, DABCO and TEA exhibited low catalytic efficiency for the PU glycerolysis and too long time was needed to reach a high level of the PU conversion, DBTDL was found to be the most efficient catalyst. The higher DBTDL concentration allowed faster PU decomposition, but the reaction yield and the product (glycerolysate, GLY) composition were insignificantly influenced. Crude glycerine (84% purity) might be applied as the reagent instead of the refined one (99.5% purity) without any negative effects on the progress of PU glycerolysis reaction. The impurities in crude glycerine slightly affected the GLY properties, only when a high amount of matter organic non-glycerol (MONG) compounds was present. Simple purification operations allowed lowering the hydroxyl value of GLY by ca. 30% (up to approx. 90 $mgKOHg^{-1}$), which extends GLY applications for different PU formulations.

The produced GLY was tested as a basic component in the cast PU formulation, replacing partially (from 25% to 75%) commercial polyol (PPG) in the prepolymer mixture. The polyol replacement with 25% by mass of GLY did not cause significant changes in comparison with the reference PU. All prepared PU were thermally stable until ca. 320 °C. Thermal decomposition takes place in two main stages at 330–340 °C and 390–400 °C. The glass transition of the PUs was shifted to higher temperatures indicating restriction due to the presence of GLY. The storage modulus of PU increases with the increased GLY concentration, while elongation at break decreases (from 500% to 130%) due to the branching of PU chains resulting from the GLY structure. The tensile strength of the PU materials based on GLY was kept on similar values (12–15 MPa) as that of reference PU. The hardness of PU slightly increased with the increasing GLY content.

Acknowledgement

The authors wish to thank Rafineria Trzebinia S.A. and Euroservice Sp. Z z.o.o. for kindly providing glycerine and PCC Rokita S.A. for providing polyol Rokopol® D2002.

Funding

Part of this work was supported by the Ministry of Education, Youth and Sports of Czech Republic, National Sustainability Program I-NPU I, Project POLYMAT LO1507.

5. References

[1] The European Parliment and the Council of the European Union, Directive 2003/30/EC of 8 May 2003 on the promotion of the use of biofuels or other renewable fuels for transport, Off. J. Eur. Union. L 123 (2003) 42–46.

[2] The European Parliament and the Council of the European Union, Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste and repealing certain Directives, Off. J. Eur. Union. L 312 (2008)

[3] The European Parliament and the Council of the European Union, DIRECTIVE (EU) 2015/720 of 29 April 2015 amending Directive 94/62/EC as regards reducing the consumption of lightweight plastic carrier bags, Off. J. Eur. Union. L 115 (2015) 11–15.

[4] European Commission, A European Strategy for Plastics in a Circular Economy, COM(2018) 28, 2018.

[5] M. Kurańska, A. Prociak, M. Kirpluks, U. Cabulis, Polyurethane–polyisocyanurate foams modified with hydroxyl derivatives of rapeseed oil, Ind. Crops Prod. 74 (2015) 849–857.

[6] J. Datta, E. Głowińska, Effect of hydroxylated soybean oil and bio-based propanediol on the structure and thermal properties of synthesized bio-polyurethanes, Ind. Crops Prod. 61 (2014) 84–91..

[7] H. Beneš, T. Vlček, R. Černá, J. Hromádková, Z. Walterová, R. Svitáková, Polyurethanes with bio-based and recycled components, Eur. J. Lipid Sci. Technol. 114 (2012) 71–83.

[8] P. Parcheta, I. Koltsov, J. Datta, Fully bio-based poly (propylene succinate) synthesis and investigation of thermal degradation kinetics with released gases analysis, Polym. Degrad. Stab. 151 (2018) 90–99.

[9] P. Kosmela, A. Hejna, K. Formela, J.T. Haponiuk, Ł. Piszczyk, Biopolyols obtained via crude glycerol-based liquefaction of cellulose: their structural, rheological and thermal characterization, Cellulose. (2016).

[10] P. Parcheta, J. Datta, Environmental impact and industrial development of biorenewable resources for polyurethanes, Crit. Rev. Environ. Sci. Technol. 47 (2017) 1986–2016.

[11] P. Kopczyńska, J. Datta, Rheological Characteristics of Oligomeric

Semiproducts Gained Via Chemical Degradation of Polyurethane Foam Using Crude Glycerin in the Presence of Different Catalysts, Polym. Eng. Sci. 57 (2017) 891–900.

[12] C. Molero, A. de Lucas, J.F. Rodríguez, Recovery of polyols from flexible polyurethane foam by “split-phase” glycolysis: Study on the influence of reaction parameters, Polym. Degrad. Stab. 93 (2008) 353–361.

[13] D. Simón, A.M. Borreguero, A. de Lucas, C. Molero, J.F. Rodríguez, Novel polyol initiator from polyurethane recycling residue, J. Mater. Cycles Waste Manag. 16 (2014) 525–532.

[14] M.M.A. Nikje, M. Haghshenas, A.B. Garmarudi, “Split-phase” Glycolysis of Flexible PUF Wastes and Application of Recovered Phases in Rigid and Flexible Foams Production, Polym. Plast. Technol. Eng. 46 (2007) 265–271.

[15] J. Datta, M. Kacprzyk, Thermal analysis and static strength of polyurethanes obtained from glycolysates, J. Therm. Anal. Calorim. 93 (2008) 753–757.

[16] J. Borda, A. Rácz, M. Zsuga, Recycled polyurethane elastomers: a universal adhesive, J. Adhes. Sci. Technol. 16 (2002) 1225–1234.

[17] M. Włoch, P. Kosiorek, K. Błażek, J. Datta, Właściwości mechaniczne i termomechaniczne kompozytów kauczuku naturalnego z krzemionką submikronową i nanokrzemionką , otrzymanych plastyfikatora, Elastomery. (2017) 75–81.

[18] J. Datta, P. Parcheta, J. Surówka, Softwood-lignin/natural rubber composites containing novel plasticizing agent: Preparation and characterization, Ind. Crops Prod. 95 (2016) 675–685.

[19] C. Molero, A. de Lucas, J.F. Rodriguez, Influence of the Use of Recycled Polyols Obtained by Glycolysis on the Preparation and Physical Properties of Flexible Polyurethane, J. Appl. Polym. Sci. 109 (2008) 617–626.

[20] J. Paciorek-Sadowska, B. Czupryński, J. Liszkowska, Glycolysis of rigid polyurethane-polyisocyanurate foams, J. Elastomers Plast. 48 (2016) 340–353.

[21] H. Beneš, J. Roesner, P. Holler, H. Synkova, J. Kotek, Z. Horak, Glycolysis of flexible polyurethane foam in recycling of car seats, Polym. Adv. Technol. 18 (2007) 149–156.

[22] T. Calvo-Correas, L. Ugarte, P. Jutrzenka Trzebiatowska, R. Sanzberro, J. Datta, M.Á. Corcuera, A. Eceiza, Thermoplastic polyurethanes with glycolysate intermediates from polyurethane waste recycling, Polym. Degrad. Stab. 144

(2017) 411–419.

[23] D. Simón, A. de Lucas, J.F. Rodríguez, A.M. Borreguero, Flexible polyurethane foams synthesized employing recovered polyols from glycolysis: Physical and structural properties, J. Appl. Polym. Sci. 134 (2017) 45087.

[24] P. Jutrzenka Trzebiatowska, A. Dzierbicka, N. Kamińska, J. Datta, The influence of different glycerine purities on chemical recycling process of polyurethane waste and resulting semi-products, Polym. Int. 67 (2018) 1368–1377.

[25] M. Duskova-Smrckova, H. Valentová, A. Ďuračková, K. DuŠek, Effect of dilution on structure and properties of polyurethane networks. Pregel and postgel cyclization and phase separation, Macromolecules. 43 (2010) 6450–6462.

[26] A. Ďuračková, H. Valentová, M. Duskova-Smrckova, K. Dušek, Effect of diluent on the gel point and mechanical properties of polyurethane networks, Polym. Bull. 58 (2007) 201–211.

[27] D. Simón, A.M. Borreguero, A. de Lucas, J.F. Rodríguez, Valorization of crude glycerol as a novel transesterification agent in the glycolysis of polyurethane foam waste, Polym. Degrad. Stab. 121 (2015) 126–136.

[28] M.M.A. Nikje, M. Nikrah, Glycerin as a new glycolysing agent for chemical recycling of cold cure polyurethane foam wastes in “split-phase” condition, Polym. Bull. 58 (2007) 411–423..

[29] J. Datta, Glikoliza poliuretanów, Wydawnictwo Politechniki Gdańskiej, Gdańsk, 2012.

[30] M. Murai, M. Sanou, T. Fujimoto, F. Baba, Glycolysis of Rigid Polyurethane Foam under Various Reaction Conditions, J. Cell. Plast. 39 (2003) 15–27.

[31] N. Hekmatjoo, Z. Ahmadi, F. Afshar Taromi, B. Rezaee, F. Hemmati, M.R. Saeb, Modeling of glycolysis of flexible polyurethane foam wastes by artificial neural network methodology, Polym. Int. 64 (2015) 1111–1120.

[32] J. Datta, P. Kopczyńska, From polymer waste to potential main industrial products: Actual state of recycling and recovering, Crit. Rev. Environ. Sci. Technol. 46 (2016) 905–946.

[33] M. Nanda, Z. Yuan, W. Qin, M. Poirier, X. Chunbao, Purification of Crude Glycerol using Acidification : Effects of Acid Types and Product Characterization, Austin J. Chem. Eng. 1 (2014) 1–7.

[34] B.T. Maru, F. López, S.W.M. Kengen, M. Constantí, F. Medina, Dark fermentative hydrogen and ethanol production from biodiesel waste glycerol using a co-culture of Escherichia coli and Enterobacter sp., Fuel. 186 (2016) 375–384.

[35] K.. Yong, W. Yunus, T.. Ooi, K. Dzulkefly, A.. Hazimah, Refining of crude glycerine recovered from glycerol residue by simple vacuum distillation, J. Oil Palm Res. 13 (2001) 39–44.

[36] J. Datta, Synthesis and Investigation of Glycolysates and Obtained Polyurethane Elastomers, J. Elastomers Plast. 42 (2010) 117–127.

[37] C. Prisacariu, Thermal behaviour of polyurethane elastomers, in: Polyurethane Elastomers, Springer-Verlag, Vienna, 2011: pp. 61–101.

[38] P. Jutrzenka Trzebiatowska, I. Deuter, J. Datta, Cast polyurethanes obtained from reactive recovered polyol intermediates via crude glycerine decomposition process, React. Funct. Polym. 119 (2017) 20–25.

[39] D.K. Chattopadhyay, D.C. Webster, Thermal stability and flame retardancy of polyurethanes, Prog. Polym. Sci. 34 (2009) 1068–1133.

[40] F.M.B. Coutinho, M.C. Delpech, T.L. Alves, A.A. Ferreira, Degradation profiles of cast films of polyurethane and poly(urethane-urea) aqueous dispersions based on hydroxy-terminated polybutadiene and different diisocyanates, Polym. Degrad. Stab. 81 (2003) 19–27.

[41] M. Zieleniewska, M. Auguścik, A. Prociak, P. Rojek, J. Ryszkowska, Polyurethane-urea substrates from rapeseed oil-based polyol for bone tissue cultures intended for application in tissue engineering, Polym. Degrad. Stab. 108 (2014) 241–249.

[42] K. Mizera, M. Kirpluks, U. Cabulis, M. Leszczyńska, M. Półka, J. Ryszkowska, M. Leszczyńska, M. Półka, J. Ryszkowska, Characterisation of ureaurethane elastomers containing tall oil based polyols, Ind. Crop. Prod. 113 (2018) 98–110.

[43] M.A. Corcuera, L. Rueda, B. Fernandez d'Arlas, A. Arbelaiz, C. Marieta, I. Mondragon, A. Eceiza, Microstructure and properties of polyurethanes derived from castor oil, Polym. Degrad. Stab. 95 (2010) 2175–2184.

[44] R.V. V Lopes, L.F.B. Osorio, M.L. Santos, M.J.A. Sales, Characterization of polyurethanes from vegetable oils by TG/DTG, DMA and FT-IR, Macromol. Symp. 319 (2012) 173–178.

[45] A. Paruzel, Sł. MichaŁowski, J. Hodan, P. Horak, A. Prociak, H. Benes, Rigid Polyurethane Foam Fabrication Using Medium Chain Glycerides of Coconut Oil and Plastics from End-of-Life Vehicles, ACS Sustain. Chem. Eng. 5 (2017) 6237−6246.

[46] J. Datta, P. Kosiorek, M. Włoch, Synthesis, structure and properties of poly(ether-urethane)s synthesized using a tri-functional oxypropylated glycerol as a polyol, J. Therm. Anal. Calorim. 128 (2017) 155–167.

Scheme 1. Proposed mechanism for PU decomposition catalysed by DBTDL. Adapted from [30]. Copyright © SAGE Publications**.**

Figure 9. a) FTIR spectra of glycerolysates obtained in the presence of various catalysts, b) the conversion of C=O group in PU during glycerolysis in the presence of various catalysts.

Figure 10. The PU conversion (X) during glycerolysis in the presence of various DBTDL concentrations**.**

Figure 11. a) FTIR spectra of glycerolysates obtained using various purity of glycerine, b) the conversion of C=O group in PU during glycerolysis with various purity of glycerine.

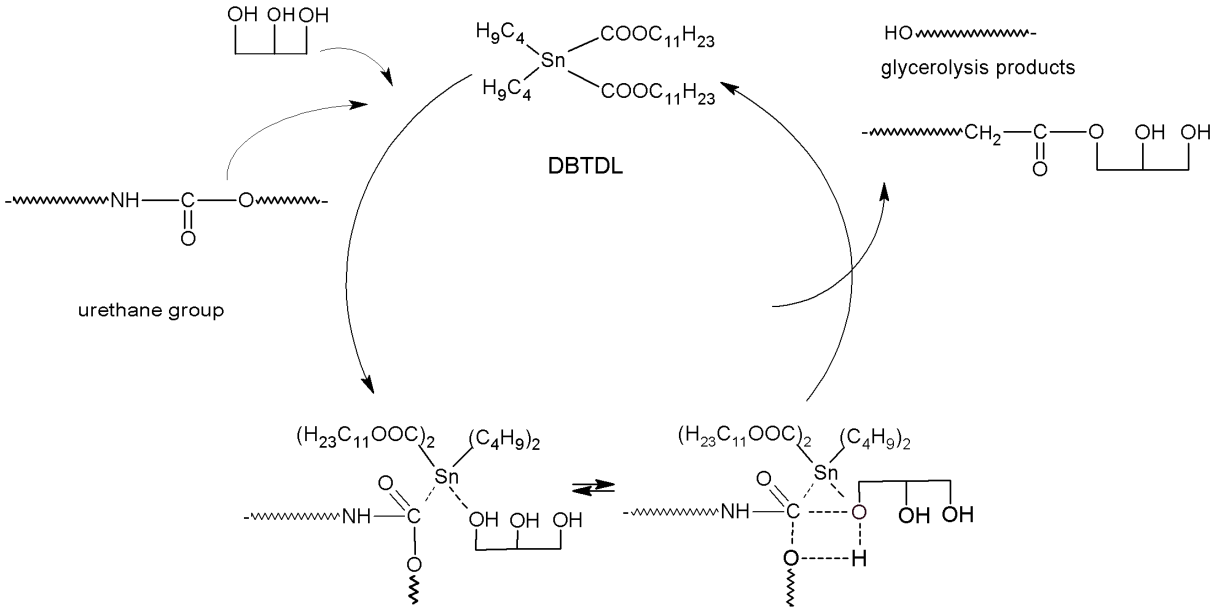
Figure 12. FTIR spectra of glycerolysate obtained in the presence of DBTDL catalyst sampled in the time intervals.

Figure 13. SEC chromatograms of glycerolysate obtained in the presence of DBTDL catalyst sampled in the time intervals

Figure 14. FTIR spectra of glycerolysate before and after purification operation (extraction and distillation) and origin polyol.

Figure 15. DTG (a) and TG (b) curves of polyurethanes with BD and bioPD as chain extenders.

Figure 16. The storage modulus and loss factor (tan δ) as a function of temperature for synthesised polyurethanes with a) BD and b) bioPD as chain extenders.


OH OH OH
H_9C_4
Sn
$COOC_{11}H_{23}$
H_9C_4
$COOC_{11}H_{23}$
DBTDL
HO-
glycerolysis products
-CH2—C—O OH OH
O
-NH—C—O-
O
urethane group
$(H_{23}C_{11}OOC)_2$
$(C_4H_9)_2$
Sn
O
-NH—C
O
OH OH OH
$(H_{23}C_{11}OOC)_2$
$(C_4H_9)_2$
Sn
O
-NH—C
O
OH OH
O
H

Scheme 1

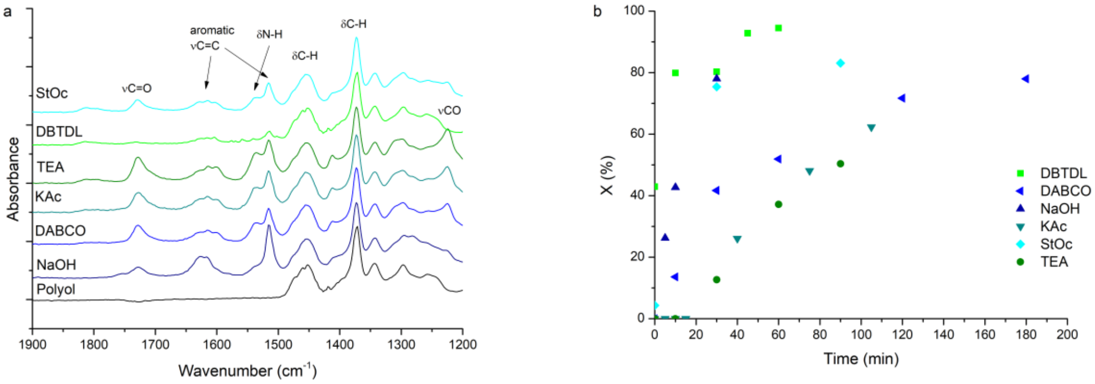

a
StOc
DBTDL
TEA
KAc
DABCO
NaOH
Polyol
νC=O
aromatic νC=C
δN-H
δC-H
δC-H
νCO
Absorbance
1900
1800
1700
1600
1500
1400
1300
1200
Wavenumber (cm-1)
b
100
80
60
40
20
0
X (%)
0
20
40
60
80
100
120
140
160
180
200
Time (min)
DBTDL
DABCO
NaOH
KAc
StOc
TEA

Figure 1

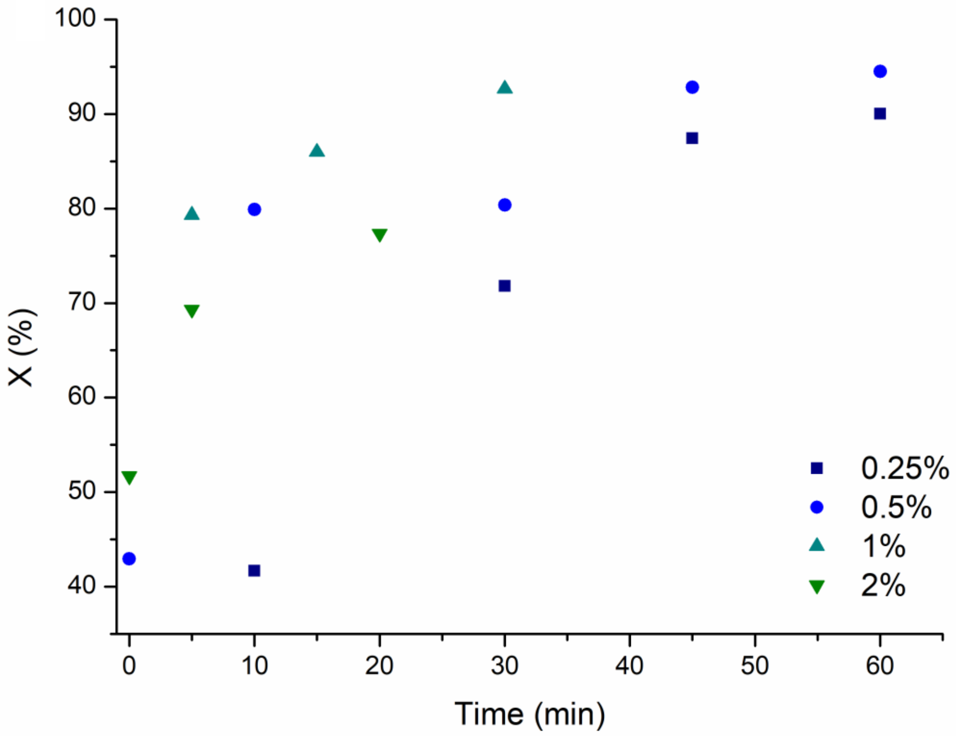


Figure 2

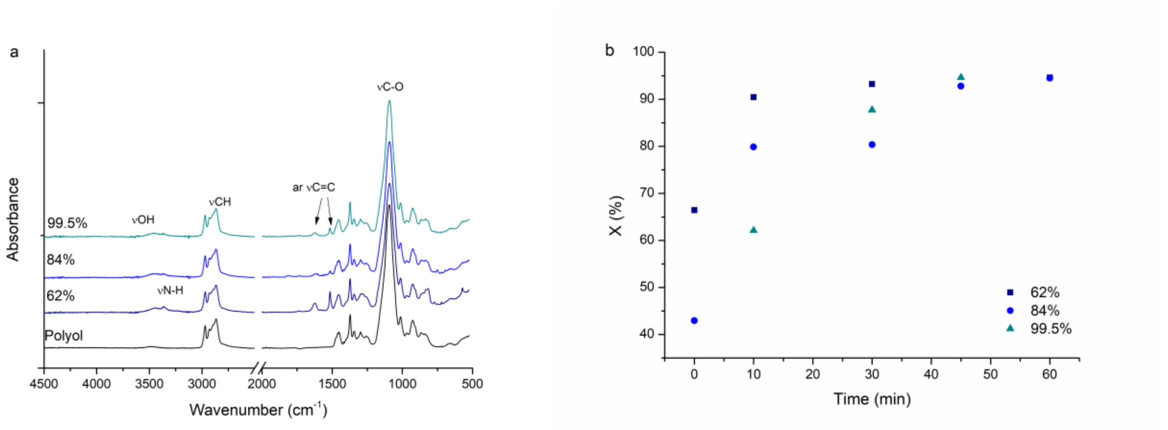

a
Absorbance
νC-O
νCH
ar νC=C
99.5%
νOH
84%
62%
νN-H
Polyol
4500
4000
3500
3000
2000
1500
1000
500
Wavenumber (cm^{-1})
b
100
90
80
70
60
50
40
X (%)
0
10
20
30
40
50
60
Time (min)
62%
84%
99.5%

Figure 3

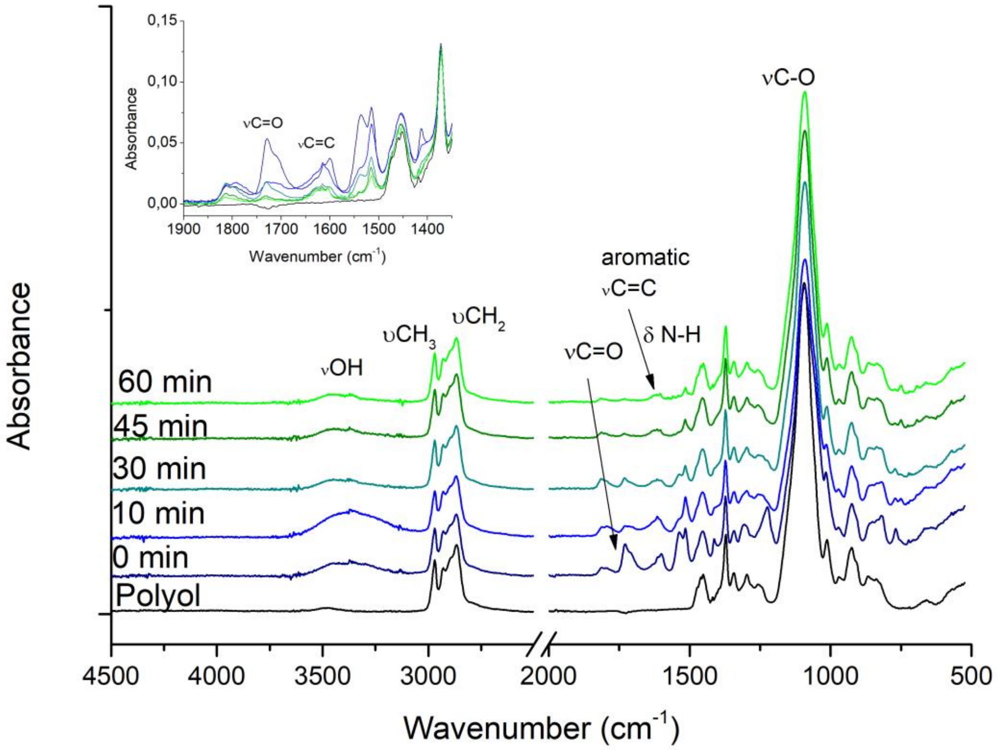

0,15
0,10
0,05
0,00
Absorbance
νC=O
νC=C
1900 1800 1700 1600 1500 1400
Wavenumber (cm^{-1})
νC-O
aromatic
νC=C
δ N-H
νC=O
υCH$_3$
υCH$_2$
νOH
60 min
45 min
30 min
10 min
0 min
Polyol
Absorbance
4500 4000 3500 3000 2000 1500 1000 500
Wavenumber (cm^{-1})

Figure 4

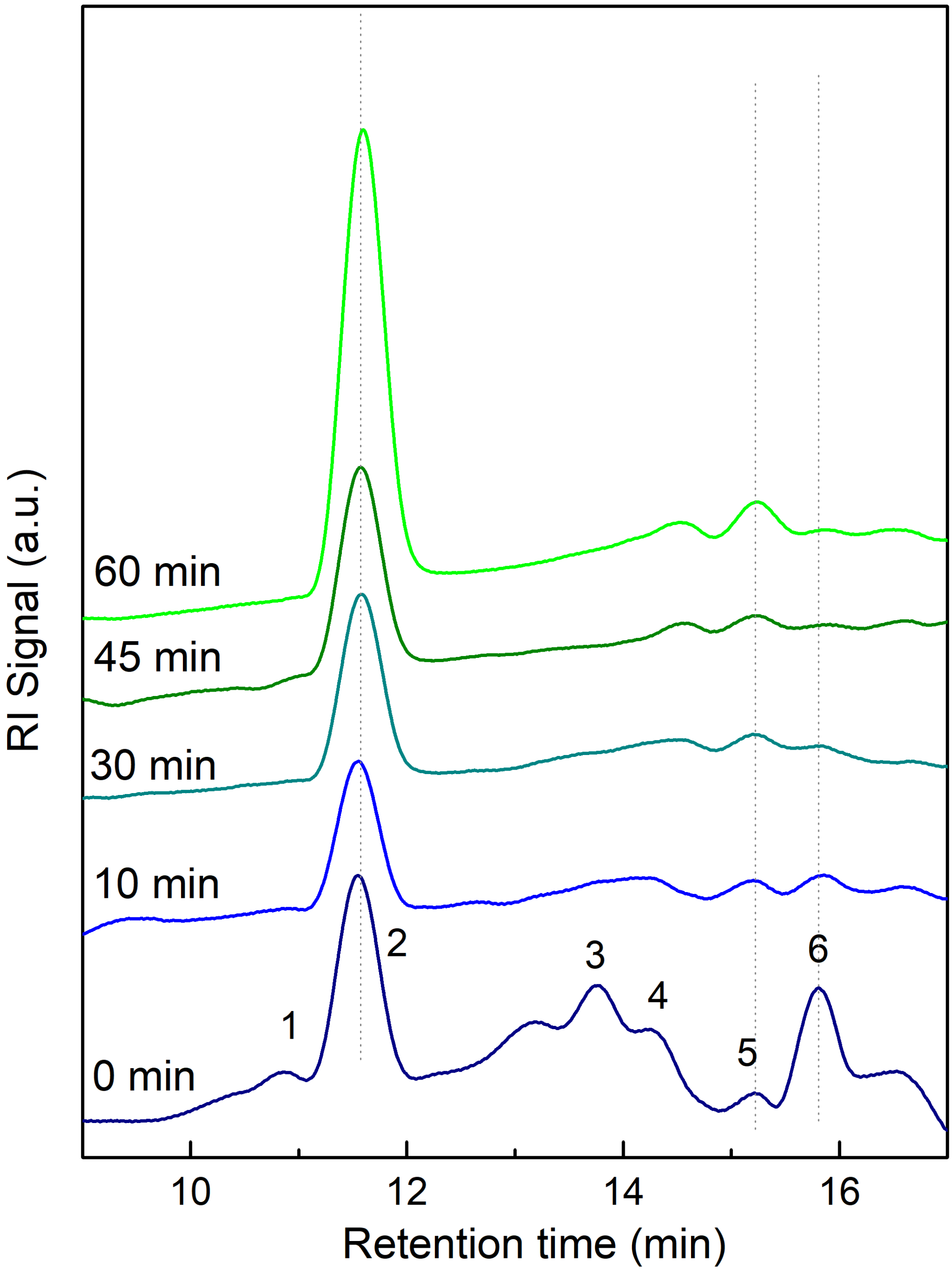

RI Signal (a.u.)
60 min
45 min
30 min
10 min
0 min
1
2
3
4
5
6
10
12
14
16
Retention time (min)

Figure 5

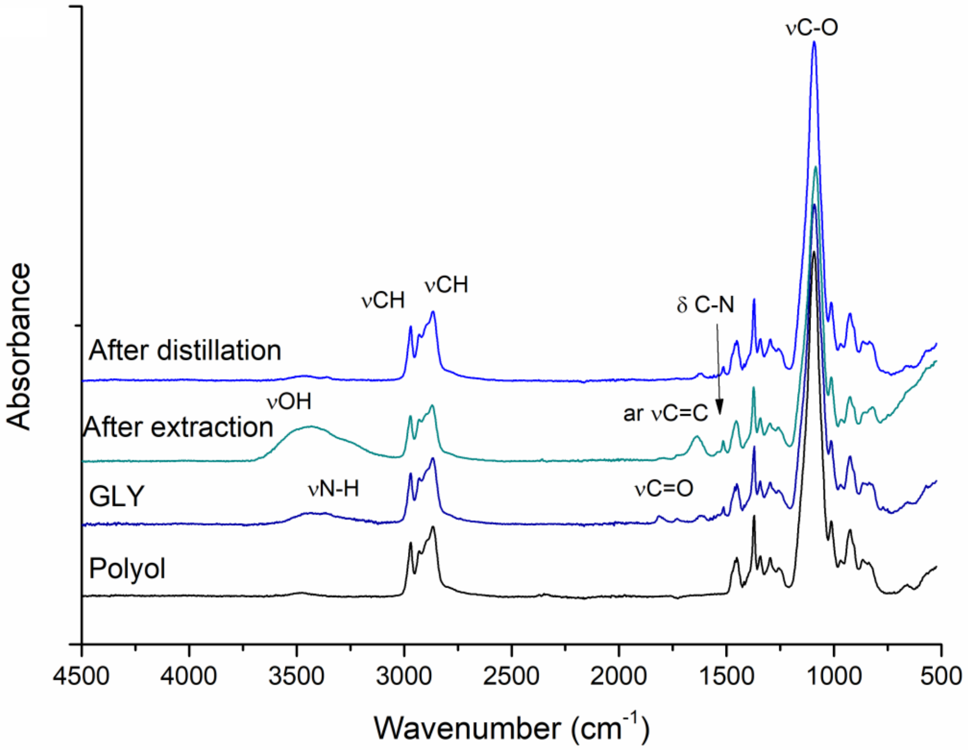

Absorbance
Wavenumber (cm^{-1})
4500
4000
3500
3000
2500
2000
1500
1000
500
After distillation
After extraction
GLY
Polyol
νCH
νCH
νOH
νN-H
δ C-N
ar νC=C
νC=O
νC-O

Figure 6

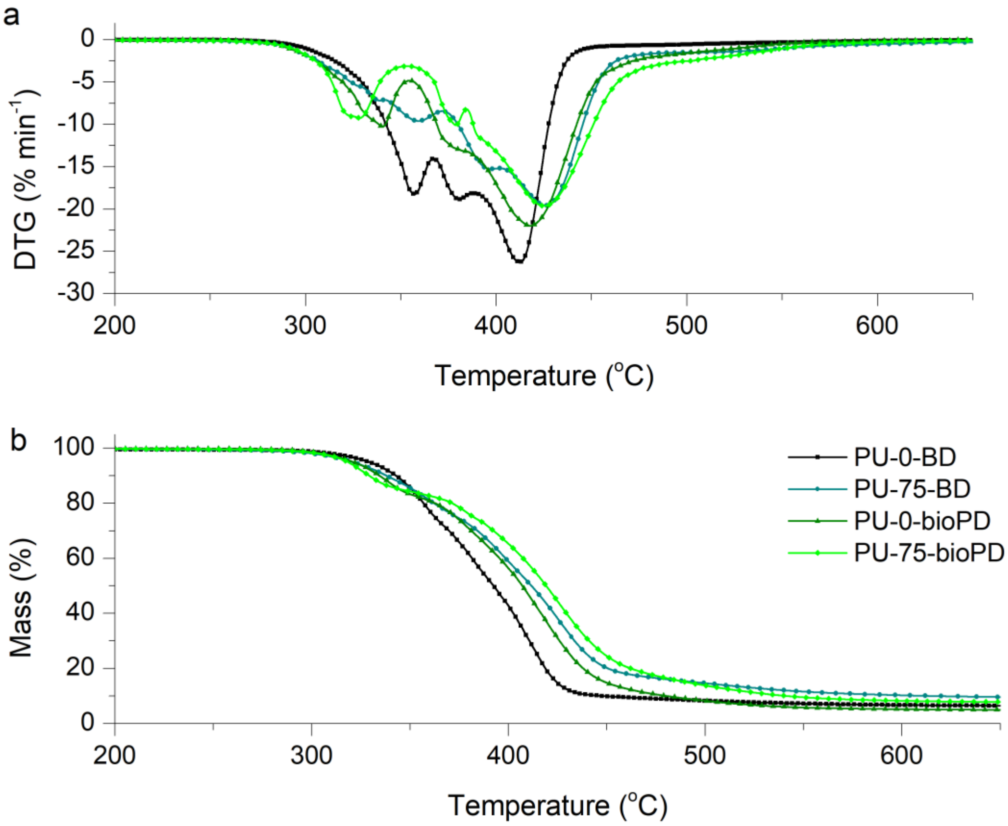
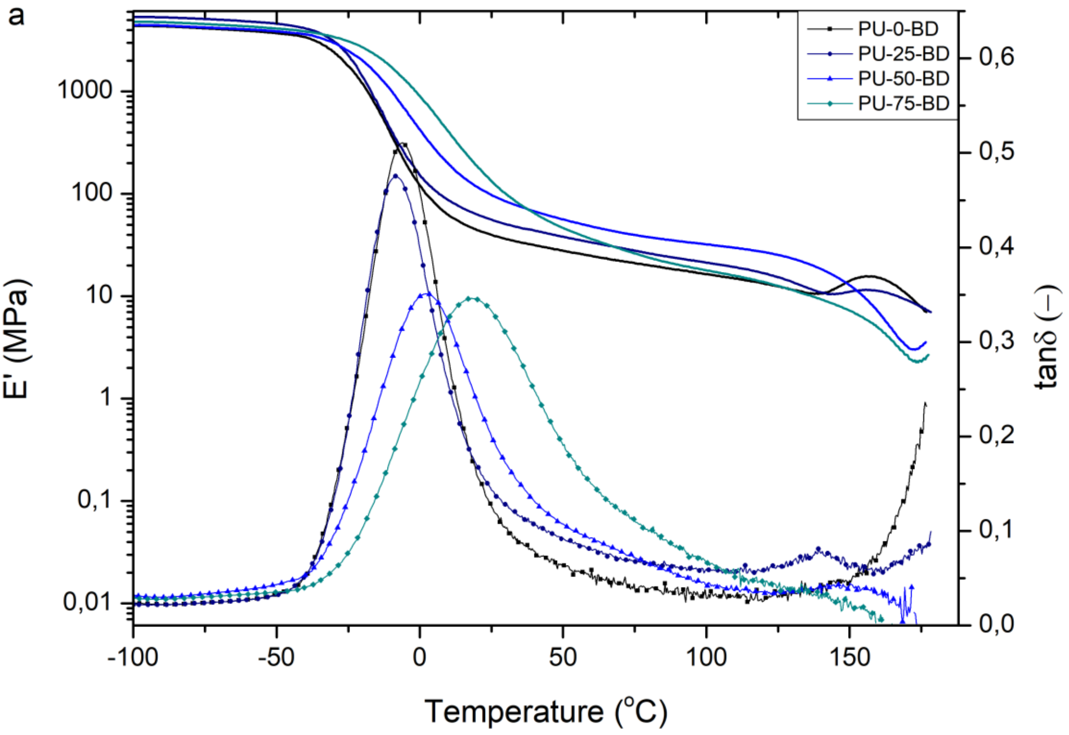

a
0
-5
-10
-15
-20
-25
-30
DTG (% min^{-1})
200
300
400
500
600
Temperature (°C)
b
100
80
60
40
20
0
Mass (%)
200
300
400
500
600
Temperature (°C)
PU-0-BD
PU-75-BD
PU-0-bioPD
PU-75-bioPD

Figure 7


a
E' (MPa)
tanδ (–)
Temperature (°C)
PU-0-BD
PU-25-BD
PU-50-BD
PU-75-BD
0,01
0,1
1
10
100
1000
0,0
0,1
0,2
0,3
0,4
0,5
0,6
-100
-50
0
50
100
150

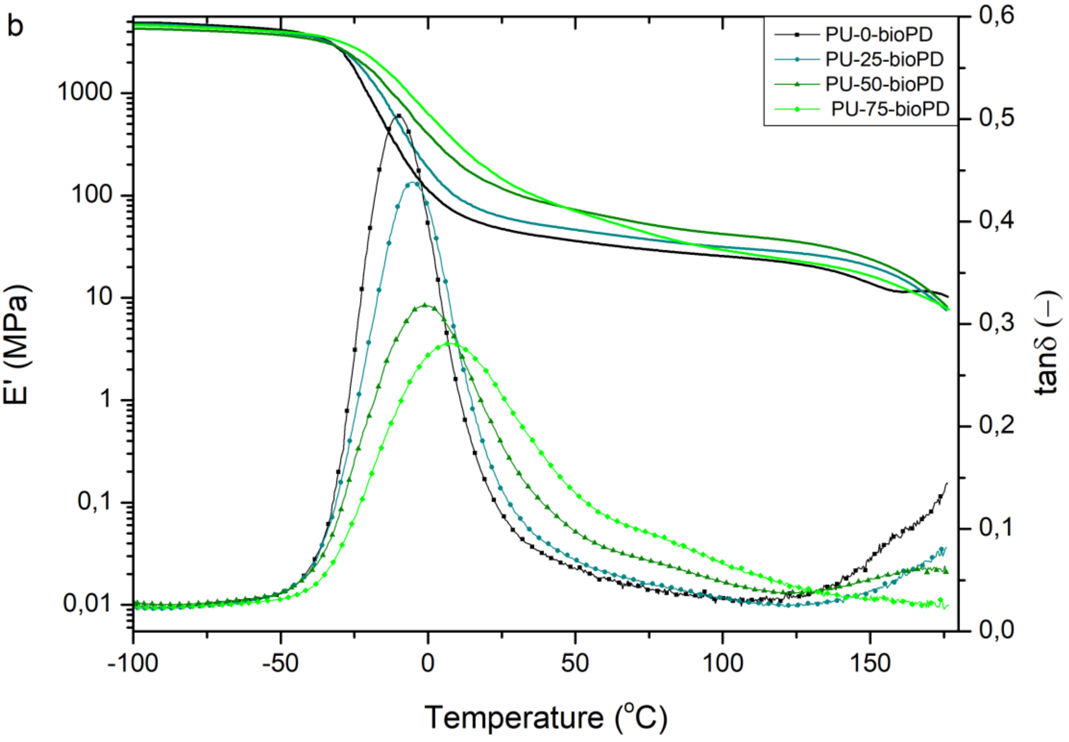

b
E' (MPa)
tanδ (–)
Temperature (°C)
PU-0-bioPD
PU-25-bioPD
PU-50-bioPD
PU-75-bioPD
0,01
0,1
1
10
100
1000
0,0
0,1
0,2
0,3
0,4
0,5
0,6
-100
-50
0
50
100
150

Figure 8

Table 7. Application of recovered intermediates in PU synthesis.

Table 8. Hydroxyl values and products concentration (% by weight) in the glycerolysates obtained using various catalysts.

Table 9. Hydroxyl value and products concentration (% by weight) in glycerolysates obtained in the presence of DBTDL catalyst at various concentrations.

Table 10. Hydroxyl values and products concentration (% by weight) on the glycerolysates obtained using various purities of glycerine.

Table 11. Hydroxyl values and products concentration (% by weight) in the glycerolysate obtained in the presence of DBTDL catalyst sampled in the time intervals.

Table 12. Hydroxyl values and products concentration (% by weight) of glycerolysate before and after purification operation (extraction and distillation) and original polyol.

Table 13. Static mechanical properties (tensile strength – TS; elongation at break – ε_b; permanent elongation after break – ε_p) and hardness of synthesised polyurethanes with BD and bioPD as a chain extender.

Table 14. Results of TGA ($T_{5\%,}$ $T_{10\%,}$ the residue at 650°C), DMA ($T_{g,}$) of polyurethanes with BD and bioPD as chain extenders.

Table 15. Application of recovered intermediates in PU synthesis.

Type of recovered polyol	Properties of recovered polyol*	Obtained material	Recovered polyol content	Properties of new material (changes)	Ref.
Glycolysate obtained from flexible PU foam by DEG	I_{OH}= 63 mgKOHg^{-1} AV= 6.23 mgKOHg^{-1}	Flexible PU foam	0–50	The compression strength decreases A slight decrease in the cell size of the foam	[19]
Glycolysate obtained from rigid PU foam by DEG+ ethanolamine	I_{OH}= 451 mgKOHg^{-1} I_{Ac}=7.1 mgKOHg^{-1}	Rigid PU foam	0–40	Higher density Heat conductivity on the same level Slightly higher compressive strengths Higher water absorption	[20]
Glycolysate obtained from flexible PU foam by DPG	I_{OH}= 372 – 341 mgKOHg^{-1}	Rigid PU foam	0–15	Cream time and gel time increased Increased thermal conductivity with a higher recovered polyol	[21]
Glycolysate obtained from PU elastomer by HD	I_{OH}=199 mgKOHg^{-1}	Thermoplastic PU	0–55	Higher Young moduli Higher tensile strength Lower elongation at break	[22]
Glycolysate obtained from flexible PU foam by DEG	I_{OH}=60 mgKOHg^{-1}	Flexible PU foam	0–50	Density slightly increased Tensile strength increased Cell size increased	[23]

Glycolysate obtained from flexible PU foam by crude glycerine	I_{OH}=51 mgKOHg^{-1}	Flexible PU foam	0–25	Density slightly increased Tensile strength increased Cell size decreased	[23]

*AV-amine value, I_{AC}-acidic number, I_{OH}-hydroxyl number.

Table 2. Hydroxyl values and products concentration (% by weight) in the glycerolysates obtained using various catalysts.

Catalyst type	Hydroxyl number (mgKOHg^{-1})	Products concentration (% by weight)			
		Oligomers	**Polyol**	**By-products**	**Glycerine**
DABCO	136	5.4	76.5	16.0	2.1
DBTDL	135	-	82.4	15.5	2.1
KAc	125	13.6	69.0	14.5	2.9
NaOH	144	4.1	59.5	34.7	1.7
StOc	124	4.2	76.1	14.5	5.2
TEA	-	9.6	61.2	17.7	11.5

Table 3. Hydroxyl value and products concentration (% by weight) in glycerolysates obtained in the presence of DBTDL catalyst at various concentrations.

DBTDL concentration	**Hydroxyl number (mgKOHg^{-1})**	**Products concentration (% by weight)**		
		Polyol	**By-products**	**Glycerine**
0.25%	155	81.5	14.8	3.7
0.5%	135	82.4	15.5	2.1
1%	182	68.5	27.4	4.1
2%	175	62.0	29.5	8.6

Table 4. Hydroxyl values and products concentration (% by weight) on the glycerolysates obtained using various purities of glycerine.

Glycerine purity	Hydroxyl number (mgKOHg^{-1})	Products concentration (% by weight)		
		Polyol	By-products	Glycerine
62%	221	65.1	31.7	3.2
84%	135	82.4	15.5	2.1
99.5%	153	78.6	19.5	1.9

Table 5. Hydroxyl values and products concentration (% by weight) in the glycerolysate obtained in the presence of DBTDL catalyst sampled in the time intervals.

Time (min)	I_{OH} (mgKOHg^{-1})	Products concentration (% by weight)			
		Oligomers	Polyol	By-products	Glycerine
0	387	3.4	35.6	33.0	16.1
10	296	-	52.1	38.8	9.1
30	167	-	67.4	22.0	6.8
45	153	-	70.2	21.6	8.2
60	135	-	82.4	15.5	2.1

Table 6. Hydroxyl values and products concentration (% by weight) of glycerolysate before and after purification operation (extraction and distillation) and original polyol.

Sample	**Hydroxyl number ($mgKOHg^{-1}$)**	**Products concentration (% by weight)**		
		Polyol	**By-products**	**Glycerine**
GLY	135	82.4	15.5	2.1
After extraction	141	69.2	25.5	5.0
After distillation	93	83.8	15.4	0.8

Table 7. Static mechanical properties (tensile strength – TS; elongation at break – ε_b; permanent elongation after break – ε_p) and hardness of synthesised polyurethanes with BD and bioPD as a chain extender.

Sample	Hardness (ºSh A/D)	TS (MPa)	ε_b (%)	ε_p (%)
PU-0-BD	85.1±0.5/34.2±0.3	15.6±0.8	560±60	78±12
PU-25-BD	87.0±0.7/31.3±0.6	13.1±1.8	330±50	41±12
PU-50-BD	90.3±0.9/38.6±0.7	12.5±1.9	110±30	27±1
PU-75-BD	89.7±0.4/38.6±0.9	12.0±0.7	130±10	7±2
PU-0-bioPD	85.5±0.6/35.0±0.7	13.7±0.4	460±10	68±4
PU-25-bioPD	87.6±0.7/34.5±1.3	15.1±1.1	280±30	27±4
PU-50-bioPD	90.9±0.4/39.2±1.1	12.5±1.3	140±30	10±5
PU-75-bioPD	88.7±1.2/36.9±0.9	14.8±1.6	150±20	13±3

Table 8. Results of TGA ($T_{5\%}$, $T_{10\%}$, the residue at 650°C), DMA (T_g,) of polyurethanes with BD and bioPD as chain extenders.

Samples	$T_{5\%}$ (ºC)	$T_{10\%}$(ºC)	Residue (%)	T_g (ºC)
PU-0-BD	329.0	342.8	6.57	-6.0
PU-25-BD	326.6	343.1	8.98	-8.5
PU-50-BD	319.1	338.8	8.51	2.0
PU-75-BD	320.5	337.9	9.71	17.9
PU-0-bioPD	320.9	334.3	5.07	-10.2
PU-25-bioPD	320.2	336.1	7.86	-5.6
PU-50-bioPD	318.6	336.1	6.92	-0.7
PU-75-bioPD	318.2	329.2	7.91	7.7

Supplemental files

Figure S1. FTIR spectra of glycerolysates obtained in the presence of DBTDL catalyst in various concentration.

Figure S2. SEC chromatograms of glycerolysates obtained in the presence of DBTDL catalyst in various concentration.

Figure S3. FTIR spectra of synthesised polyurethanes.

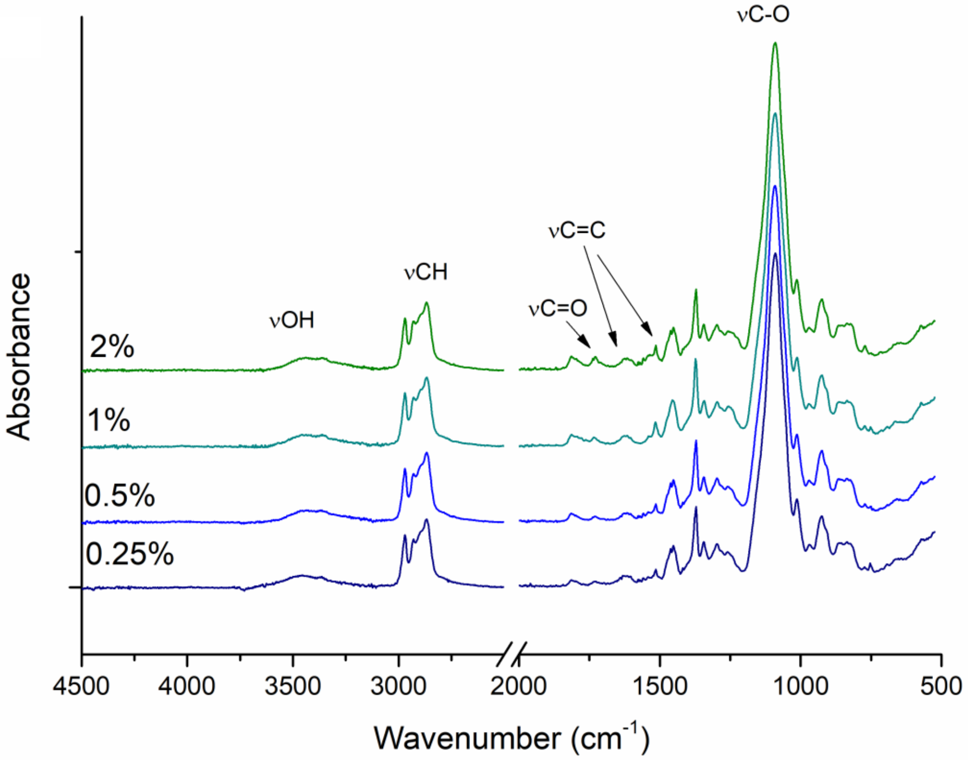

νC-O
νC=C
νCH
νC=O
νOH
2%
1%
0.5%
0.25%
Absorbance
4500
4000
3500
3000
2000
1500
1000
500
Wavenumber (cm^{-1})

Figure S1

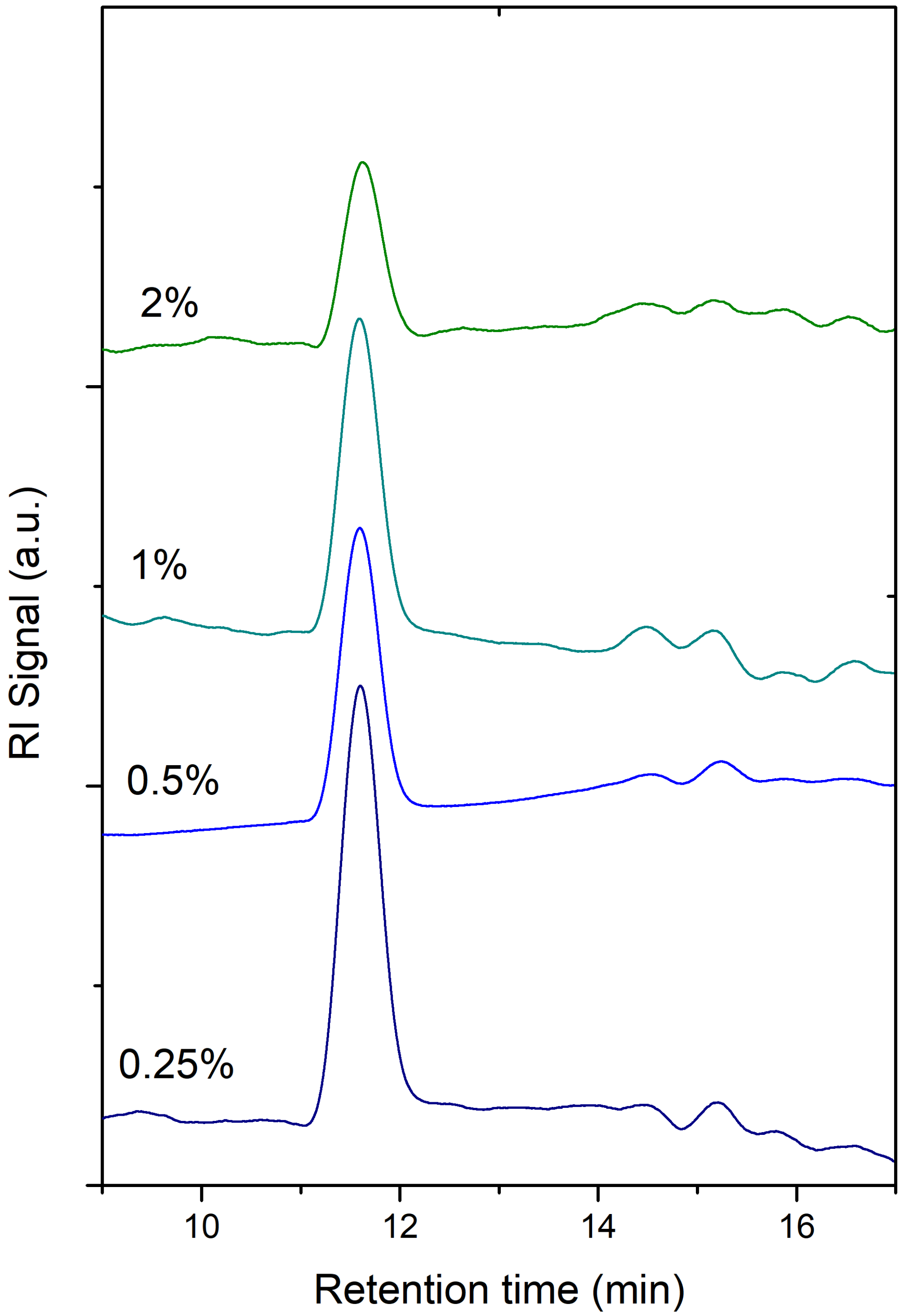


Figure S2

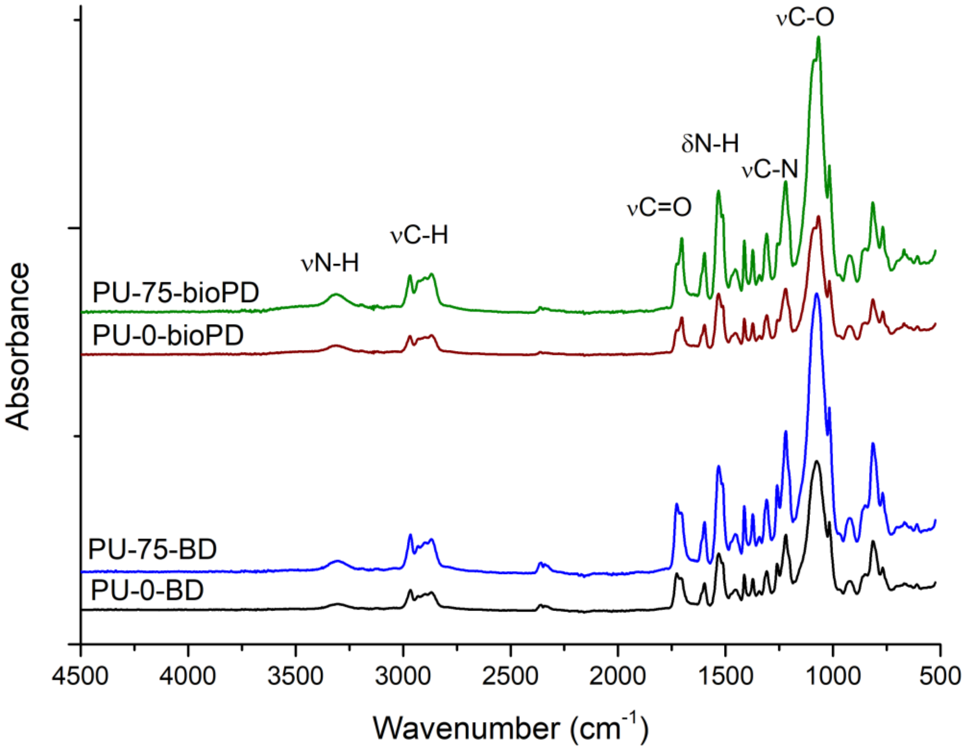

νC-O
δN-H
νC-N
νC=O
νC-H
νN-H
PU-75-bioPD
PU-0-bioPD
PU-75-BD
PU-0-BD
Absorbance
4500
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})

Figure S3