

THERMAL ANALYSIS AND STATIC STRENGTH OF POLYURETHANES OBTAINED FROM GLYCOLYSATES

J. Datta* and M. Kacprzyk

Gdańsk University of Technology, Chemical Faculty, Department of Polymer Technology, 80-952 Gdańsk, Poland

In this work thermal stability and tensile strength of polyurethanes obtained from glycolysates was investigated. The glycolysates were produced via glycolysis of waste polyurethane foam (PUR) in the reaction with 1,3-propylene glycol (PG). Polyurethanes were synthesized from the obtained intermediates by the prepolymer method using diisocyanate (MDI) and glycolysis product of molecular mass ranging from 700 to 1000, while 1,4-butylene glycol (BDO) was used as a chain elongation agent. The influence of NCO group concentration in prepolymer on tensile strength and elongation at break of polyurethanes was investigated using Zwick universal tensile tester.

Thermal decomposition of the obtained glycolysates and polyurethanes was followed by TG coupled with FTIR spectroscopy. The main products of thermal decomposition have been identified.

Keywords: glycolysates, polyurethane wastes, tensile strength, TG, TG-FTIR, thermal analysis, thermal stability

Introduction

The most frequently used agents that stimulate glycolysis in recycling of scrap polyurethanes are diols such as, ethylene glycol (EG), 1,2- and 1,3-propylene glycol (PG), and 1,4-butylene glycol (BDO), and 1,6-hexane glycol as well as dimers, e.g. diethylene glycol (DEG), dipropylene glycol (DPG) and trimers, e.g. triethylene glycol and tripropylene glycol [1–3]. Sometimes oligomerols of low molecular mass, ranging from 300 to 750, are applied, e.g. polyoxyethylene and polyoxypropylene glycols. Mixtures of glycol and amines or alkylamines (e.g. monoethylamine, diethylamine and triethylamine) are also used in chemical reactions. The type of glycol used influences the rate of the process because the maximal temperature cannot exceed the glycol's boiling point [1–7]. The application of glycols with side carbon chains prevents lamination in final products [8–10]. Lamination can be influenced by varying the mass ratio of scrap polyurethane, PU to glycolysis initiating agent, as well as via the application of reaction catalysts. The addition of amines and alkylamines speeds up the reaction at lower temperatures [4, 5, 11, 12].

The investigations of the possible use of glycolysates in polyurethane production allow defining practical suitability of the chemical compounds obtained from waste. In such studies the utilitarian properties of the products obtained from commercially available polyols as well as by applying gly-

colysates are compared; the reactivity of commercial polyols and glycolysates in the polyurethane production processes are also researched. The R-RIM products containing even up to 50 mass% of scrap polyol (glycolysate) and not displaying a significant loss of mechanical properties have been described [13–15].

The possibility of using glycolysates from rigid foams to produce new foam products has been confirmed [16, 17]. The addition of 30 mass% of glycolysate did not change in a significant way the characteristics of such products. Borda *et al.* [18] used the glycolytic products obtained from elastomers to synthesize polyurethane glues. Gassan *et al.* [19] described a method for producing rigid polyurethane insulating foams of the improved thermal stability with the use of glycolytic products. The authors of the patent [20] obtained rigid insulating foams of high thermal stability and good mechanical properties by applying a mix of commercial polyol and glycolysate as polyol component. The amount of added glycolysate ranged from 10 to 50% of the total mass of the substrates. Matko *et al.* [21] undertook an attempt to obtain polyurethane foams and partially biodegradable, polyurethane composites of decreased flammability. The basic components of these materials were the products of glycolysis of urethane elastomers [17, 22, 23], MDI and, in the case of composites, wood shavings. Inexpensive, commercially available phosphorus compounds were used as agents lowering flammability.

* Author for correspondence: datta@urethan.chem.pg.gda.pl

The purpose of our work was to use glycolysates obtained in the reaction between scrap polyurethane foam and 1,3-propylene glycol in the synthesis of polyurethanes, and to investigate the thermal stability and tensile strength of the PU products.

Experimental

Materials

The utilized elastic PUR foam was a production waste received from the company Eurofoam Polska (Poland). 1,3-propylene glycol (PG) (DuPont, USA) and sodium hydroxide (KOH) (POCH, Poland) were used as decomposing agent and catalyst, respectively. The glycolysates were produced via glycolysis which was carried out at the following PUR foam/PG mass ratios: 2:1, 4:1, 6:1, 8:1 and 10:1. The amount of catalyst equaled 0.4% of the PUR foam mass. The reaction was carried out in a 2 L steel reactor with a mechanical stirrer and reflux condenser in the temperature 170/190°C. The reaction time ranged from 29 to 39 min, depending on the PUR foam/PG mass ratio. 1,3-propylene glycol was not separated from the product after the process of glycolysis.

Polyurethanes (PU) were synthesized by the prepolymer method (two-stage) using 4,4'-methyl-diphenyl diisocyanate (MDI) (Borsodchem, Hungary), glycolysates of the highest molecular mass and phosphoric acid (POCH, Poland) as side reactions inhibitor (first stage). However glycolysate or 1,4-butylene glycol (BDO) (BASF, Germany) was added to the obtained urethane prepolymer (second stage) as a chain extender agent of the prepolymer.

Methods

Thermal stability of polyurethanes obtained from glycolysates was investigated by thermogravimetry coupled with Fourier transform infrared spectroscopy using NETZSCH TG 209 Iris-FTIR. All samples had approximately 10 mg. The analysis was conducted in an argon atmosphere (flow rate of 2 mL min⁻¹) at temperatures ranging from 20 to 600°C and at a heating rate of 10°C min⁻¹.

Mechanical properties of the polyurethanes obtained from glycolysates were determined by tensile strength at break using ProLine Zwick Z020. The analysis was conducted in an air atmosphere at 200 mm min⁻¹ tensile speed. Determinations were performed on samples with dimension of 100×8×2 mm.

Results and discussion

Thermal decomposition study

The results of thermogravimetric analysis of polyurethanes obtained from glycolysates are shown in Figs 1 to 4. Thermal stability of PU samples synthesized from the glycolysates (GL) that had been obtained for different values of the PUR foam/PG ratio (from 2/1 to 10/1) was similar based on the curve similarity in curves depicting the relationship between the mass loss and temperature. It can be concluded that the onset of thermal degradation of polyurethanes produced from glycolysates most frequently occurs within the temperature range between 274 and 292°C, while a 10% mass loss starts at 300°C for the majority of PUs. In comparison to the polyurethanes obtained from commercial raw materials, PUs from glycolysates are characterized by slightly lower thermal stability.

Based on DTG curves (Figs 2 and 4), it was concluded that polyurethanes obtained from glycol-

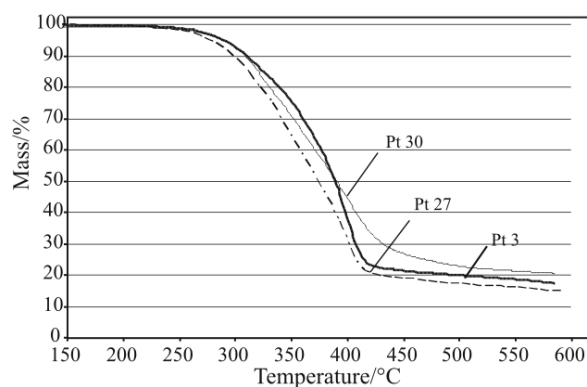


Fig. 1 TG of polyurethanes obtained from glycolysates of different structure. Pt 3 curve – polyurethane obtained from GL9 [10:1]; Pt 27 – from GL5 [2:1] and GL11 [4:1]; Pt 30 – from GL12 [6:1] and GL10 [2:1]

Table 1 Thermal resistance (TG/DTG) of polyurethane samples obtained from glycolysates

Polyurethane's code	$T_{5\%}/^{\circ}\text{C}$	$T_{10\%}/^{\circ}\text{C}$	$T_{\text{maxI}}/^{\circ}\text{C}$	$T_{\text{maxII}}/^{\circ}\text{C}$	$T_{\text{maxIII}}/^{\circ}\text{C}$
Pt 3	274.2	309.3	317.2	350.1	397.6
Pt 12	275.3	309.4	330.3	362.8	389.0
Pt 24	278.6	311.2	331.1	363.3	399.3
Pt 27	267.3	298.3	335.2	369.5	396.0
Pt 30	273.5	308.4	322.1	356.8	402.0

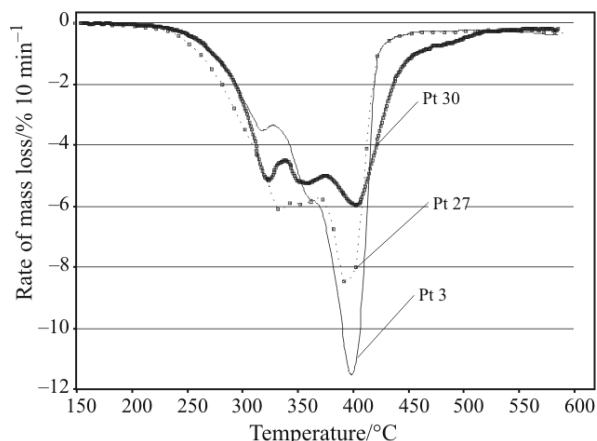


Fig. 2 DTG of polyurethanes obtained from glycolysates (GL) of different structure. Pt 3 curve – polyurethane obtained from GL9 [10:1]; Pt 27 – from GL5 [2:1] and GL11 [4:1]; Pt 30 – from GL12 [6:1] and GL10 [2:1]

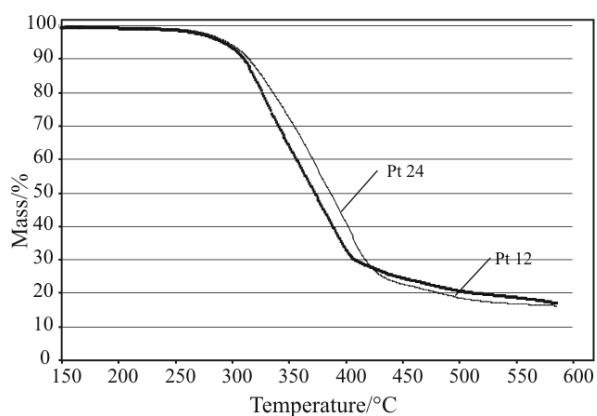


Fig. 3 TG of polyurethanes obtained from glycolysates of different structure. Pt 12 curve – polyurethane obtained from GL12 [6:1] with BDO (chain extender); Pt 24 – from GL14 [10:1] with BDO

ysates have different chemical structure. This has been manifested by the three temperature ranges for which a mass loss occurred with the highest rate.

The first rate maximum for PU decomposition occurs within the temperature range from 317 to 335°C (Table 1).

The analysis of gaseous products (Fig. 5) originating during this mass loss indicated that the compounds containing $-\text{CH}_3$, $-\text{CH}_2-$, $-\text{C}-\text{O}-\text{C}-$ and $-\text{OH}$ groups had been present. Probably, short-chain aliphatic compounds of simple chemical structure form. The second rate maximum was registered for the temperature range 350–369.5°C. The analysis of gaseous products pointed to the presence of compounds containing $-\text{CH}_3$, $-\text{CH}_2-$ and $-\text{C}-\text{O}-\text{C}-$ groups. Moreover, $-\text{OH}$ group was very noticeable. Compounds that form under such thermal conditions most likely belong to ethers with hydroxyl end groups. The third decomposition rate maximum for PU

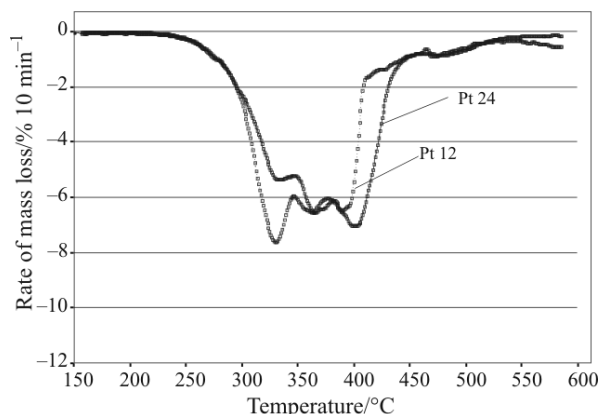


Fig. 4 DTG of polyurethanes obtained from glycolysates (GL) of different structure. Pt 12 curve – polyurethane obtained from GL12 [6:1] with BDO (chain extender); Pt 24 – from GL14 [10:1] with BDO

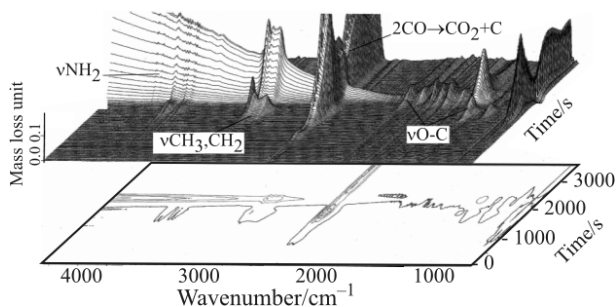


Fig. 5 Infrared absorption spectrum of gaseous decomposition products of polyurethane (Pt 24) obtained from glycolysate

obtained from glycolysates was observed within the temperature range from 389 to 402°C. The analysis of gaseous products allowed identification of the compounds with $-\text{NH}-$ and $-\text{NH}_2$ groups. Moreover, the increased band intensity of signal characteristic for ether group ($-\text{C}-\text{O}-\text{C}-$) and free CO was noted. Most likely, this was caused by the forming amines and amides that contained ether groups in their structure.

Infrared analysis of gaseous products (Fig. 5) forming during the thermal degradation of polyurethanes showed that their main component is CO, as proven by the intensive band corresponding to the wavenumbers range 2350–2300 cm^{-1} . As the temperature increases, carbon monoxide(II) transforms into CO_2 and C.

Mechanical properties

Polyurethanes produced with the use of glycolysate as prepolymer and/or chain extender were characterized by varying tensile strength that ranged from 1 to over 12 MPa. This may be a proof of the big influence the glycolysis conditions have on the structure and prop-

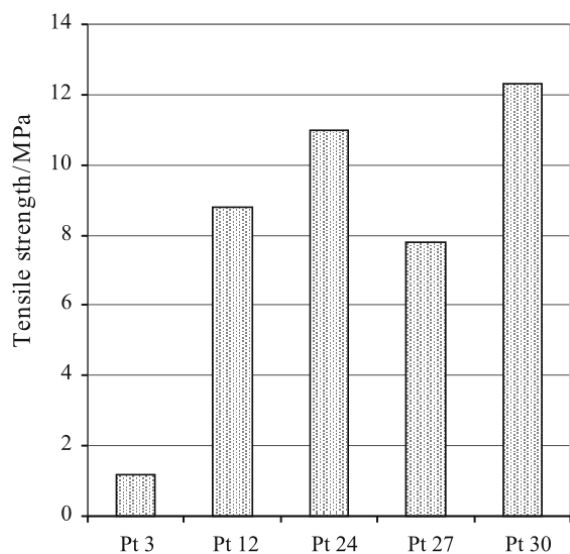


Fig. 6 Influence of glycolysates on tensile strength at break of polyurethanes. Pt 3 – polyurethane obtained from GL9 [10:1]; Pt 12 – from GL12 [6:1] with BDO (chain extender); Pt 24 – from GL14 [10:1] with BDO; Pt 27 – from GL5 [2:1] and GL11 [4:1]; and Pt 30 – from GL12 [6:1] and GL10 [2:1]

erties of glycolytic semiproducts, and therefore on their applicability to the synthesis of polyurethanes.

In Fig. 6 the structural effect of the polyurethane obtained from glycolysate on its tensile strength at break is shown. It can be concluded that the studied polyurethanes, exclusive of a PU sample coded Pt 3 (obtained without the chain extender), are characterized by the similar tensile strength, i.e. from 8 to 12 MPa.

The mechanical strength of samples synthesized with the use of glycolysate as prepolymer extender, i.e. Pt 29 and Pt 30 was not lower than that of the materials obtained with the use of commercial glycol BDO (samples Pt 12 and Pt 24). Despite the high variability of glycolysates, their suitability for synthesizing polyurethanes of increased rigidity has been established.

Based on the results presented in Fig. 7, it was observed that polyurethanes obtained from glycolysates are characterized by even higher differentiation of elongation at break values, namely from 9 to 195%. A particularly high elongation at break of almost 200% was noted for the sample with the lowest tensile strength. The remaining PU samples had similar elongation at break values of about 20%. The authors assume that such small elongations may indicate high cross-linking. The reaction between glycolysates and diisocyanates was occurring at high rate which could disturb or prevent the rigidity improving cross-linking process. As can be seen in Figs 6 and 7, the relationship between tensile strength

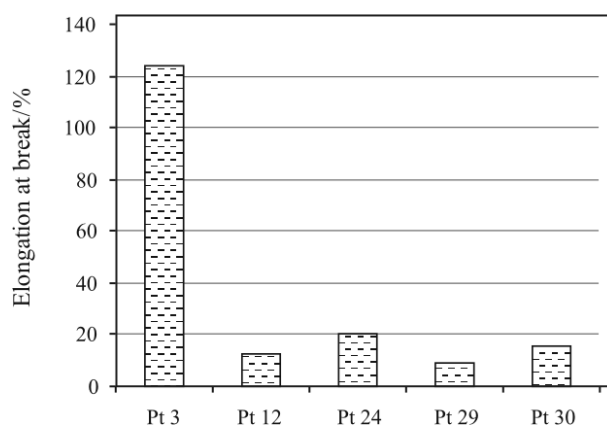


Fig. 7 Influence of glycolysates on elongation during the stretching of polyurethanes. Pt 3 – polyurethane obtained from GL9 [10:1]; Pt 12 – from GL12 [6:1] with BDO (chain extender); Pt 24 – from GL14 [10:1] with BDO; Pt 29 – from GL5 [2:1] and GL11 [4:1]; and Pt 30 – from GL12 [6:1] and GL10 [2:1]

and elongation for the studied samples is inversely proportional.

For the increasing stretching force used to extend the studied sample, the elongation value was decreasing.

Conclusions

Based on TG curves, it was concluded that polyurethanes obtained from glycolysates were thermally stable up to 270°C. That is about 30°C lower as compared to the PUs synthesized from the commercial raw materials. Infrared spectral analysis (TG-FTIR) of gaseous products originating during decomposition of the polyurethanes obtained from glycolysates has shown that both PU types differ only slightly in chemical composition.

Polyurethanes synthesized with the use of prepolymers obtained from glycolysates of higher molecular mass (700–1000) have higher tensile strength, however their elongation at break values are small as compared to those for polyurethanes from glycolysates of low molecular mass (200–700). Therefore, in the case of glycolysates, the rule concerning the choice of long-chain oligomerols for synthesizing polyurethanes having the most advantageous properties has been confirmed.

Acknowledgements

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