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GLASS TRANSITION TEMPERATURES OF POLYURETHANE–UREA ELASTOMERS BASED ON N, N'-ETHYLENETHIOUREA AND N, N'-ETHYLENEUREA AS CHAIN EXTENDERS

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Abstract

Glass transition temperatures of polyurethane–urea elastomers (*PU*) based on two urea derivatives, have been investigated with differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) methods. The DMTA measurements have been proved as more useful to determine an optimal annealing time and to controlling polyurethane-urea synthesis then the DSC analysis.

Keywords: DSC, glass transition temperature, polyurethane–urea elastomers

Introduction

Polyurethane–urea elastomers are obtained in a variety of products, differing in properties and performance, due to a great choice of chemicals, which may be used in their synthesis. Nevertheless, the major group of polyurethane elastomers is based on diisocyanates, long chain components (polyesters, polyethers or polyamines) and on short chain di- or more functional alcohols or amines, acting as chain extenders. Polyurea dispersion are used in reaction injection moulding (RIM) applications [1]. Urea derivatives as chain extenders in syntheses of polyurethanes are less known. In this work thermal and tensile properties of polyurethane–urea elastomers from typical urethane prepolymers terminated with N, N'-ethylene urea (EU) and N, N'-ethylene thiourea (*ETU*) in regard to annealing conditions were estimated.

Experimental

Materials

4,4'-diphenylmethane diisocyanate (*MDI*) (ICI) was melted and pressure filtered at 60°C. The oligo(ethylene-butylene adipate) (Bydgoszcz Chemical

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Works "Zachem") was dewatered in reactor with a mechanical stirrer at 80°C, under vacuum of ca. 250 Pa, during 6 h. N, N'-ethyleneurea (2-imidazolidone) (*EU*) (Fluka AG) was dried at a vacuum oven (250 Pa) at 70°C to water quantity below 0.05% N, N'-thylenethiourea (2-imidazolidinethione) (*ETU)* (Aldrich) and 3,3'-dichloro-4,4'-diaminodiphenylomethane (*MOCA*) (Bydgoszcz Chemical Works "Zachem") were used without further purification. 1,4-Butanediol (1,4-*BD*) (BASF) was dried at vacuum oven (250 Pa) at 50°C during 4 h. Dimethylacetamide (*DMA*) (Reachim) was dried with P_2O_5 and distilled once before use.

Preparation

To oligo(ethylene-buthylene adipate) at 80°C a predetermined quantity of *MDI* was added, so the molar ratio of NCO to OH groups was 3.5. The synthesis of the prepolymer was carried out at 100°C for 15 min. At the final stage the prepolymer was degassed under vacuum of ca. 250 Pa. Because of high melting points *EU* and *ETU* could be used only in solution. Appropriate quantity of the chain extender (*EU* or *ETU*) was dissolved in DMA (40 cm^3 of DMA per 40 g prepolymer), then the prepolymer was dissolved in this solution. The quantity of the chain extender were such as to allow for the maintaining of a constant molar ratio of NCO to NH groups = 1.05. The mixture was poured into a centrifuge drum running at a speed of ca. 3500 rpm. Forming of elastomers was carried at 20°C (*ETU*) and at 80°C (*EU*). The forming time was approximately 30 min for *ETU* and 90 min for *EU*. Due to ventilating air stream in the centrifuge drum a possible effect of air moisture could not be eliminated. The obtained specimens were 0.15 to 0.30 mm thick. The solvent evaporated partly during forming in the centrifuge and finally during annealing in a heated vacuum oven. PU based on 1,4-*BD* and *MOCA* was cast into moulds without any solvent in the reactions mixture.

Methods

DSC measurements have been carried out on Perkin-Elmer DSC-7 thermal analyser with 3700 data station at the heating rate of 20 $deg \cdot min^{-1}$. DMTA measurements have been carried out in the bending mode on Polymer Laboratories DMTA-Mk III with a standard head at the heating rate of 2 $deg \cdot min^{-1}$ at the frequency of 10Hz and at the strain of 4× for *ETU*, *MOCA*, 1,4-*BD* based samples, and 2× for *EU* based samples.

Results and discussion

Cast polyurethane–urea elastomers reach optimal properties in an annealing process, when the reaction and phase separation into soft and hard segment domains are completed. The primary goal of this work was the use of DMTA and DSC to characterisation of obtained elastomers and to estimation of optimal annealing time.

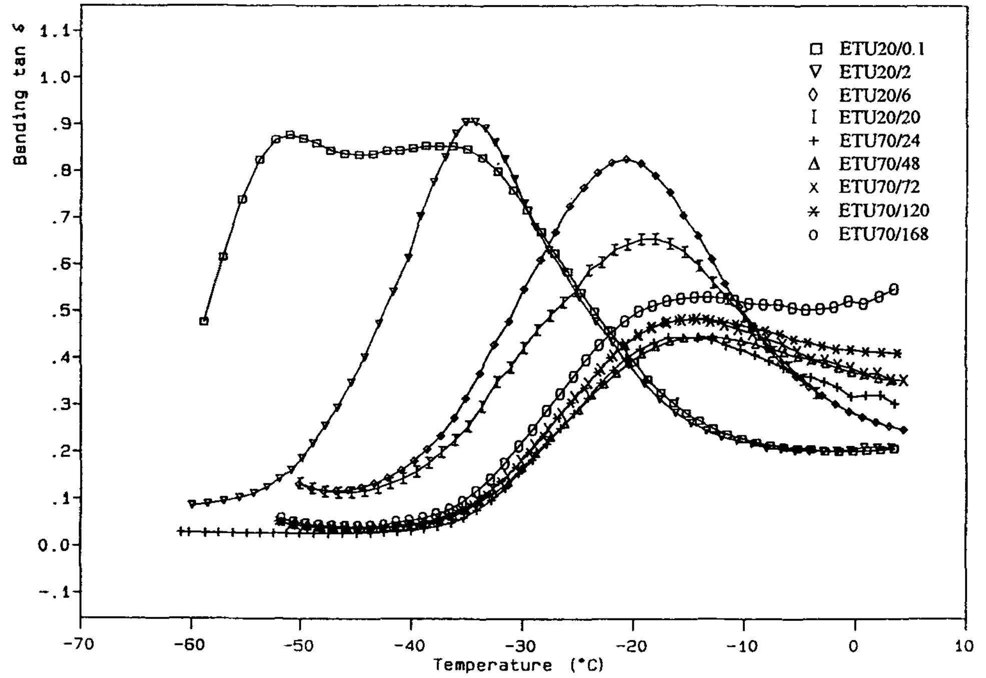

Fig. 1 Effect of annealing time on loss tangent of polyurethane-urea elastomers obtained with N, N'-ethylenethiourea

In a DMTA experiment, second order transition, observed as the α peak at the dissipation factor, tan δ, curve, is regarded as the same glass transition, as observed from the heat capacity change during DSC measurements. Transitions discussed below refer to changes in the soft segment phase, formed from the polyester molecules. The glass transition could be directly connected with the conversion of thermosetting systems containing diisocyanates [2], but the annealing of fully reacted polyurethane–urea elastomers mainly leads to perfection of the two phase structure, which could be discussed from DMTA and DSC traces. The DMTA curves of PU extended with *ETU* are shown in Fig. 1. Glass transitions occurred between –52°C and –14°C. The curve *ETU* 70/0.1 (desig-

Table 1 DSC results and tensile properties of investigated poliurethane–ureas

Sample	Chain extender	Annealing temperature/ °C	Annealing time/ h	Glass transition temperature/ °C	Glass transition onset/ °C	Enthalpy/ $J\cdot g^{-1}\cdot K^{-1}$	Tensile at break/ MPa	Elongation at break/ %
ETU 70/24	*ETU*	70	24	–36.06	– 41.52	0.2350	40.4	1193
ETU 70/48	*ETU*	70	48	–37.86	– 41.39	0.2481	41.0	1366
ETU 70/72	*ETU*	70	72	–37.99	– 42.35	0.2611	45.5	1380
ETU 70/120	*ETU*	70	120	–38.63	– 42.51	0.2514	51.0	1293
ETU 70/168	*ETU*	70	168	–38.61	– 42.65	0.2551	45.0	1273
EU 70/24	*EU*	70	24	–38.37	– 41.98	0.2755	6.29	433
EU 70/48	*EU*	70	48	–38.76	– 40.99	0.2338	10.8	960
EU 70/72	*EU*	70	72	–35.47	–39.89	0.2712	12.6	953
EU 70/120	*EU*	70	120	–35.39	–39.98	0.2660	12.5	947
EU 70/168	*EU*	70	168	–35.38	–39.98	0.2720	12.5	940
*MC**	*MOCA*	110	24	–27.78	–34.08	0.2183	40.0	460
BD	1,4-*BD*	110	24	–28.52	–34.91	0.3401	44.8	628

* based on 2,4-toluenediizocianate (TDI)

nations as in the Table 1) exhibits a double peak. The lower one is connected with non bonded prepolymer which is still present in the sample 0.1 h after forming process. The higher one indicates transition in the soft segment polymer phase. Stabilisation of the T_g value is reached after 25–30 h at the temperature of 20°C. Even annealing of the samples during 24 to 168 h at 70°C have not more influence on T_g (all differences between curves *ETU* 70/24-*ETU* 70/168 are in the range of mistakes). The not eliminated effect of ventilating air moisture during curing process in the centrifuge drum should not alter the position of the tan δ peak of the soft phase transition, as it was determined at investigation of water blown microcellular polyurethane elastomers [3]. The DSC measurements of *ETU* extended samples are shown in the Table 1. T_g's for *ETU* 20/0.1..*ETU* 20/20 samples are not observed down to –60°C. Differences observed between T_g values obtained from DMTA and DSC curves are approximately 25 deg, resulting from frequency shifting of the T_g transition and from different heating rates. The DSC results are closer to the true of T_g but in cases of minor heat capacity changes they might be not enough sensitive to detect this transition, as at the first hours of annealing, when the phase separation is not completed. The DMTA results of PU based on *EU* are shown in Fig. 2. The curve *EUSO* belongs to a sample which was investigated immediately after the

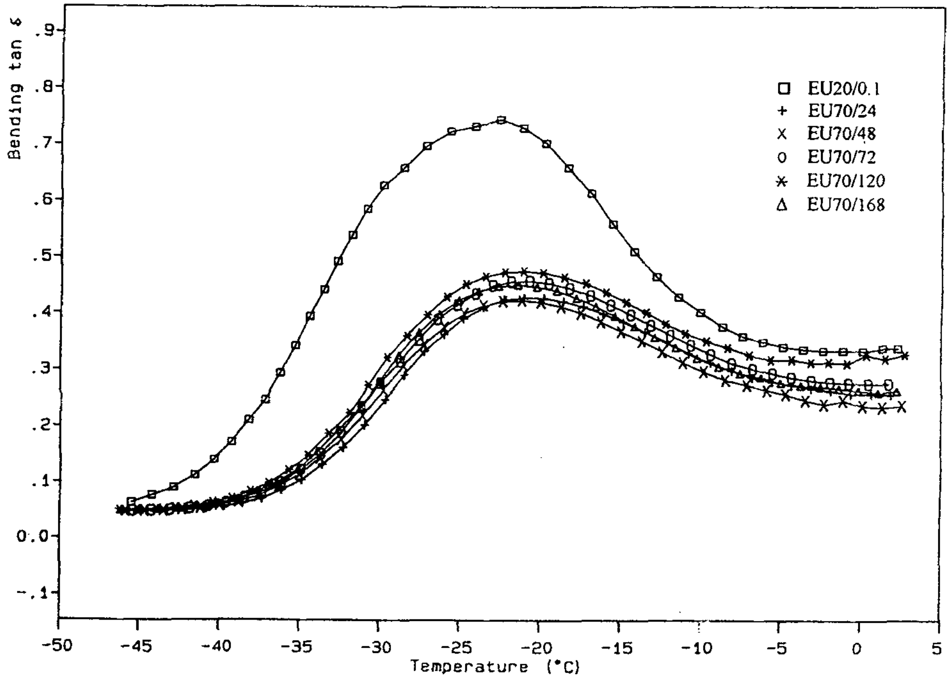

Fig. 2 Effect of annealing time on loss tangent of polyurethane-urea elastomers obtained with N, N'-ethyleneurea

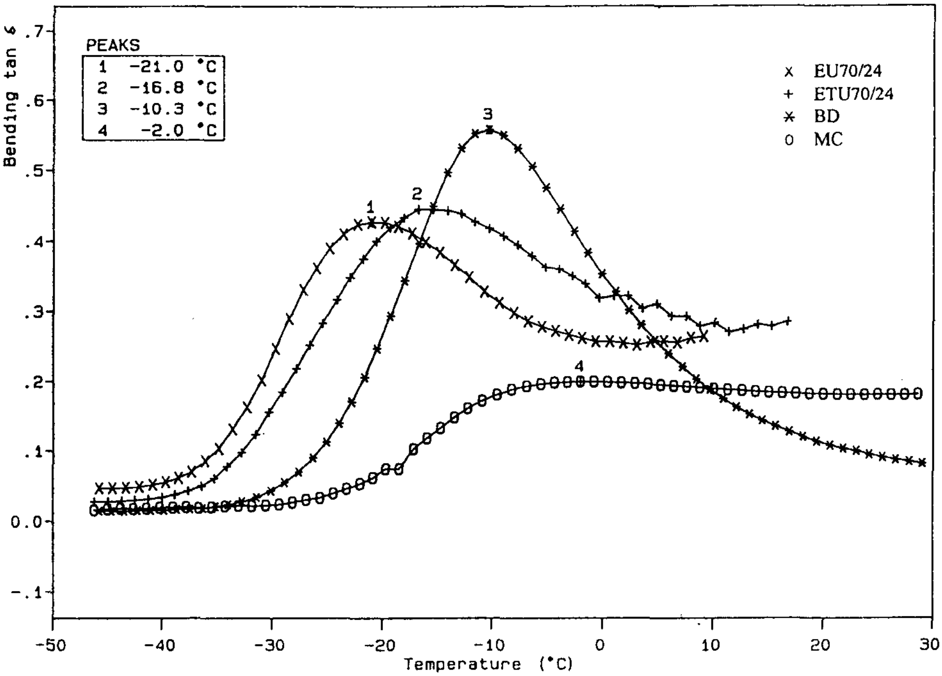

Fig. 3 Comparison of the loss tangent peaks of polyurethane-urea elastomers obtained with N, N'-ethyleneurea, N, N'-ethylenethiourea, 1,4-BD and MOCA

forming process (in fact ~1.5 h after start of synthesis). A differences between *EU* 20/0.1 and *EU* 70/24..*EU* 70/168 at T_g peaks are about one point distance at the data collecting (~2°C). Such fast reaching of the final T_g value could be an effect of better possibility to phase separation during longer time until gelation and at higher temperature of forming than in the synthesis of PU based on *ETU*. Similar like for *ETU* based samples, any glass transitions were not detected by DSC measurements for samples *EUSO* during first 20 h of conditioning at 20°C. DMTA glass transitions of PU based on *EU* and on *ETU* and of well known PU cured with *MOCA* and 1,4-*BD* are depicted in Fig. 3. Because in the temperature dependency of the loss tangent better phase separation is indicated by increased slope and by narrowing of the transition peak [4, 5], used derivatives seem to deliver elastomers showing higher degree of phase separation, then these extended with diamine.

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Zusammenfassung — Mittels DSC und DMTA wurden die Glasumwandlungspunkte von Polyurethan-Harnstoff Elastomeren (PU) auf der Basis zweier Harnstoffderivate untersucht. DMTA-Messungen erwiesen sich als nutzbringender zur Bestimmung einer optimalen Temperungsdauer und zur Überwachung der Polyurethan-Harnstoff-Synthese als die DSC-Analyse.