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DYNAMIC MECHANICAL PROPERTIES AND THERMAL DEGRADATION PROCESS OF THE COMPOSITIONS OBTAINED FROM UNSATURATED POLY(ESTER URETHANES) CROSS-LINKED WITH STYRENE

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Dynamic mechanical and thermal properties of poly(ester urethanes) (PEU) cross-linked with styrene have been studied. The investigated polyurethanes were obtained from 4,4'-diphenylmethane diisocyanate and unsaturated oligo(alkyleneester)diol based on *cis*-2-butene-1,4-diol. The conducted analyses dealt with the correlation between the chemical structure of poly(ester urethanes) and their ability to phase separate as well as their thermal stability. The products of PEU thermal degradation were characterized using infrared spectroscopy.

Keywords: *dynamic mechanical thermal analysis, poly(ester urethanes), thermal decomposition*

Introduction

The importance of cross-linked polyurethanes (PUR) follows from their wide applicability both as constructional materials and coatings. Moreover, the properties they exhibit allow for utilizing them as elastomers, polyurethane foams and rubbers cross-linked using diisocyanates, sulphur, low molecular mass chain extenders or peroxide compounds.

The cross-linking process is one of the most popular methods of polymers modification. The introduction of allophanate and urea groups results in the creation of cross-linked systems [1, 2]. Another way to obtain cross-linked polyurethanes is to use hydroxyl or amine terminated low molecular mass chain extenders with at least three functional groups, such as 2-ethyl-2-(hydroxymethyl)propane-1,3-diol [3]. However, many researchers have focused on the reactivity of free isocyanate groups and on obtaining cross-linked polyurethanes in the synthesis of isocyanurate ring-containing materials [4–7]. This kind of polyurethanes exhibits high thermal stability obtained via trimerization in the presence of organometallic catalysts.

PUR with unsaturated bonds in soft or hard segments is a particularly interesting group of polymers [8–18]. The most common are hydroxyterminated polybutadiene (HTPB)-based polyurethanes [10–16]. Because of their importance in many fields, such as electronics, automotive industry and medicine, the thermal stability measurements and characteristics of thermal degradation products deemed necessary. The results obtained in [10–16] indicate that the thermal properties largely depend on the urethane groups content, whereas the mechanical properties are strongly influenced by the HTPB presence.

The purpose of our research was to obtain a novel group of polymers characterized by the increased elasticity and being an alternative solution to the cross-linked polyester resins. The goal has been achieved via the synthesis of novel poly(ester urethanes) based on unsaturated oligomerols and 4,4'-diphenylmethane diisocyanate. A pioneering approach has been applied, i.e. the use of *cis*-2-butene-1,4-diol as the carrier of unsaturated bonds in the synthesis of oligomerols.

It has been presumed that the introduction of such monomer type would increase the elasticity of the obtained polyurethanes with the concurrent retention of appropriate thermal stability as compared to the systems based on maleic anhydride [19, 20]. The experimental studies allowed to conclude that the application of styrene as cross-linking co-monomer results in a composition characterized by higher resistance to stretch as compared to the systems cross-linked with methyl methacrylate.

In this paper the results of dynamic mechanical and thermal measurements of poly(ester urethanes) cross-linked with styrene are presented. The influence of the polyurethanes chemical structure on their properties was investigated. We also focused our attention

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on the chemical structure of the thermal decomposition products of poly(ester urethanes).

Experimental

Materials

For the synthesis of oligo(alkyleneester)diols (OAE) the following compounds were used: adipic acid and phthalic anhydride (Sigma-Aldrich) in the form received from the manufacturer, without further purification; ethylene glycol (POCh) distilled under reduced pressure (1.4 hPa) (*b.p.* 117–118°C); *cis*-2-butene-1,4-diol distilled under reduced pressure (1.4 hPa) (*b.p.* 125–127°C); and hydroquinone (POCh) in the commercially available form.

For the synthesis of poly(ester urethanes) (PEU) the following components were used: the obtained unsaturated oligo(alkyleneester)diols, 4,4'-diphenylmethane diisocyanate (MDI) (Borsodchem) filtered in melt; styrene (St) (Sigma-Aldrich) from which the inhibitor was removed by washing in 10% NaOH solution and distilled water, dehydrated over anhydrous $MgSO_4$, initiator: methyl ethyl ketone peroxide (36% solution in dimethyl phthalate); accelerator: cobalt(II) 2-ethylhexanoate.

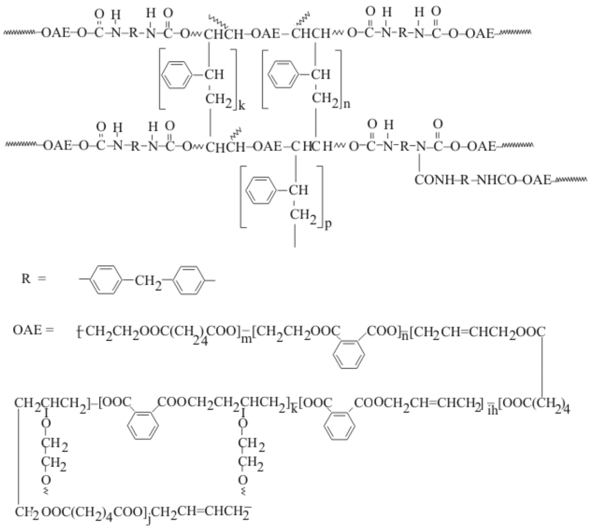
Synthesis of oligo(alkyleneester)diol and poly(ester urethanes)

Oligo(alkyleneester)diols, with –COOH contents below 2 mg KOH g^{-1}, were obtained via the polycondensation reaction of 1.44 mol of ethylene glycol, 1 mol of adipic acid, 0.5 mol of phthalic anhydride, and 0.5 mol of *cis*-2-butene-1,4-diol. The synthesized oligo(alkyleneester)diols and 4,4'-diphenylmethane diisocyanate were used for the synthesis of unsaturated urethane prepolymers and later for the cross-linked poly(ester urethanes) (Scheme 1). The step of prepolymers synthesis with a molar excess of NCO or OH groups (Table 1) was carried out at 60°C for 1 h. The second step was the preparation of a solution of the obtained prepolymers in styrene which was a cross-linking agent. Styrene was used at the concentration equaled to 30 mass% of the OAE content. The curing process was carried out at 80°C for 24 h [19].

Table 1 Content of co-monomers in the compositions obtained from the unsaturated poly(ester urethanes) cross-linked with styrene

Symbol	Molar ratio [NCO/OH]	MDI content/ mass%	OAE content/ mass%	St content[*]/ mass%
PEU 1	1.5/1	18.0	82.0	30
PEU 2	1.1/1	14.2	85.8	
PEU 3	1/1.1	11.6	88.4	
PEU 4	1/1.3	9.9	90.1	
PEU 5	1/2	6.8	93.2	
PEU 6	1/2.6	5.2	94.8	

[*] St *w/w* per OAE



Scheme 1 Chemical structure of poly(ester urethanes) cross-linked with styrene

Methods

The measurements of poly(ester urethanes) dynamic mechanical thermal properties were carried out using Ares Solids Rheometer. They were conducted with the frequency of 10 Hz within the temperature range from –60 to 220°C, and at the heating rate of 5°C min^{-1}.

Thermogravimetric analyses (TG) were performed on Pyris 1 TGA apparatus (Perkin Elmer) in a nitrogen atmosphere at the heating rate of 10°C min^{-1}. Samples were heated from 20 to 600°C.

Thermogravimetric analyses combined with infrared spectroscopy (TG-FTIR) of the thermal decomposition products of cross-linked poly(ester urethanes) were performed using TG209 (Netzsch) and ISS66 (Bruker) apparatus at the heating rate of 15°C min^{-1} in a nitrogen atmosphere.

Results and discussion

Dynamic mechanical thermal analysis (DMTA) of poly(ester urethanes) cross-linked with styrene reveals the evident influence of their chemical structure on the relationships between the temperature and storage shear modulus (*G*'), loss shear modulus (*G*") and the glass transition temperature (T_g), defined as the maximum of tanδ(T) curves.

The relationships between the storage shear modulus of cross-linked poly(ester urethane) and temperature are shown in Fig. 1. All curves reveal the same behaviour in the temperature range from –50 to –20°C in the glassy region, whereas in the rubbery region visible differences are present. For the temperature range from 0 to 220°C, one can notice the influence of MDI content in compositions on the storage shear modulus. As the 4,4'-diphenylmethane diisocyanate content increases, the polyurethanes G' values increase simultaneously (Table 1, Fig. 1). Therefore it has to be concluded that the increased crosslink density of PEU via allophanate bonds formation influences the increased values of the storage shear modulus above the glass transition temperature range. In the case of PEU cross-linked with styrene, the wide plateau in the rubber elasticity region was also well established.

Despite the various chemical structures of the obtained poly(ester urethanes) two maxima in tanδ(T) and logG''(T) curves can be observed. These results confirm the phase separation of the polymers which is determined by the molar content of oligo(alkylene-ester)diol, 4,4'-diphenylmethane diisocyanate and the cross-link density of compositions. The low-temperature peaks of log(G'')(T) and tanδ(T) curves resulted from the presence of oligo(alkyleneester)diols which have been used in the PEU synthesis. Furthermore, the high-temperature peaks are related to some motion of the pendant polystyrene side chains in the compositions [20]. The logG'' *vs.* temperature curves for PEU 1, PEU 2, PEU 3, PEU 4, PEU 5 and PEU 6 show peaks at: –15 and 116; –13 and 118; –15 and 120; –13 and 121; –13 and 125 and –13°C, respectively (Fig. 2). Moreover, the glass transition temperatures for these compositions were observed at: –6 and 117; –6 and 118; –8 and 120; –6 and 124; –4 and 126; –7 and 122.0°C, respectively (Fig. 1).

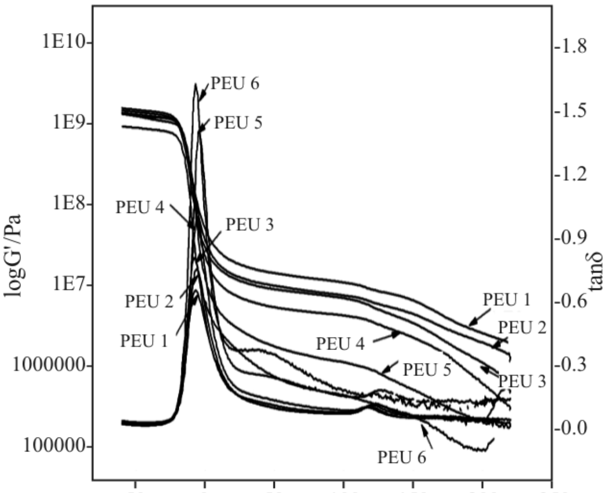


Fig. 1 Dynamic storage moduli (G') and loss tangent (tanδ) *vs.* temperature dependence of PEU cross-linked with styrene;
1 – PEU[NCO/OH] 1.5/1, 2 – PEU[NCO/OH] 1.1/1,
3 – PEU[NCO/OH] 1/1.1, 4 – PEU[NCO/OH] 1/1.3,
5 – PEU[NCO/OH] 1/2, 6 – PEU[NCO/OH] 1/2.6

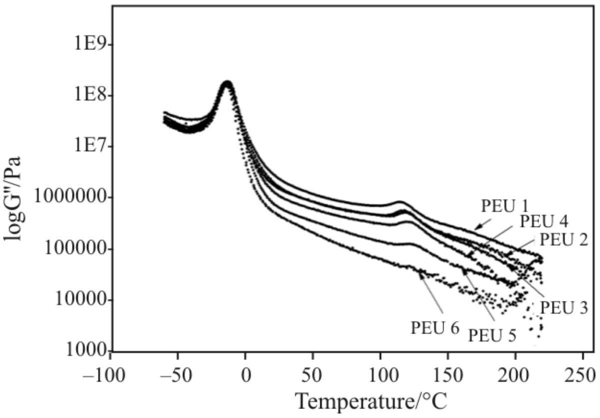


Fig. 2 Dynamic loss moduli (G'') *vs.* temperature dependence of PEU cross-linked with styrene;
1 – PEU[NCO/OH] 1.5/1, 2 – PEU[NCO/OH] 1.1/1,
3 – PEU[NCO/OH] 1/1.1, 4 – PEU[NCO/OH] 1/1.3,
5 – PEU[NCO/OH] 1/2, 6 – PEU[NCO/OH] 1/2.6

A comparison of the present outcome with the previously obtained results [19, 20] has led to the conclusion that the presence of *cis*-2-butene-1,4-diol in PEU results in the lowered temperature values for low-temperature glass transition. This is associated with the higher mobility of PEU segments that had originated from the oligomerol containing unsaturated diol as compared to poly(ester urethanes) based on maleic anhydride. It was also found out that the phase change temperatures for the investigated compositions within the high-temperature range were higher than those for poly(ester urethanes) based on the oligomerol synthesized from adipic acid, maleic anhydride and ethylene glycol, and cross-linked with styrene or methyl methacrylate.

Thermal stability measurements of the investigated poly(ester urethanes) exhibit the single-step degradation process in a nitrogen atmosphere. As depicted in Fig. 3 the relationship between the PEU mass loss and temperature shows a similar trend. From the presented results one may easily infer that PEU remain stable in the initial phase, while beyond the temperature of 280°C their degradation increases rapidly. The temperature values corresponding to the initial stages of thermal decomposition ($T_{5\%}$, $T_{10\%}$) and the temperatures at which the maximal rate of degradation occurs (T_{max}) are presented in Table 2. The first stage of PEU degradation is observed for the temperature ranging from 288 to 308°C, and it in-

Table 2 Outcome of TG analysis of poly(ester urethanes) cross-linked with styrene

Symbol	PEU 1	PEU 2	PEU 3	PEU 4	PEU 5	PEU 6
$T_{5\%}$/°C	288.3	295.6	308.3	304.9	304.8	308.2
$T_{10\%}$/°C	307.9	319.7	330.3	329.6	329.7	330.3
T_{max}/°C	398.2	412.1	402.0	409.7	409.8	402.1

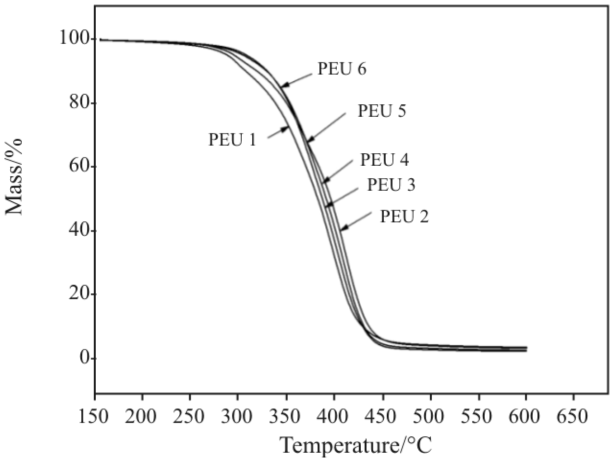


Fig. 3 TG curves of PEU cross-linked with styrene; 1 – PEU[NCO/OH] 1.5/1, 2 – PEU[NCO/OH] 1.1/1, 3 – PEU[NCO/OH] 1/1.1, 4 – PEU[NCO/OH] 1/1.3, 5 – PEU[NCO/OH] 1/2, 6 – PEU[NCO/OH] 1/2.6

volves the decomposition of urethane groups, as reported in [21–26]. These results explain some differences between the thermal stability of poly(ester urethanes) obtained from prepolymers synthesized with NCO molar excess (PEU 1–2) and the polymers synthesized from prepolymers with an excess of OH molar groups (PEU 3–6). The latter compositions have lower content of urethane and allophanate bonds, therefore the temperatures of their initial decomposition stages and maximal rate of degradation are higher than those of obtained from prepolymers with NCO-end groups. On the basis of the obtained results, it can be concluded that the increase of polymers cross-link density by the introduction of allophanate bonds leads to the decrease of PEU thermal stability. In the course of the study, it was established that the introduction of *cis*-2-butene-1,4-diol as the unsaturated bonds carrier into the PEU structure results in the lowered thermal stability of polymers by 10 to 20°C in comparison to the compositions synthesized with maleic anhydride. Nevertheless, PEU described in this work can be considered as polymers characterized by thermal resistance that allows their application in construction materials.

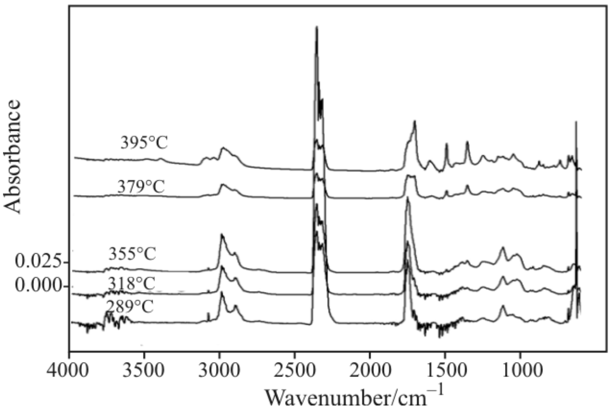


Fig. 4 FTIR spectra of PEU-2 thermal degradation products at temperatures from 289 to 395°C

In order to study more thoroughly the thermal degradation process of the investigated polymers, FTIR spectra of PEU thermal degradation products were analyzed. In Fig. 4 the absorbance spectra of PEU 2 are presented. The bands with the maxima within the range from 2233 to 2360 and at 669 cm^{-1} are characteristic for carbon dioxide being the main product of polyurethanes thermal decomposition. The bands observed from 3550 to 3700 cm^{-1} are attributed to –OH stretching vibrations. Furthermore, the presence of absorbance regions in the vicinity of 1750, 1280, 1154 and 1054 cm^{-1}, which originate from C=O and C–O–C groups, has confirmed the participation of carbonyl and ester-containing fragments. The bands in the vicinity of 2967, 2887 and 1382 cm^{-1} are associated with the alkylene groups, whereas the appearance of –N–H absorptions at 1619 cm^{-1} has confirmed the presence of –NH$_2$-end fragments.

Conclusions

A novel group of poly(ester urethanes) cross-linked with styrene via radical copolymerization cross-linking has been obtained. Unsaturated oligomerols based on *cis*-2-butene-1,4-diol as unsaturated bonds carrier were used for the polyurethanes synthesis. The results of dynamic mechanical thermal analysis showed that the introduction of unsaturated diol into the OAE structure and later on into PEU increases the mobility of oligomerol chains as compared to the systems containing maleic anhydride. This phenomenon manifests itself by the lowered glass transition temperature within the low-temperature range. Moreover, the presence of double maxima for the curves describing the relationship between the temperature and dynamic loss moduli and loss tangent indicates that the phase separation has occurred in these compositions. The analyzed effect is the result of the presence of styrene homopolymer in the compositions or of polystyrene one-side bonded to PEU.

Thermogravimetric measurements indicate that poly(ester urethanes) synthesized from the unsaturated oligo(alkyleneester)diols based on *cis*-2-butene-1,4-diol remain stable below 280°C. The analysis of the obtained results indicates that both chemical structure of the unsaturated bonds carrier and the molar ratio of NCO/OH groups in urethane prepolymers are the decisive factors in regard to thermal resistance of the synthesized compositions. The poly(ester urethanes) described in this study have lower thermal resistance by 10–20°C as compared to the compositions containing maleic anhydride. Therefore the future studies will be focused on increasing the thermal stability of these polymers. The use of TG-FTIR technique allowed the conclusion that the main decomposition products of PEU are carbon dioxide, carbonyl and ester-containing fragments as well as fragments with –OH and –NH_2-end groups.

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