THERMAL AND DYNAMIC MECHANICAL ANALYSIS OF CROSS-LINKED POLY(ESTERURETHANES)

Lidia Jasińska[1]*, A. Balas*[1]*, J. T. Haponiuk*[1]*, G. Nowaczyk*[2] *and S. Jurga*[2]

[1]Gdańsk University of Technology, Faculty of Chemistry, Department of Polymer Technology, Narutowicza St 11/12
80-952 Gdańsk, Poland
[2]Adam Mickiewicz University, Faculty of Physics, Department of Macromolecular Physics, Umultowska St 85, 61-614 Poznań, Poland

New cross-linked poly(esterurethanes) (PEU) based on unsaturated olygo(alkyleneester)diol (OAE), 4,4'-diphenylmethane diisocyanate (MDI) and styrene or methyl methacrylate as curing monomers were prepared. The synthesis of PEU was performed in two steps. In the first step OAE was obtained from adipic acid, maleic anhydride and ethylene glycol. In the second step a prepolymer was obtained in a reaction of OAE with different amounts of 4,4'-diphenylmethane diisocyanate followed by cross-linking using previously mentioned curing monomers. The influence of structure of the poly(esterurethanes) on thermal and dynamic mechanical properties is studied. Thermogravimetric analysis shows that cross-linked poly(esterurethanes) demonstrate high thermal stability. Moreover the dynamic mechanical thermal analysis shows that the presence of styrene cross-linking chains in polymers lead to the phase separation in cross-linked poly(esterurethanes).

Keywords: dynamic-mechanical analysis, poly(esterurethanes), thermal stability

Introduction

From the recent studies of a new group of polyurethanes containing unsaturated bonds one may extract a few trends. One of them focuses on poly(urethaneacrylates) (PEUA) and poly(urethaneurea-methacrylates) (PEUMA) in which the presence of unsaturated bonds allows for their cross-linking by a radical polymerization [1–5]. In the papers by Oprea *et al.* [1–3] concerning thermal stability of PEUA and PEUMA two maxima of mass loss in their thermograms were revealed. Furthermore, these authors showed that polymers containing cross-linking bonds exhibit an increase of degradation temperature of up to 15–25°C in comparison with polymers containing double bonds. Their thermogravimetric analysis revealed also a decrease in activation energy of up to 20–30% for PEUA [1] and 10–15% for PEUMA [2], respectively. These changes, in authors' opinion, may be caused by the dehydration of the $-COO^-NH_3$ structure and polymerization of double bonds.

The group of polymers containing unsaturated bonds includes also poly(ester-siloxane)urethanes [6, 7]. The presence of urethane groups and fragments of polysiloxane chains allows for obtaining polymers with sufficiently thermal and mechanical properties. The studies on mechanical properties and thermal stability of cross-linked elastomers revealed their dependence on chemical composition and cross-linking density. As shown in [6–8], these properties are strongly influenced by hard segment content in the structure of elastomers. Dynamic-mechanical thermal analysis measurements of poly(ester-siloxane)urethanes exhibited an influence of chemical composition of polymers and the type of the used cross-linking agent on their thermo-mechanical properties [6].

The intercross-linked networks of siliconized polyurethane-epoxy/unsaturated polyester coatings also constitute an important group of cross-linked polymers [8]. The thermal stability of these systems was studied using a differential scanning calorimetry and thermogravimetric analysis. The studies proved that the presence of urethane groups in these systems reduces their thermal stability. Moreover, the polymers containing urethane groups have lower glass transition temperatures (T_g) than the unmodified ones. Urethane groups in elastomers increase their tensile strength and thus provide possibilities of wide application.

The present paper discusses the influence of a chemical structure on the thermal and dynamic-mechanical properties of cross-linked poly(esterurethanes). In particular, the influence of the [NCO/OH] molar ratio and the type of the used cross-linking monomer was studied. The obtained results show also that the poly(esterurethanes) which contain cross-linking agent are more stable than the reference materials without cross-linking.

Experimental

Materials

In the synthesis of cross-linked poly(esterurethanes) the following substrates were used:

Adipic acid (Sigma-Aldrich) was used as received without further purification. Maleic anhydride (Sigma-Aldrich) used as received without further purification. Glycol ethylene (POCh) purified by distillation under reduced pressure. 4,4'-diphenyl-methane diisocyanate (Borsdochem) used after being filtrated in melt. Styrene and methyl methacrylate (Sigma Aldrich) used after being washed in 10% NaOH solution and distilled water to remove the inhibitor, dehydrated over anhydrous $MgSO_4$. Catalysts: methyl ethyl peroxide (36% solution in dimethyl phthalate), cobalt(II) 2-ethylhexanoate.

Synthesis of poly(esterurethanes)

Poly(esterurethanes) (PEU) were prepared from unsaturated oligo(alkyleneester)diol, 4,4'-diphenyl-methane diisocyanate and a curing monomer. In the first step of the synthesis, the OAE was obtained from adipic acid, maleic anhydride, and ethylene glycol. The reaction was carried out in a nitrogen atmosphere at the temperature of 190°C. In the next step a prepolymer was obtained in the reaction of the OAE with different amounts of 4,4'-diphenylmethane diisocyanate (MDI) followed subsequently by cross-linking with styrene or methyl methacrylate as a curing monomer. The prepolymers were synthesized in melt at the temperature of 60°C for 1 h and dissolved in 30 mass% of styrene (St) or methyl methacrylate (MMA). The PEU curing process was carried out for 24 h in the presence of 1 mass% of the methyl ethyl peroxide and of 0.003 mass% of the cobalt(II) 2-ethylhexanoate at the temperature of 80°C. The details of the synthesis and properties of poly(esterurethanes) cross-linked by methyl methacrylate were described in [9]. The obtained polymers were prepared from prepolymers with various [NCO/OH] molar ratios, namely, 1.5/1, 1.2/1, 1/1 and 1/1.5. Hereafter, these poly(esterurethanes) shall be called PEU [NCO/OH] 1.5/1, PEU [NCO/OH] 1.2/1, PEU [NCO/OH] 1/1, PEU [NCO/OH] 1/1.5, respectively.

Methods

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}. Dynamic mechanical thermal analysis (DMTA) was performed using Ares Solids Rheometer in the temperatures ranging from –60 to 220°C at the heating rate of 5°C min^{-1}, with the frequency of 10 Hz.

Results and discussion

Thermogravimetric analysis (TG) is a widespread technique used for the characterization of materials thermal stability. In the present work TG measurements were used to study the initial temperatures of PEU's thermal decomposition ($T_{5\%}$) and the temperatures of the maximal rate of decomposition (T_{max}). The work focuses on two aspects: the influence of the contents of urethane groups in PEU and the type of the used cross-linking agent on their thermal stability.

The investigations were accomplished for poly(esterurethanes) obtained from prepolymers with various [NCO/OH] molar ratios, namely, 1.5/1, 1.2/1, 1/1 and 1/1.5 and cross-linked by styrene (PEU/St) and methyl methacrylate (PEU/MMA). The mass loss as a function of temperature of poly(esterurethanes) cross-linked by styrene and methyl methacrylate is presented in Figs 1 and 2, respectively. The thermogravimetric data presented in Table 1 show that cross-linked polyurethanes exhibit high thermal stability. On the basis of the obtained results one can observe that the degradation process of PEUs initiates at the temperature of about 300°C. Furthermore, the thermogravimetric analysis showed that polymers synthesized from prepolymers with OAE molar excess (PEU [NCO/OH] 1/1.5) are more stable in comparison with polymers synthesized with MDI molar excess (PEU [NCO/OH] 1.5/1 and PEU [NCO/OH] 1.2/1). The explanation of this fact is the lower thermal stability of urethanes groups, which are generated in a reaction of MDI and OAE. The measurements of the temperature of a maximal
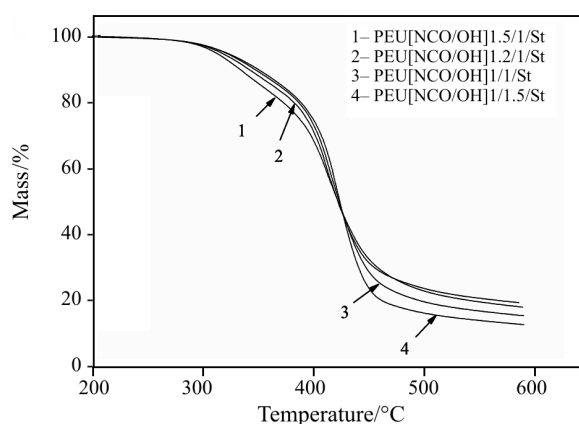

Fig. 1 The mass loss as a function of temperature of PEU cross-linked by styrene performed in nitrogen atmosphere at the heating rate of 10°C min^{-1}
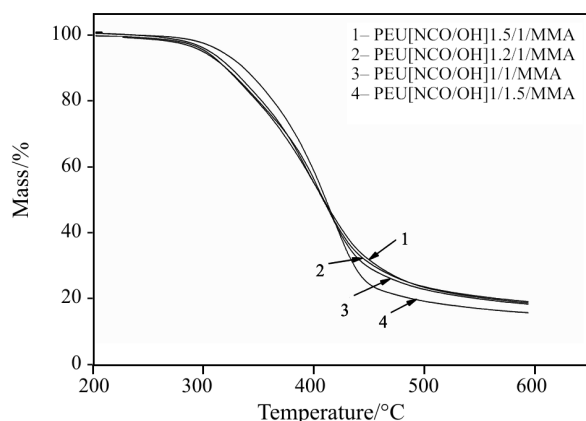
Fig. 2 The mass loss as a function of temperature of PEU cross-linked by methyl methacrylate performed in nitrogen atmosphere at the heating rate of 10°C min^{-1}

Table 1 Degradation parameters measured on cross-linked poly(esterurethanes) in nitrogen atmosphere at the heating rate of 10°C min^{-1}

PEU/St [NCO/OH]	1.5/1	1.2/1	1/1	1/1.5
$T_{5\%}$/°C	309.1	313.9	317.3	318.2
T_{max}/°C	409.5	409.5	412.5	417.5
PEU/MMA [NCO/OH]	1.5/1	1.2/1	1/1	1/1.5
$T_{5\%}$/°C	299.2	302.6	295.5	317.8
T_{max}/°C	406.6	410.1	412.8	422.4

mass loss have also confirmed this fact. Simultaneously, it can be observed that the polymers crosslinked by styrene are slightly more stable than polyurethanes cross-linked by methyl methacrylate.

Dynamic mechanical thermal analysis (DMTA) was used to study the dynamic mechanical behaviour of cross-linked poly(esterurethanes) and poly(esterurethanes) without cross-linking (PEU 0). Temperature dependencies of logarithms of storage modulus (G'), loss modulus (G''), and loss tangent (tanδ) of the PEU cross-linked by styrene are presented in Figs 3–5. The obtained results of DMTA demonstrate that the chemical structure of polyurethanes and the presence of cross-linking agent strongly influence their mechanical and thermal properties. This conclusion follows from the fact that the storage moduli G' of the cross-linked PEU exhibits nearly constant temperature dependence above the glass transition, in contrary to poly(esterurethanes) synthesized without styrene, as depicted in Fig. 3. Moreover, the temperature dependencies of logarithms of storage moduli G' of crosslinked poly(esterurethanes) indicate that G' of PEU are less temperature sensitive, especially in the rubber elasticity region.

Comparing the temperature dependencies of the logarithms of loss modulus G'' and loss tangent tanδ
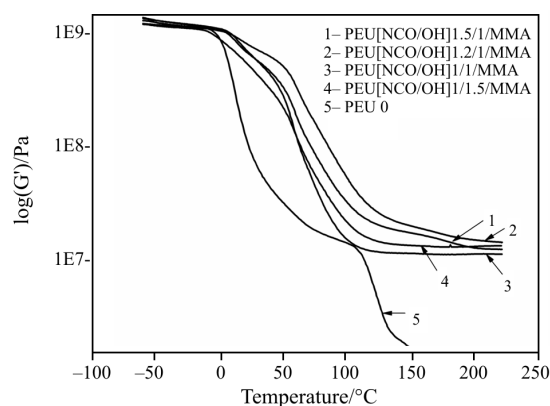

Fig. 3 Dynamic storage moduli (G') of PEU cross-linked by styrene as functions of temperature performed in the temperature range from –60 to 220°C at the heating rate of 5°C min^{-1}, at the frequency of 10 Hz
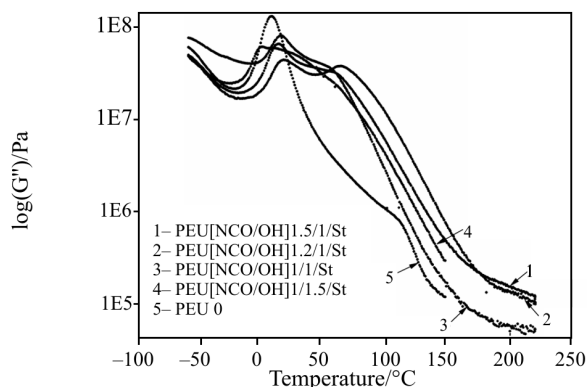

Fig. 4 Dynamic loss moduli (G'') of PEU cross-linked by styrene as functions of temperature performed in the temperature range from –60 to 220°C at the heating rate of 5°C min^{-1}, at the frequency of 10 Hz

of the cross-linked PEU with PEU 0 one can notice that the presence of styrene cross-linking chains in polymers lead to the phase separation in cross-linked poly(esterurethanes). The log$G''(T)$ curves (Fig. 4) for cross-linked polymers have two peaks at: 12 and 55, 15 and 62, 13 and 52, –3 and 51°C for PEU synthesized from prepolymers with the [NCO/OH] molar ratio 1.5/1, 1.2/1, 1/1, 1/1.5 respectively. The behaviour of tanδ in the function of temperature (Fig. 5) shows the same trends as the loss modulus for all investigated samples. Temperature dependencies of the loss tangent (tanδ) for PEU/St [NCO/OH] 1.5/1, 1.2/1, 1/1, 1/1.5 and PEU 0 have maxima at the following temperatures: 14 and 78, 17 and 93, 16 and 73, 2 and 78 and 15°C. These results demonstrate the influence of presence of styrene on the PEU/St glass transition temperatures. The maxima present on the curves of tanδ in temperature range from 70 to100°C may follow from presence of pendant polystyrene side chains in cross-linked PEU, while maxima pres-
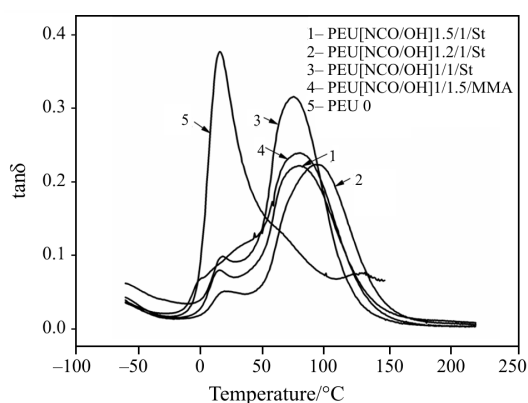
Fig. 5 Loss tangent (tanδ) values of PEU cross-linked by styrene performed in the temperature range from –60 to 220°C at the heating rate of 5°C min^{-1}, at the frequency of 10 Hz

Fig. 7 Dynamic loss moduli (G'') of PEU cross-linked by methyl methacrylate as functions of temperature performed in the temperature range from –60 to 220°C at the heating rate of 5°C min^{-1}, at the frequency of 10 Hz

ent in temperature range 2–17°C may follow from oligo(alkyleneester)diol chains. Rutkowska *et al.* [10] described the similar scientific problem which concerns the phase behaviour of partly sulfonated polystyrenes containing polyurethane grafts. The analyses of phase separation were described also for polyurethane-polystyrene interpenetrating polymer networks [11]. Moreover, dynamic mechanical thermal analysis of rubber waste-urethane composites [12] and polymer blends based on poly(ether-urethane) ionomer and ion-containing styrene-acrylic acid copolymer [13] confirms that the dynamic mechanical properties depend on the phase separation of hard and soft segments and on the density of physical networks.

Figures 6–8 present the temperature dependencies of logarithms of storage modulus G', loss modulus G'' and loss tangent tanδ of poly(esterurethanes) cross-linked by methyl methacrylate. The plots of PEU/MMA show the behaviour typical

Fig. 8 Loss tangent (tanδ) values of PEU cross-linked by methyl methacrylate performed in the temperature range from –60 to 220°C at the heating rate of 5°C min^{-1}, at the frequency of 10 Hz

for one-phase systems. Temperature dependencies of the logG'' reveal maxima at 19, 20, 16, 13 and 6°C for PEU [NCO/OH]: 1.5/1, 1.2/1, 1/1, 1/1.5 and PEU0, respectively.

The curve of loss tangent tanδ *vs.* temperature *T* for these PEU also shows single maxima at 33, 39, 30, 33, and 15°C for PEU obtained from prepolymers with [NCO/OH] molar ratios, 1.5/1, 1.2/1, 1/1, 1/1.5, and PEU 0, respectively. Furthermore temperature dependencies of the logG', shown in Fig. 6, exhibit no melting behaviour in the rubber elasticity region unlike the non cross-linked polymers.

Conclusions

In our analysis we focused on the influence of chemical structure of poly(esterurethanes) cross-linked by styrene and methyl methacrylate on their
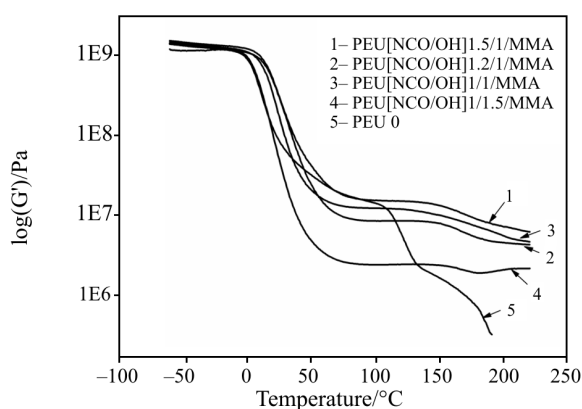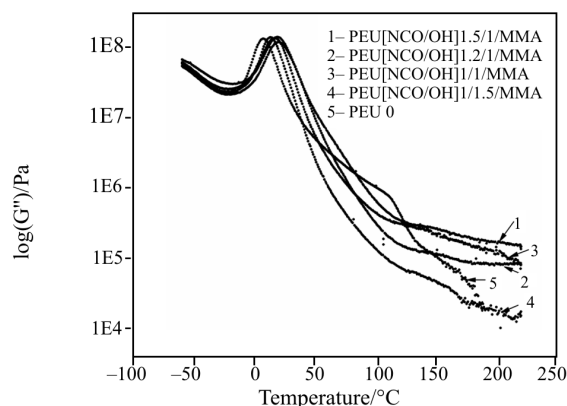

Fig. 6 Dynamic storage moduli (G') of PEU cross-linked by methyl methacrylate as functions of temperature performed in the temperature range from –60 to 220°C at the heating rate of 5°C min^{-1}, at the frequency of 10 Hz
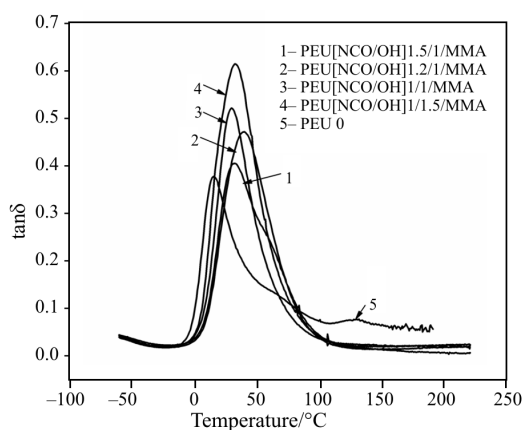
thermal and dynamic-mechanical properties. The thermogravimetric analysis shows that poly(esterurethanes) exhibit high thermal stability. The initial temperatures of PEU's thermal decomposition are at about 300°C.

DMTA analysis of the investigated poly(esterurethanes) confirmed that the presence of cross-linking agent strongly influences their mechanical and thermal properties. This influence is especially visible in the rubber elasticity region. The investigations indicated also phase separation in poly(esterurethanes) cross-linked by styrene, which may follow from the presence of pendant polystyrene side chains.

References

1 S. Oprea, S. Vlad and A. Stanciu, Polymer, 42 (2001) 7257.
2 S. Oprea, S. Vlad, A. Stanciu, C. Ciobanu and M. Macoveanu, Eur. Polym. J., 35 (1999) 1269.
3 S. Oprea, Polym. Degrad. Stab., 75 (2002) 9.
4 J. Ledru, B. Youssef, J. M. Saiter and J. Grenet, J. Therm. Anal. Cal., 67 (2002) 767.
5 T. Yilmaz, O. Ozarslan, E. Yildiz, A. Kuyulu, E. Ekinci and A. Gungor, J. Appl. Polym. Sci., 69 (1998) 1837.
6 S. Ioan, G. Grigorescu and A. Stanciu, Polymer, 42 (2001) 3633.
7 A. Stanciu, V. Bulacovschi, S. Oprea and S. Vlad, Polym. Degrad. Stab., 72 (2001) 551.
8 A. Anand Prabu and M. Alagar, Prog. Org. Coat., 49 (2004) 236.
9 L. Jasinska, A. Balas and J. T. Haponiuk, e-Polymers, 003 (2007).
10 M. Rutkowska, M. Jastrzębska, J. S. Kim and A. Eisenberg, J. Appl. Polym. Sci., 48 (2003) 521.
11 D. J. Hourston, F.-U. Schafer, M. H. S. Gradwell and M. Song, Polymer, 39 (1998) 5609.
12 A. Danch, S. Ilisch, W. W. Sułkowski, M. Moczyński, A. Radoń and H. J. Radusch, J. Therm. Anal. Cal., 79 (2005) 623.
13 O. Slisenko, E. Lebedev, P. Pissis, A. Spanoudaki, E. Kontou and O. Grigoryeva, J. Therm. Anal. Cal., 84 (2006) 15.