Effect of glycols used as glycolysis agents on chemical structure and thermal stability of the produced glycolysates

J. Datta

Abstract In this study, the influence of glycols on chemical structure and thermal stability of glycolysates as polyurethane intermediates were investigated. The intermediates were obtained by the glycolysis process of waste polyurethane foams in the reaction with different glycols ranging from ethylene glycol to hexane-1,6-diol. The used glycols were not separated from the product after the glycolysis process has been terminated. The effects of different weight ratio of glycols to polyurethane (PU) foam on chemical structure and thermal stability were investigated by FTIR, GPC, and TG/DTG. FTIR analysis of the glycolysates revealed their similar chemical architecture as manifested by the similarity of absorption peaks within the entire wavenumber range of spectra. This may indicate that the glycol has no influence on the chemical composition of glycolysates. GPC analysis showed that the glycolysates were characterized by polydispersity smaller than 2 which is lower as compared to some commercial polyols used for PU synthesis. GPC chromatograms showed that the applied glycols and the conditions of PU glycolysis allowed recreation of the original polyol as documented on the chromatograms by a single, well-formed peak at the beginning of retention time. Based on TG thermograms, it was established that glycol used in transesterification of PUs affected the temperature at which the loss of glycolysate mass by 5 and 10 % occurs. It was also observed that glycol affected the temperature at which the decomposition rate of glycolysates was the highest.

Keywords Glycols · Glycolysis process · Thermal stability · TG · FTIR · Waste polyurethane foam

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Introduction

Research on polyurethane (PU) glycolysis has been conducted worldwide with a stable intensity for many years [1–9]. Studies are aimed at elaborating technologies which would allow the production of semi-products useful for industry and therefore possessing certain functionality, molecular mass, medium reactivity, and low viscosity at room temperature. Reactions are studied under atmospheric pressure at temperatures lower than the boiling point of low-molecular-mass glycol or diol which serve as glycolysis agents. Usually, the catalysts are used, and in some cases, amines are added which results in aminoglycolysis. The products of glycolysis are the so-called glycolysates, which consist of a homogenous mix of various compounds, also including those with amphiphilic properties. The conditions of PU depolymerization via transesterification and the applied glycolysis agents influence the direction of the reaction and therefore the amount of the obtained glycolysate [10, 11]. Based on our studies, we can conclude that the use of low-molecular-mass glycols, ranging from ethylene glycol (EG) to hexane-1,6-diol (HDO), during PU glycolysis allows obtaining glycolysates with such chemical structure and thermal stability which make them suitable for the direct application in PU synthesis and the production of elastoplastic materials characterized by significant elastoplastic deformation.

Experimental

Materials

Elastic PU foam was a production waste from Eurofoam Gdańsk LLC (Poland). EG (POCH Gliwice, Poland),

propane 1,3 diol (PG) (Sigma Aldrich, Germany), butane 1,4 diol (BDO) (BASF, Germany), pentane 1,5 diol (GP) (BASF, Germany), HDO (POCH, Gliwice Poland) as decomposing agent, and potassium acetate (KAc) (POCH, Poland) as catalyst were used. Glycolysis reaction was carried out at PU foam/glycols mass ratio of 10:1. The amount of catalyst was 0.5 % of PU foam mass. Reaction was carried out in a 2-l steel reactor with mechanical stirrer and reflux condenser at the temperature between 190 and 250 °C. Reaction time was 33/80 min depending on glycolysis agent. Two phases were obtained. The weight ratio of upper/lower glycolysate phase ranged from 90:10 to 70:30. The upper glycolysate phase was decanted after 24 h and analyzed.

Measurements

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

The measurements were performed at the Gdansk University of Technology, Department of Physical Chemistry.

The mass values and the molecular mass distributions of the glycolysates were determined by chromatography with a Knauer 64 GPC System. A set up consisting of five PL-gel columns (250 × 8 mm, 10 μm particle size) and refractometric or UV–Vis detector was used. Column calibration was performed using polystyrene standards (Watters).

The measurements were performed at the Cracow University of Technology, Faculty of Chemical Engineering and Technology, Independent Department of Chemistry and Technology of Plastics.

The hydroxyl number (LOH) was determined according to PN-EN ISO 2554. Based on hydroxyl value, the number average molecular mass (Mn) was calculated from Eq. (1):

$$Mn = \frac{56.1 \times 1000 \times f}{LOH} \tag{1}$$

where f is the assumed functionality of glycolysate.

TG analysis was carried out by using a NETZSCH TG 209 apparatus. Samples were heated between 20 and 600 °C at the rate of 10 °C min^{-1}. The analysis was performed under argon atmosphere. Temperature values for which the loss of glycolysate mass by 5 and 10 % ($T_{5\%}$ and $T_{10\%}$) had occurred were assessed from TG thermograms. The temperatures at which the highest rate of mass loss (T_{max}) had been observed were determined from the DTG curve. The measurements were performed at the University of Gdansk, Physicochemical Laboratories.

Results and discussion

FTIR spectra of the glycolysates produced for the same mass ratio of PU: glycol of 10:1 and with the use of various glycols are presented in Fig. 1. An outstanding peak for the wavenumber value of 1,085 cm^{-1} is interpreted as originating from υ_{C-O-C} polyol group. The peaks characteristic for –OH groups of hydroxyl compounds (υ_{OH} 3,440 cm^{-1}) and NH groups of urethane bonds (υ_{NH} 3,343 cm^{-1}) are also noticeable. Intensive absorption bands at wavenumber 3,000–2,800 cm^{-1} correspond to symmetric and asymmetric bending oscillations of –CH_2– and –CH_3 groups. Bands present at 1,550–1,350 cm^{-1} are interpreted as deformational oscillations of –CH_3 groups and other oscillations from the bonds between carbon atoms. The >C=O interactions from urethane groups correspond to $\upsilon_{C=O}$ band with two or three peaks at the wavenumber value of ca. 1,730 cm^{-1}. The $\upsilon_{C-O,ureth}$ bands of urethane bonds at 1,222 cm^{-1} and $\upsilon_{C-O,alc}$ band at 1,008 cm^{-1} from hydroxyl compounds present in glycolysates are also visible.

Similar results can be found in the reports of other authors, who have researched the glycolysis process of PUs [4, 5, 12].

It is noticeable that the obtained spectra indicate the presence of similar chemical substances in glycolysates irrespective of the glycolysis agent used. GPC chromatograms of glycolysates obtained during glycolysis of PU foam with EG and propylene glycol are presented in Figs. 2 and 3, respectively. For a similar retention time (ca. 22–24 min) well-defined peaks of high intensity are present in the chromatograms. This indicates that the applied glycolysis conditions allowed foam degradation until the total decomposition of PU chains and the separation of specific components, including the main ingredient originally used for producing the foam, i.e., polyether polyol. The shape of the peak 1 with a very visible maximum (M_{p1} = 957 in Fig. 2 and M_{p1} = 1,068 in Fig. 3) confirms
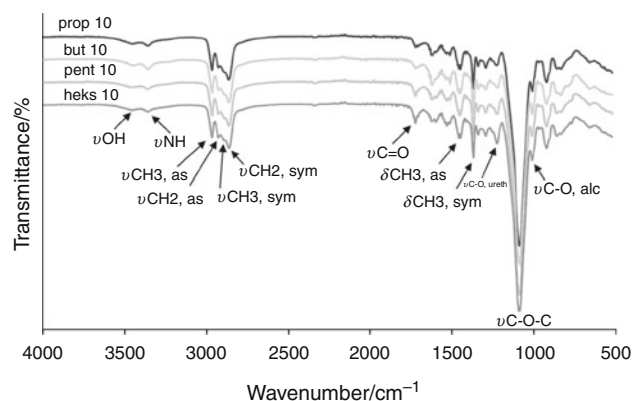

Fig. 1 FTIR spectra of glycolysates obtained for the mass ratio of polyurethane:glycol of 10:1 and various glycols
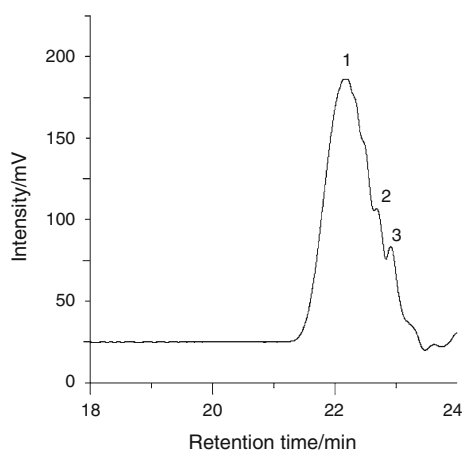
Fig. 2 GPC chromatogram of the glycolysate coded Et10. *Peak 1* recovered polyether polyol ($M_{p1} = 957$); *peaks 2, 3* reaction by-products ($M_{p2} = 331$, $M_{p3} = 199$)
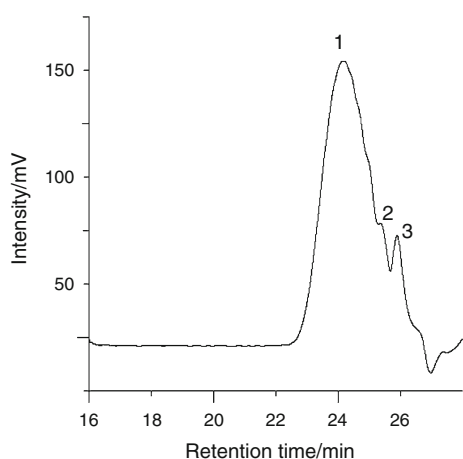

Fig. 3 GPC chromatogram of the glycolysate coded Prop10. *Peak 1* recovered polyether polyol ($M_{p1} = 1{,}068$); *peaks 2, 3* reaction by-product ($M_{p2} = 325$, $M_{p3} = 182$)

the aforementioned conclusion. The peaks marked 2 and 3 are interpreted as mixtures of post-reaction adducts most likely containing, inter alia, mono- and dicarbamates. At the same time, the author's assumption that unreacted glycol in the glycolysate obtained for the 10:1 mass ratio is practically gone has been confirmed. This manifested itself by the lack of a well-defined single peak of low intensity which

otherwise would have been present in the chromatogram as peak 4 for the above mentioned retention time.

Chromatographic analysis showed that glycolysis, conducted according to the method previously described by the author [11], allowed obtaining glycolysates with the mean polydispersity lower than 2. This is advantageous because glycolysates are supposed to serve as semi-products in the production of urethane polymers. High polymolecularity could significantly reduce or exclude the production of PUs characterized by ordered structure that influences sought after properties of the product. Number average molecular masses ($\overline{\mathrm{Mn}}$) of glycolysates calculated by GPC method from LOH values obtained from titration of terminal hydroxyl groups (Table 1) are similar. This finding proves that the assumed functionality of glycolysate in Eq. (1) is correct.

TG–DTG analysis indicates that the thermal stability of glycolysates increases with the increasing molecular weight of the glycol used in glycolysis. This phenomenon occurs for the temperature at which degradation is marked by the loss of glycolysate mass by 5 % ($T_{5\%}$), as well as for the temperature at which such mass loss is 10 %. Our research results, which have been partially published [10, 11], indicate that a 5 % loss of glycolysate mass was mainly caused by evaporation of the remnants of unreacted glycol (temperature range 225–242 °C). Within this temperature range, there is no serious damage to oligomerol chains that contain PU-specific groups. Above 242 °C urethane bonds probably break, and that initiates degradation of glycolysates. This hypothesis has been confirmed by other studies, inter alia [13]. Within the temperature range between 260 and 314 °C a glycolysate loses ca. 10 % of its mass, while the main degradation process, which is very rapid, occurs above 360 °C. Destruction is initiated inside rigid segments via decomposition of urethane groups which is followed by the decomposition of ether groups in elastic segments [1, 4, 14]. I described the products originating during this process, i.e., amine compounds and carbon monoxide (IV) in the earlier report [4].

TG–DTG thermogram obtained from the sample coded Heks10 is presented in Fig. 4.

The loss of glycolysate mass occurs at the highest rate at ca. 368 and 399 °C for EG and hexanediol, respectively. We

Table 1 Average molecular mass and polydispersity of glycolysates

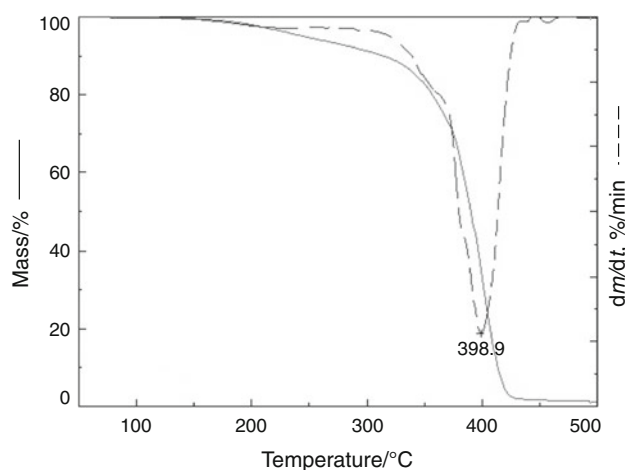| Glycolysate code	Number average molecular mass GPC	Mass average molecular mass GPC	Polydispersity GPC	Hydroxyl number/ mg KOH g^{-1}	Average mass calculated from hydroxyl number
Et10	615	1,192	1.94	152	737
Prop10	655	1,435	1.67	148	756
But10	735	1,540	1.76	144	776
Pent10	810	1,780	1.85	136	822
Heks10	914	1,990	1.42	121	927

Fig. 4 TG and DTG curves of the glycolysate coded heks10 (10:1)

Table 2 Results of thermal stability analysis of the glycolysates. Mass ratio of PU foam to glycol equals 10:1

Glycolysate code	$T_{5\%}$/°C	$T_{10\%}$/°C	T_{max}/°C
Et10	225	260	368
Prop10	235	274	380
But10	240	285	385
Pent10	243	297	392
Heks10	244	314	399

assume that the former temperature value results, partially or wholly, from the presence of the glycolysate remnants in the evaporated product. The values of temperature at which the degradation of all glycolysates starts (TG) and at which the rate of mass loss is the fastest (DTG) are listed in Table 2.

Conclusions

The used analytical methods confirmed that during the glycolysis of waste PU foam glycols, ranging from EG to 1,6-hexanediol, have less significant influence on chemical architecture and probably also on chemical composition of glycolysates as demonstrated by similar absorption bands, as well as much the same intensities of the peaks appearing in FTIR spectra. The peak intensity at $1,085$ cm^{-1} indicates the presence of oligomerols that contain ether groups and therefore the probable presence of polyols used in the synthesis of PU subjected to glycolysis. This observation has been confirmed by the analysis of GPC chromatograms. For the similar retention time value (ca. 22–24 min) well-defined peaks of high intensity appear in the chromatograms. This is an indication that the used glycols and chosen reaction conditions allow for conducting intermolecular transesterification of

urethanes and urethane groups, as confirmed by the results obtained by other authors [1, 10, 13]. It also shows that the foam degradation reached the level of complete decomposition of PU chains and the separation of specific components, including the main component, i.e., polyetherol. The results of TG–DTG analysis indicates that thermal resistance of glycolysates increases with the increasing molecular weight of glycol used in glycolysis. Moreover, glycolysates display thermal resistance up to ca. 240–260 °C. The temperature at which a 5 % mass loss occurs most likely does not result from degradation but from evaporation of unreacted glycol. The shape of DTG curves proves it.

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