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DSC AND THERMAL STABILITY INVESTIGATION OF NOVEL POLY(ESTER-ETHER) GLYCOLS AND POLY(ESTER-ETHER)URETHANES

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Abstract

A new group of poly(ester-ether) glycols was obtained by polycondensation of adipic acid with poly(alkylene glycol) or of adipic acid with mixture of poly(alkylene glycol) and ethylene glycol. Poly(ester-ether) glycols were synthesised in a two-step method at comparable laboratory conditions. We prepared series of poly(ester-ether) glycols where molar ratios [COOH]:[OH] were changed in the range from 1:1.20 to 1:2.10. The molecular mass of synthesized substances was in the range from 850 to 2500 g mol^{-1}.

Thermal stability of poly(ester-ether) glycols and obtained polyurethanes was investigated by thermogravimetric analysis and DSC method.

We have found that obtained oligomerols obtained from adipic acid and poly(tetramethylene glycol) have the highest thermal stability.

The differential scanning calorimetry shown occurrence of two-phase transitions for examined polyurethanes, which are described by glass transition temperature T_g and the melting temperature T_t.

Keywords: DSC, polyglycols, polyols, polyurethanes, TG, thermal stability

Introduction

Polyester polyols, polyether polyols, aliphatic or aromatic diisocyanates and low molecular mass glycols or diamines as chain extenders are monomers which are used in the polyurethanes’ synthesis [1–5].

Polyurethanes obtained from above-mentioned monomers are block copolymers with soft and hard segments. The soft segments are mainly built from polyester polyol or polyether polyol, and their content usually varies from 60 to 80 mass%. Diisocyanates and chain extenders form hard segments.

The soft segments are responsible for elasticity, elongation and thermal stability of polyurethanes. By planning of the structure of the soft segment it is possible to influence properties of polyurethanes. Polyester polyols and polyether polyols differ significantly regarding their chemical and applicable properties.

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Polyesterurethanes have better mechanical properties, better thermal and weathering resistance and hydrolysis resistance than polyetherurethanes.

Mothe, de Araujo obtained polyurethanes based on castrol oil or polybutadiene liquid hydroxyl (PBLH). Thermal behaviour of polyurethanes was analyzed by thermogravimetry. TG curves showed three decomposite stages for polyurethanes obtained from castrol oil. At 290°C they observed 15% mass loss and a principal degradation at 400°C of the polyurethanes from PBLH [6].

Wang and Hsieh investigated thermal stability of segmented poly(urethane-ureas). These polymers they obtained from 4,4'-diphenylmethane (MDI), three kinds of polyol, and diamine (EDA) chain extender. Thermogravimetric analysis (TG) and differential thermal analysis (DTA) showed that polyurethanes base on polytetramethylene glycol (PTMG) are generally more stable than polyurethanes which have soft segments built from polypropylene glycol (PPG). The authors explain that lower stability for PPG-based polyurethanes may be attributed to the lower extent of inter-urethane hydrogen bonding arising from the incomplete phase separation between the soft and hard segments [7].

The thermal degradation of different thermoplastic polyurethanes elastomers (TPU) investigated Herrera, Matuschek, Kettrup [8]. Polymers were obtained from 4,4'-diphenylmethane (MDI) and two polyols. For all polyurethanes 1,4-butanediol was used as the short chain diol. The long chain diols were tetrahydrofuran as polyether and butanediol adipate as polyester. The authors affirmed that for both polymers the mass loss take place in range 280–485°C.

The polyether–polyurethane losses are 85% of initial mass while the polyester–polyurethane losses are 90%. The difference they explain through the oxygen-content of used polyols or through dehydration reactions.

Polyurethane coating synthesised from a stoichiometric mixture of diol and diisocyanate [9] were investigated using modulated and pressure differential scanning calorimetry (TMDSC, PDSC). The authors of the article have proved that obtained PU coating closely match to the rubber compound [10].

Araujo and Pasa were synthesized polyurethanes based on biopitch (wood tar obtained by condensing smoke given off Eucalyptus charcoal production masonry kilns) and poly(ethylene glycol) (PEG) of distinct molecular masses (M_w 1500, 4000 and 6000 g mol^{-1}) and polymeric MDI 4,4'-diphenylmethane diisocyanate. Thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) were used to determine polyurethane's thermal properties. The authors of the article have found that polyurethanes show decrease in thermal stability with addition of biopitch, regardless of the molecular mass of PEG and the NCO/OH ratio used. PUs with higher concentration of hard segments has lower stability. TG curves of polyurethanes (air atmosphere) showed that addition of biopitch on PUs retards thermal degradation above 400°C. This behavior can be important in the development of applications in which safety is an essential aspect [11].

Polyurethane composites with bagasse of sugar cane (BSC) at different proportions (5, 10 and 20 mass/mass%) were prepared by melt mixing method [12]. The thermal behaviour of these composites were investigated by thermogravimetry. The composite with 5% of BSC exibited the best performance with respect to thermal stability.

The aim of our work was to obtain a new group of polyglycols which would have ester and ether groups chemically bound in the structure of the oligomerol and could be utilized at preparation of soft segments in different types of polyurethanes.

Experimental

Materials

The poly(ester-ether) glycols were obtained from adipic acid (POCH Gliwice, Poland) and one of the following diols:

- poly(propylene glycol) average molecular mass (M_w) 450, (Aldrich Chemie, Germany)
- poly(ethylene glycol) M_w 600, (Aldrich Chemie, Germany)
- poly(tetramethylene glycol) M_w1000, (Aldrich Chemie, Germany)

or adipic acid and mixture of ethylene glycol (Poch Gliwice, Poland) with one of polyalkylene glycols in the polycondensation reaction. Before reaction all diols and glycol were dried under pressure reduced to 300 Pa.

Synthesis of oligo(ester-ether)diols

The reactions were carried out under nitrogen in two temperature steps:

- In the first step the temperature was 160, 180 or 200°C under atmospheric pressure.
- The second step of the polycondensation started when the determined conversion degree was more than 0.90. This step was always carried out at 200°C and at the pressure reduced to 300 Pa [13].

Water was being removed by distillation during all processes.

Synthesis of polyurethanes

Two-stage method was used to obtaining cast urethane elastomers. The prepolymer was synthesised from the novel poly(ester-ether) glycols and 4,4'-diphenylmethane diisocyanate (MDI). In the second stage dehydrated buthylene glycol was added to the obtained prepolymer at 80°C. The molar ratio free [NCO]:glycol [OH] was 1.05.

Measurements

Thermogravimetric analysis was performed on Pyris 1 TG Perkin Elmer instrument at heating rate 20°C min^{-1} under nitrogen.

Glass transition temperature and melting point of the polyurethanes was determined by Differential Scanning Calorimeter (DSC-7, Perkin Elmer). Data were collected from –100 to 200°C, at a heating rate of 10°C min^{-1}.

Results and discussion

The results of thermogravimetric analysis of obtained oligomerols are given in Tables 1–3.

Table 1 Thermal characteristic of poly(ester-ether) glycols obtained from adipic acid (KA) and poly(propylene glycol) (POP) or mixture poly(propylene glycol) with ethylene glycol

Poly(ester-ether) glycols	Molar ratio [COOH]:[OH$_p$]:[OH$_g$] at synthesis	Temperature/°C at mass loss of		
		5%	10%	50%
KA-POP	1:1.20	220	250	370
	1:1.30	230	270	390
	1:1.40	240	255	380
	1:1.50	240	260	380
KA-POP-GE	1:0.525:0.525	260	290	380
	1:0.575:0.575	270	290	385
	1:0.625:0.625	260	285	390
	1:0.675:0.675	270	290	390

Table 2 Thermal characteristic of poly(ester-ether) glycols obtained from adipic acid (KA) and poly(ethylene glycol) (POE) or mixture poly(ethylene glycol) with ethylene glycol

Poly(ester-ether) glycols	Molar ratio [COOH]:[OH$_p$]:[OH$_g$] at synthesis	Temperature/°C at mass loss of		
		5%	10%	50%
KA-POE	1:1.20	230	320	400
	1:1.30	235	325	400
	1:1.40	230	330	410
	1:1.50	240	330	410
KA-POE-GE	1:0.55:0.55	250	330	400
	1:0.60:0.60	255	325	400
	1:0.65:0.65	260	330	410
	1:0.70:0.70	260	335	410

The obtained poly(ester-ether) glycols from adipic acid and poly(propylene glycol) or poly(ethylene glycol) or their mixture with ethylene glycol have similar thermal stability which is shown in Tables 1 and 2. Two groups of investigated oligomerols have similar temperatures of certain mass loss. Particularly, similar thermal behaviour was observed at the beginning of the destruction process.

The temperatures of 5% mass loss of the synthesised poly(ester-ether) glycols was observed in the range of 220–270°C, respectively. The fastest mass loss was observed at higher temperatures in the range of 370–400°C, and poly(ester-ether) glycols synthesised from poly(ethylene glycol) show higher thermal stability than those containing polypropylenediol moieties (Table 2).

Table 3 Thermal characteristic of poly(ester-ether) glycols obtained from adipic acid (KA) and poly(tetramethylene glycol) (PTMG) or mixture poly(tetramethylene glycol) with ethylene glycol

Poly(ester-ether) glycols	Molar ratio $[COOH]:[OH_p]:[OH_g]$ at synthesis	Temperature/°C at mass loss of		
		5%	10%	50%
KA-PTMG	1:1.80	290	320	420
	1:1.90	280	325	430
	1:2.00	290	330	430
	1:2.10	290	330	435
KA-PTMG-GE	1:0.60:0.60	320	360	415
	1:0.65:0.65	320	365	420
	1:0.70:0.70	330	370	425
	1:0.75:0.75	330	370	420

The poly(ester-ether) glycols obtained from poly(tetramethylene glycol) or mixture of ethylene glycol and poly(tetramethylene glycol) have the highest thermal stability from all synthesised oligomerols. The 5% mass loss is reached at 290°C. We have found that with addition of ethylene glycol the temperature of 5% mass loss increases to 320°C.

We have observed that 10% mass loss is reached at the temperature 320°C for poly(ester-ether) glycols (Table 3). This temperature is about 20–40°C higher in case of poly(ester-ether)glycols obtained from poly(ethylene glycol) (Table 2) and about 70–90°C higher in case of polyglycols which are presented in Table 1.

We have found that the temperatures of the 50% mass loss are the highest for all synthesised poly(ester-ether) glycols from adipic acid and poly(tetramethylene glycol) or mixture with ethylene glycol.

The cast urethane elastomers which have soft segments built from novel poly(ester-ether) glycols based on poly(tetramethylene glycol) have the highest thermal stability of all investigated polyurethanes. The temperatures of the highest rate is in the range of 370–400°C.

Thermal stability of obtained (ester-ether)urethane elastomers is similar to 250°C to the stability of polyesterurethanes which have soft segments built from commercial polyols (Fig. 1). Upper this temperature the higher temperature resistance have polyesterurethane.

The results of thermal analysis of polyurethanes from novel poly(ester-ether) glycols determinated by DSC method are shown in Table 4.

Table 4 DSC results of polyurethanes synthesised from the novel poly(ester-ether) glycols

Polyurethanes obtained from the novel polyglycols	Onset/ °C	T_g/ °C	ΔC_p/ J g^{-1} °C^{-1}	Onset/ °C	T_t/ °C	ΔH/ J g^{-1}
KA-POP	–43.5	–40.1	1.4	122.6	140.5	4.5
KA-POE	–55.5	–48.4	1.2	92.2	128.6	9.5
KA-PTMG	–55.3	–49.7	3.5	–	–	–

The differential scanning calorimetry show occurrence of two-phase passages in examined polyurethanes, which are described by glass transition temperature (T_g) and melting temperature (T_t).

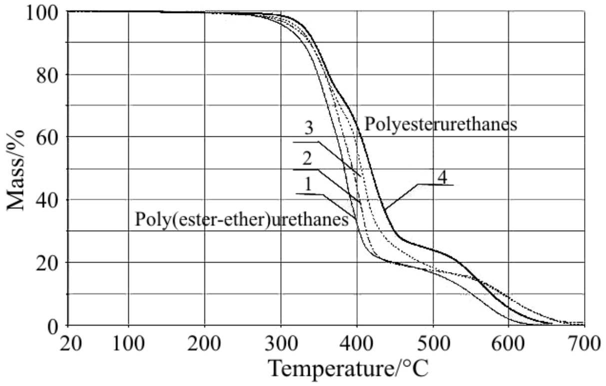

Fig 1 Thermogravimetric curves of polyurethanes (PU) obtained from the novel poly(ester-ether) glycol: 1 – KA+POP; 2 – KA+POE; 3 – KA+PTMG and of 4 – PU from commercial polyester glycol

On the basis of the results of investigations by DSC we can affirm that novel polyurethanes characterize good low temperature resistance. The glass transition temperature of the soft segment is in the range from –55 to –43°C. We can observe that received polyurethanes have good thermal stability to 140°C.

Conclusions

The presence of ethylene glycol moieties in the structure of the obtained new linear poly(ester-ether) glycols causes an increase of thermal stability, as compared with poly(ester-ether) glycols obtained without ethylene glycol.

Temperature of mass loss changes only about a few degrees, for samples obtained at increasing excess of polyalkylene glycol or mixture of polyalkylene glycol with ethylene glycol per one mol of adipic acid, which suggests that molecular mass of investigated poly(ester-ether) glycols only in insignificantly influence their thermal stability.

Thermal stability of obtained poly(ester-ether) glycols is comparable to the stability of the commercial polyester glycols, therefore we confrm that poly(ester-ether) glycols can be used in the polyurethanes synthesis. The new polyurethanes have similar thermal stability to known polyesterurethanes.

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