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THERMAL PROPERTIES OF POLYURETHANES SYNTHESIZED USING WASTE POLYURETHANE FOAM GLYCOLYSATES

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In this work thermal transitions and thermal stability of polyurethane intermediates and polyurethanes were investigated. The intermediates were obtained by glycolysis of waste polyurethane (PUR) in the reaction with hexamethylene glycol (HDO). The excess of HDO was not separated from the product after the glycolysis process was finished. The effects of different mass ratio of HDO to PUR foam on selected physicochemical properties (hydroxyl number, Brookfield viscosity and density) were also determined.

The polyurethanes were synthesized from the obtained intermediates by the prepolymer method using diisocyanate (MDI) and glycolysis product of molecular mass in range 700/1000 g mol^{-1}. Hexamethylene glycol, 1,4-butanediol and ethylene glycol were used as chain extender agents. Influence of NCO groups concentration in prepolymer on glass transition temperature (T_g) and storage and loss modulus (E', E'') of polyurethanes were investigated by the DMTA method. Thermal decomposition of obtained glycolysates and polyurethanes was followed by thermogravimetry coupled with Fourier transform infrared spectroscopy. Main products of thermal decomposition were identified.

Keywords: *DMTA, elastomer, glycolysis, polyurethane, TG, TG-FTIR, thermal analysis, thermal stability, waste foam*

Introduction

Glycolysis is the most promising method of feedstock recycling of polyurethanes. Many researchers have investigated this process using different waste type, glycolysis agents, catalyst and different conditions [1–16]. It was confirmed that glycolysis products could be used as polyol components in synthesis of new polyurethanes alone or in mixture with commercial polyols. Polyurethanes of different types like flexible and rigid foams, integral skin foams, elastomers and adhesives was made using recycled polyols [7–9, 17–21]. In some cases using glycolysis product as polyol component brings improved thermal stability of obtained polyurethanes [18, 19].

Aim of the current work was to obtain glycolysates from waste flexible PU foam and to use one of them in synthesis of cast PU elastomer as the only polyol component. Thermal decomposition of obtained glycolysates and elastomer was investigated by thermogravimetry coupled with Fourier transform infrared spectroscopy.

Experimental

Materials

Elastic PU foam was a production waste from MZCh Organika Malbork (Poland). 1,6-hexanediol (HDO) (BASF, Germany) as decomposing agent and potassium acetate (KAc) (POCH, Poland) as catalyst were used. Glycolysis reaction was carried out at following PU foam/HDO mass ratios: 1:1, 2:1, 4:1, 6:1, 8:1, 10:1. The amount of catalyst was 0.5% by PU foam mass. Reaction was carried out in 1 liter steel reactor with mechanical stirrer and reflux condenser in the temperature 230/245°C. Reaction time was 9/70 min (dependent on the PU foam/HDO mass ratio).

Polyurethane elastomers were synthesized by the prepolymer method using 4,4’-methyldiphenyl diisocyanate (MDI) (Borsodchem, Hungary), glycolysates of highest molecular mass and phosphoric (V) acid as side reactions inhibitor. Ethylene glycol (POCH, Poland), 1,4-butanediol (BDO) (BASF, Germany) and 1,6-hexanediol (BASF, Germany) were used as chain extender agents.

Measurements

Hydroxyl value was estimated by titration method using acetic acid anhydride and 0.1M KOH solution. Number average molecular mass was calculated in assumption that all glycolysis products are difunctional. Viscosity was measured by a rotational viscometer Brookfield DV-II. Density was measured at 50°C.

Physicomechanical properties of the polyurethane elastomers were determined by tensile strength (Zwick/Roell Z020) and hardness (Zwick/Roell

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HPE 3130 electronic hardness tester) measurements. Glass transition temperatures, storage and loss modulus were measured on Polymer Laboratories Mk III thermomechanical analyzer. Samples were tested with 4°C min^{-1} heating rate and at fixed frequency 10 Hz.

Thermal stability of glycolysis products and PU elastomer was investigated by thermogravimetry coupled with Fourier transform infrared spectroscopy (Netzsch TG–FTIR). Analysis was conducted in argon atmosphere at 10°C min^{-1} min heating rate.

Results and discussion

Glycolysis

The variations in the hydroxyl value and number average molecular mass with different PU foam/HDO ratio is shown in Fig. 1. Hydroxyl value decreases when PU foam/HDO ratio is increased. For PU elastomer synthesis glycolysates of molecular mass 670 and 600 g mol^{-1} were selected (both obtained at PU foam/HDO ratio 10:1). It was found that glycolysis run depends on reactants ratio. For PU foam/HDO ratios 1:1, 2:1 and 4:1 single phase, liquid product is obtained. The unreacted glycol may slowly crystallize at room temperature, but phase separation does not occur. For PU foam/HDO ratios 6:1, 8:1 and 10:1 reaction run as ‘split phase’ glycolysis. Upper phase was liquid at room temperature. Lower phase was a very viscous liquid at the reaction temperature with solidification temperature about 100°C.

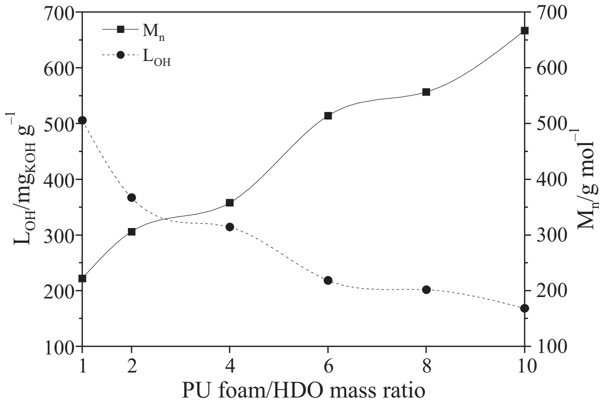


Fig. 1 Variations in the hydroxyl value and number average molecular mass with different PU foam/HDO mass ratio

Thermal decomposition study

Fig. 2 DTG curves of glycolysis products

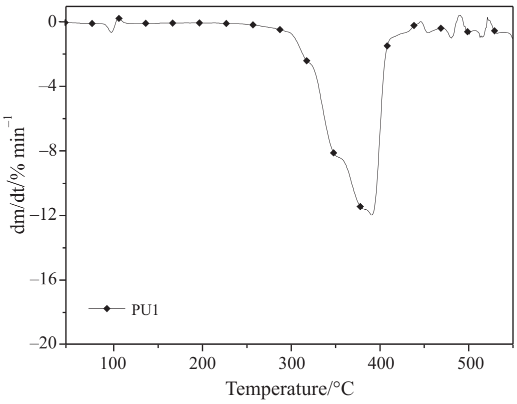


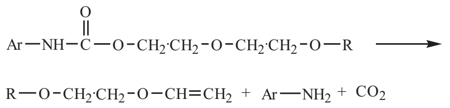
Fig. 3 DTG curve of the polyurethane elastomer

DTG curves of the glycolysates and PU elastomer are shown in Figs 2 and 3. The glycolysates have one or two temperatures of the maximum decomposition rate dependent on the PU foam/HDO mass ratio. Glycolysates which have the largest amount of unreacted HDO (GL1.1, 1:1 and GL1.3, 4:1) have the first DTG minimum at 245°C. This corresponds to the unreacted HDO evaporation. The DTG minima at about 400°C corresponds to the polyether chain thermal degradation.

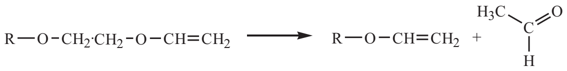
FTIR spectra of decomposition products of glycolysates and PU elastomer at maximum decomposition rates are shown in Figs 4 and 5. As the main products of the thermal decomposition of glycolysates and PU elastomer CO_2 (2360, 2320 cm^{-1}), CO (2180, 2117 cm^{-1}) and compounds containing ether and hydroxyl groups were identified (3587, 1108 cm^{-1}). Carbon dioxide can be formed in reaction (1). Vinyl ether decomposes fast forming acetaldehyde (absorption peak at 1745 cm^{-1}, Fig. 4) in reaction (2) [21]. Perhaps in the thermal decomposition of the glycolysates 1-ethoxy-2-propanol or similar compound is formed as a product of fragmentation of the polyether chain (3) [21].

DMTA study

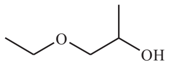
Variations of storage modulus, loss modulus and tangent delta with temperature are presented in Figs 6, 7 and 8.



$$Ar-NH-\overset{\overset{O}{\|}}{C}-O-CH_2{\cdot}CH_2-O-CH_2{\cdot}CH_2-O-R \longrightarrow R-O-CH_2{\cdot}CH_2-O-CH{=}CH_2 + Ar-NH_2 + CO_2 \quad (1)$$



$$R-O-CH_2{\cdot}CH_2-O-CH{=}CH_2 \longrightarrow R-O-CH{=}CH_2 + H_3C-\underset{\underset{H}{|}}{C}{=}O \quad (2)$$



(3)

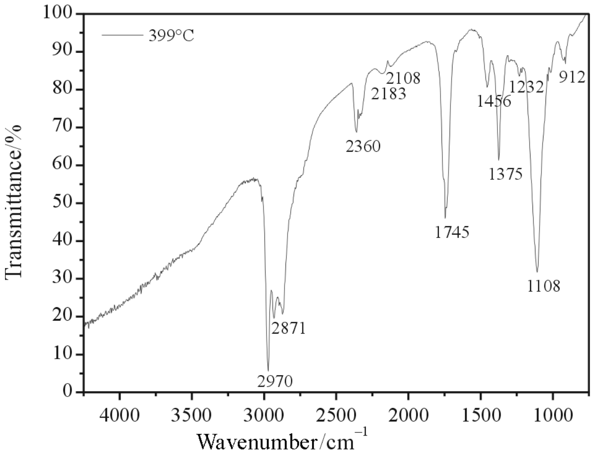


Fig. 4 FTIR spectrum of the glycolysis product GL1.6 (PU foam/HDO mass ratio 10:1) at maximum decomposition rate

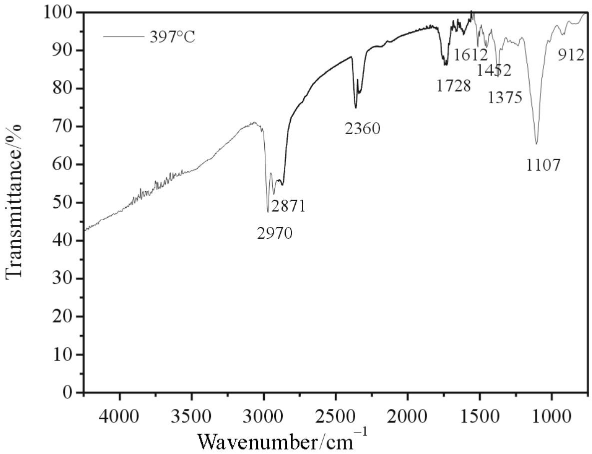


Fig. 5 FTIR spectrum of the PU elastomer at maximum decomposition rate

There is interesting phenomena in the temperature dependency of the storage moduli of elastomers PU1 and PU2. As expected, higher hard segment content results in higher modulus values in the viscoelastic state above the glass transition, but the glassy state the previously ‘soft’ segments changed to rigid structures therefore enhancing the modulus of PU1 over the modulus of PU2.

The peak maxima, which would be taken as the glass transition temperatures are almost the same (PU1=0.5°C, PU2=0.8°C) indicating the same level of phase separation.

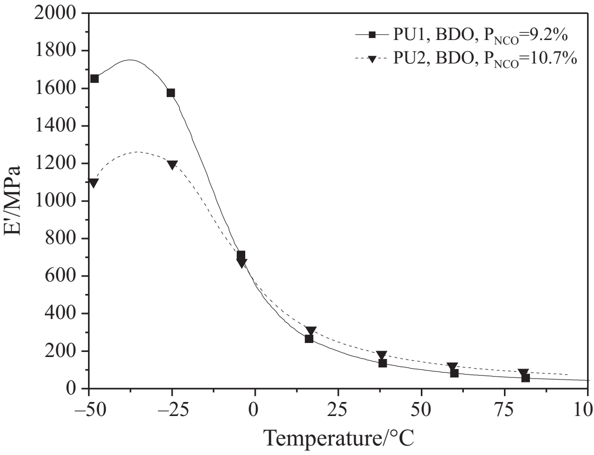


Fig. 6 Variation of the storage modulus of the PU elastomers with temperature

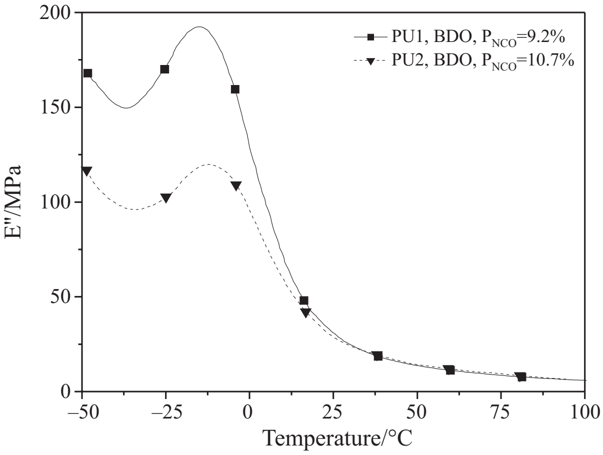


Fig. 7 Variation of the loss modulus of the PU elastomers with temperature

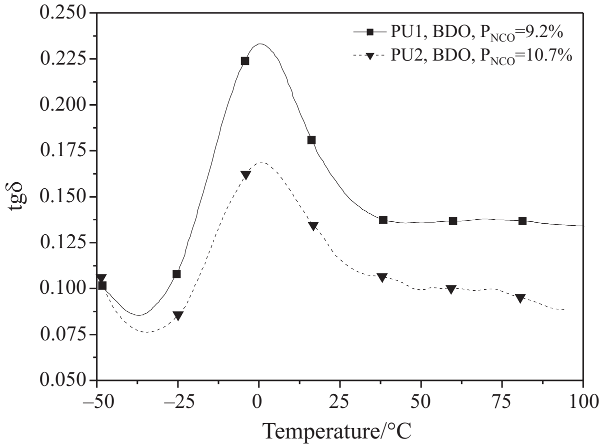


Fig. 8 Variation of the tangent delta of the PU elastomers with temperature

Conclusions

From glycolysis of waste flexible polyurethane foam oligodiols a product useful for new polyurethane synthesis was obtained. Glycolysates of highest molecular mass were successfully used as the only polyol components in polyurethane elastomers synthesis. Obtained PU elastomers have tensile strength in range 13.4/15.6 MPa and hardness in range 85/94 °Sh A. Elastomers have glass transition temperatures (DMTA) at 0.5 and 0.8°C. Thermal stability investigation shows that main decomposition occurs at temperature about 400°C in both cases of glycolysates and PU elastomer. The main products of thermal decomposition are carbon monoxide, carbon dioxide, compounds containing ether and hydroxyl groups and probably acetaldehyde. Future works could focus on comparing thermal stability of recycled and commercial polyols or thermal stability of polyurethanes obtained from recycled and commercial polyols.

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