

STEFAN OPREA

“Petru Poni” Institute of Macromolecular Chemistry
Aleea Grigore Ghica Voda No. 41-A
700487, Iasi, Romania
e-mail: stefop@icmpp.ro

Effect of structure on the thermal stability of crosslinked poly(ester-urethane)

Summary — Polyurethane (PUR) crosslinked copolymers composed of 4,4'-diphenylmethane diisocyanate (MDI), poly(ethylene adipate)diol (PEA), glycerine (Gly), and diol [1,2-ethanediol (ED), diethylene glycol (DEG), 1,3-propanediol (PD), 1,4-butanediol (BD), 1,5-pentanediol (PTD) or 1,6-hexanediol (HD)] as a chain extender were synthesized in a two-step process. The effect of structural hard segments on the thermal stability of crosslinked poly(ester-urethane) was studied. Increase in the length of the hard segment decreased the thermal stability within a given series of compounds. The thermal oxidative stability of the polyurethane crosslinked system was investigated under an air atmosphere using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Interchain crosslinking improves thermal stability and chemically crosslinked PUR behaves as an elastomer capable of shape memory. The decomposition of PUR crosslinked with various hard segments has been compared.

Key words: poly(ester-urethane), crosslinking, thermal stability, hard segments, soft segments.

WPLYW STRUKTURY NA STABILNOŚĆ TERMICZNĄ USIECIOWANYCH POLI(ESTRO-URETANÓW)

Streszczenie — Usieciowane kopolimery poliuretanowe (PUR) syntezowano dwuetapowo z diizocyanianu 4,4'-difenylometanu (MDI), diolu poli(adipinianu etylenu) (PEA), glicerolu (Gly) i diolu jako przedłużacza łańcucha [1,2-etanodiolu (ED), glikolu dietylowego (DEG), 1,3-propanodiolu (PD), 1,4-butanodiolu (BD), 1,5-pentanodiolu (PTD) lub 1,6-heksanodiolu (HD)] (tabela 1). Metodą analizy termogravimetrycznej (TGA) i skaningowej kalorymetrii różnicowej (DSC) badano w atmosferze powietrza stabilność termiczną otrzymanych materiałów. W badanych seriach związków różniących się stosunkiem substratów (PUR1—PUR2 i PUR7—PUR12) metodą TGA stwierdzono zmniejszanie się stabilności termicznej ze wzrostem długości segmentów sztywnych (tabela 2, rys. 1—4). Wyznaczono energię aktywacji (E_a) procesu degradacji w funkcji stopnia przemiany (α) (rys. 5 i 6). Zaobserwowano zwiększanie się wartości E_a ze wzrostem ciężaru cząsteczkowego segmentów sztywnych podczas pierwszego etapu degradacji, a zmniejszanie się podczas drugiego etapu. Metodą DSC wyznaczono temperaturę zeszklenia (T_g) otrzymanych materiałów. Stwierdzono zmniejszanie się wartości T_g ze wzrostem zawartości grup metylenowych w segmentach sztywnych PUR.

Słowa kluczowe: poli(estro-uretan), sieciowanie, stabilność termiczna, segmenty sztywne, segmenty giętkie.

Recently, it was found that polyurethanes (PUR) with phase separation morphology have shape memory effect and especially, in some cases, have some specific tendency in mechanical and thermal properties, such as higher recovery strain, lower residual strain, higher hardness, increased modulus and strength [1—3]. The shape memorizing phase consists of physical or chemical crosslinking in the polymer, which allows PUR to remember the primary shape [4—6]. Generally speaking, these polymers often have crosslinked structures (either chemical crosslinking [7, 8] or physical crosslinking) which determine their permanent shapes.

The shape memory effect can be controlled *via* molecular weight of soft segment, molar ratio between hard and soft segments, and polymerization process [9, 10].

The soft or flexible segments, which are in a viscous or rubbery state, provide the elastomeric character to the polyurethane chain. The hard or rigid segments, which are in a glass or semicrystalline state, provide dimensional stability by acting as thermally reversible and multifunctional crosslinks and also as reinforcing fillers [11].

Thermal stability is an important aspect of the technological applications of polymeric materials like PUR elastomers. Thermogravimetry is a suitable method to

evaluate the thermal properties. It was proposed that the thermal degradation of PUR is primarily a depolycondensation process, which starts at about 250 °C [12]. In general, thermal degradation of PUR involves an initial stage where trapped volatile materials are released; this is followed by the scission and depolymerization, resulting in weight loss and deterioration of mechanical properties, and finally a complete thermal breakdown of the chain [13–15].

Usually, at a low heating rate, the degradation process results in differential thermogravimetric curves (DTG) with several peaks, which indicate of the complexity of the degradation [16]. The urethane linkages may be broken due to the high shear and stress at elevated processing temperature [17].

This study was conducted using thermogravimetric analysis (TGA) in an air atmosphere. Weight loss in an air arise from a combination of thermodynamic (bond scission) and oxidative degradation.

The nature of the components present in a formulation is clearly the most important factor affecting the thermal stability.

In this work we will discuss the effect of hard segment composition on the thermal properties of cross-linked poly(ester-urethane), and explore the thermal degradation of PUR with various hard segments.

EXPERIMENTAL

Materials

4,4'-Diphenylmethane diisocyanate (MDI) characterized by melting temperature $T_m = 42\text{--}44$ °C, density $d = 1.180$ g/cm³ and boiling temperature $T_b = 200$ °C/5 mmHg (Sigma-Aldrich) was used without further purification.

Polyethylene adipate diol (PEA) with molecular weight $M_w = 2000$, $T_m = 50\text{--}55$ °C, $d = 1.175$ g/cm³, hydroxyl number $L_{OH} = 56$ mg KOH/g (Bayer) was dried in a vacuum oven before use.

1,2-Ethandiol (ED), diethylene glycol (DEG), 1,3-propanediol (PD), 1,4-butanediol (BD), 1,5-pentanediol (PTD), 1,6-hexanediol (HD), glycerine (Gly) (all from Fluka), were checked for the moisture content and, if necessary, dried under a vacuum until the water content was below 0.03 %.

Polymer synthesis

The poly(ester-urethane)s were prepared, based on aromatic hard segments derived from MDI, Gly and one of diols ED, DEG, PD, BD, PTD or HD, with PEA as the soft segments. The average hard segment composition was controlled by the molar ratios of PEA/MDI/(diol and triol) used in the syntheses, which was stated as 1/2/1 or 1/3/2. The diol/Gly molar ratio used was 3/2 in all of polyurethane samples synthesized. The compo-

sitions used and their hardness values are shown in Table 1. In this way, the average soft segment length was kept constant, while the hard segment length was systematically varied.

Table 1. Formulations and hardness of the polyurethanes obtained

Symbol of sample	PEA/MDI/(diol and triol) molar ratio	Type of chain extender	Hardness Shore A
PUR1	1/2/1	ED and Gly	60
PUR2	1/2/1	DEG and Gly	56
PUR3	1/2/1	PD and Gly	55
PUR4	1/2/1	BD and Gly	46
PUR5	1/2/1	PTD and Gly	58
PUR6	1/2/1	HD and Gly	48
PUR7	1/3/2	ED and Gly	70
PUR8	1/3/2	DEG and Gly	65
PUR9	1/3/2	PD and Gly	72
PUR10	1/3/2	BD and Gly	62
PUR11	1/3/2	PTD and Gly	67
PUR12	1/3/2	HD and Gly	53

First NCO-terminated prepolymer was prepared by reaction of MDI and PEA at a specified NCO/OH equivalent ratio. In a 500 mL four neck cylindrical vessel which was equipped with a mechanical stirrer, thermometer, heating mantle and a gas inlet and outlet for continuous flow of nitrogen, appropriate amounts of MDI and PEA were stirred under nitrogen at 80 °C for 3 h to make prepolymer. Next the extender diol (ED, DEG, PD, BD, PTD or HD) and Gly were added dropwise to the reaction mixture according to the specified in Table 1 ratios, and the remaining isocyanate groups' content was intermittently checked by di-*n*-butylamine back-titration during polymerization to determine the progress of polymerization. The reaction mixture became sticky during polymerization, and the reaction was carried out until the unreacted isocyanate groups were not observed.

The resulting PUR material poured into a mold and left to cure at 100 °C for 24 h and post-curing of PUR proceeded at ambient temperature for 7 days. Under these conditions the use of catalyst was not necessary. The polyurethane sheets thus prepared were used for the determination of thermal stability.

Methods of testing

The thermal stability of polyurethanes was tested in an air atmosphere by thermogravimetric analysis (TGA) using a DERIVATOGRAPH Q-1500 D apparatus (Hungary). The rate of TGA scans was 10 °C/min. The initial weight of the sample was about 50 mg and the temperature range 30–700 °C. A differential scanning calorimeter (DSC) type DSC-7 Perkin-Elmer was used for thermal

analysis and was operated with a heating rate of 10 °C/min. In the first scan, the PUR sample was heated up to 250 °C (10 °C/min), kept at this temperature for 5 min, and quickly cooled to -100 °C. In the second scan, the sample was heated again to 250 °C with a heating rate of 10 °C/min, and the second scan was used to find glass transition temperature (T_g).

Kinetic analysis of TG data was carried out using a single curve method described by Coats and Redfern [18], and Reich and Levi [19].

RESULTS AND DISCUSSION

In this study, several diols were examined as chain extenders in polyurethanes crosslinking. The effects of the hard segments of structure were studied.

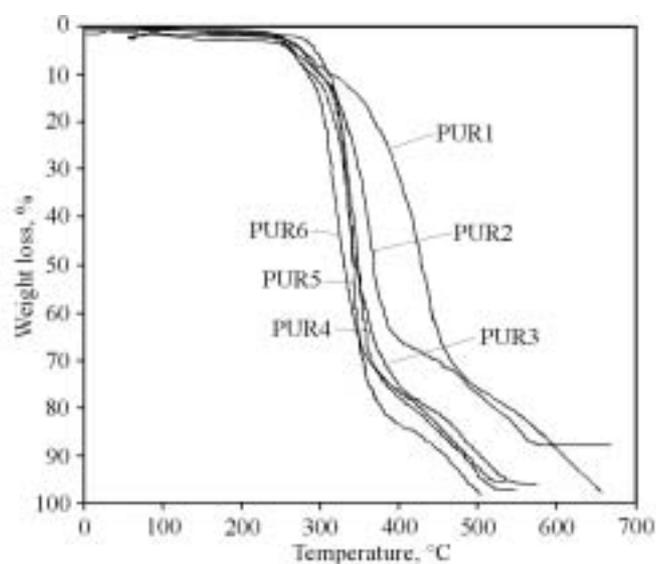


Fig. 1. Thermogravimetric curves of PURs with PEA/MDI/(diol and triol) molar ratio equal to 1/2/1

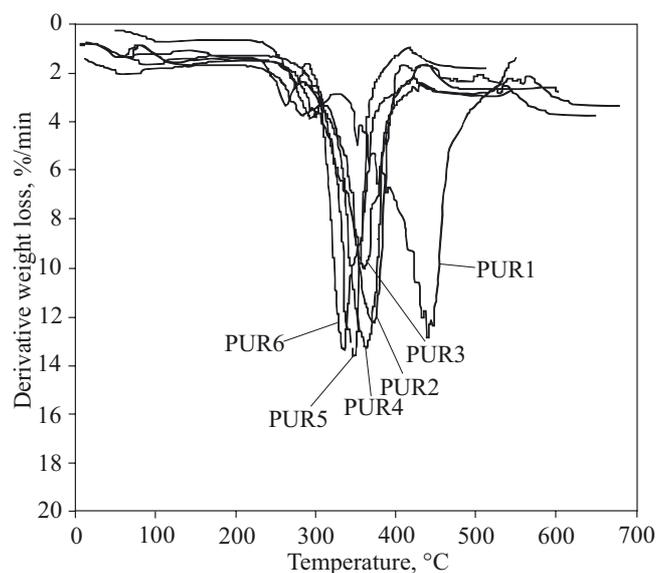


Fig. 2. Differential thermogravimetric curves of PURs with PEA/MDI/(diol and triol) molar ratio equal to 1/2/1

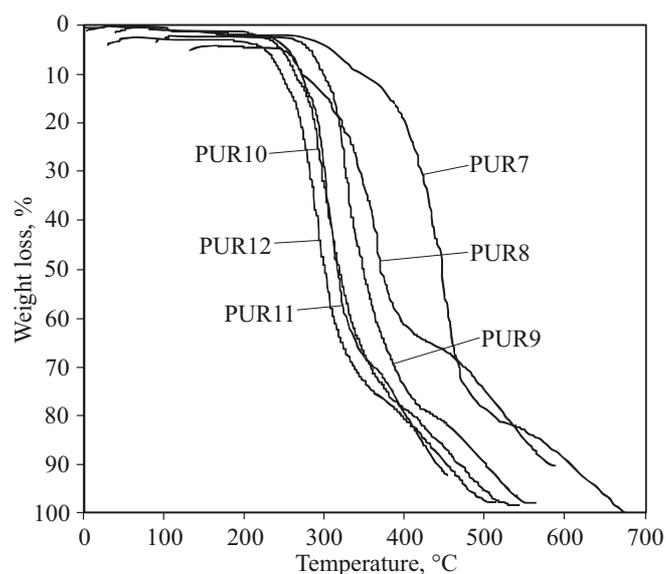


Fig. 3. Thermogravimetric curves of PURs with PEA/MDI/(diol and triol) molar ratio equal to 1/3/2

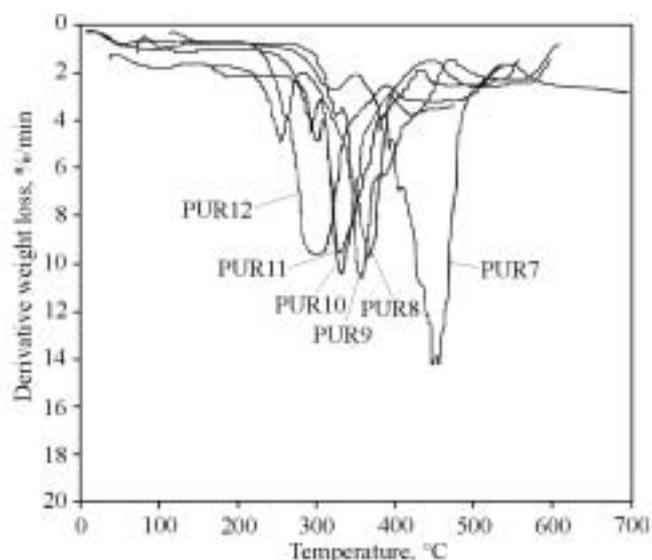


Fig. 4. Differential thermogravimetric curves of PURs with PEA/MDI/(diol and triol) molar ratio equal to 1/3/2

Figures 1—4 show the degradation profiles of cross-linked polyurethanes with variation of hard segment length and components' ratios.

The same testing conditions were used for all the copolymer samples being analyzed. The onset degradation temperature (T_i) was defined as the initial temperature of degradation, corresponding to the intersection of the tangent drawn at the inflection point of the decomposition step with the horizontal zero line of TG curve [20].

All polymers showed initial weight losses in the temperature range of 100—320 °C, suggesting that degradation started at the urethane bond [22]. It can be observed that T_i value shifts to lower temperature with increasing the ratio of the hard and soft segments. The weight loss with a maximum rate at temp. about 400 °C is associated

with other segments of the remaining structure. Thermal stability of these PURs depends strongly on urethane groups per unit volume and an increase in the initial weight loss was observed as a result of the increase in the amount of urethane groups.

Thermogravimetric characteristics, which include temperature ranges, are listed in Table 2. Data shown in Table 2 indicate that thermal degradation mechanisms of studied samples are very complex and consist of several steps.

were reduced. The speed of the onset weight losses is higher and it proceeds at lower temperatures.

Following the initial degradation in the hard segments, the second stage of the degradation was related to the soft segments and started at about 310 °C. The reaction orders are close to unity, what suggests that some diffusion processes accompany the decomposition in various conditions.

The increase in the temperature of maximum rate of decomposition indicates a lower rate of diffusion of the

Table 2. Thermogravimetric data of weight losses (%) and decomposition temperature ranges for poly(ester-urethane)s

Symbol of sample	Total weight loss, %	Step I		Step II		Step III	
		weight loss, %	temp. range, °C	weight loss, %	temp. range, °C	weight loss, %	temp. range, °C
PUR1	95	11	120–280	75	280–480	9	480–650
PUR2	88	12.5	100–300	68	300–390	7.5	390–580
PUR3	95	3	100–310	72	310–520	20	520–690
PUR4	96	4	100–250	76	250–440	16	440–620
PUR5	96	8	100–320	77	320–530	11	530–635
PUR6	96	3	100–260	77	260–440	16	440–580
PUR7	98	9,6	115–290	78	290–470	10,4	470–660
PUR8	92	11	100–280	65	280–400	16	400–580
PUR9	96	2	100–300	80	300–530	14	530–700
PUR10	97	4	100–270	76	270–500	17	500–650
PUR11	96	4	100–300	72	300–530	20	530–670
PUR12	96	4	100–280	75	280–500	17	500–680

Heat-ageing weight loss for this series shows a distinct order of thermal stability as follows: ED > PD > BD > PTD > HD. We note that during decomposition in an air, thermal stability of PUR7–PUR12 elastomers (Fig. 3) are somewhat lower than those of PUR1–PUR6 elastomers (Fig. 1). In the temperature range 320–500 °C, TG curves of the latter are shifted towards higher temperatures.

The soft segments of polyurethanes are all made up of PEA, suggesting that the structures of PUR are different only in the hard segments' part. It can be concluded that the thermal stability of PUR is affected by hard segments. Because of the tendency of the formation of hydrogen bond between the oxygen atom in the soft segment (carbonyl of the hydroxyl group) and the urethane hydrogen atom in the hard segment, the interaction between the soft segment and the hard one in poly(ester-urethane) will be stronger.

Figures 3 and 4 show the thermograms of crosslinked PUR synthesized with MDI/PEA/(diol and triol) ratios equal to 1/3/2 (PUR7–PUR12). These thermograms show that all the polymers synthesized with these ratios of components reach the maximal weight losses at lower temperatures than PUR synthesized at a ratio 1/2/1 (PUR1–PUR7). The temperature of onset of degradation is higher for PUR1–PUR6 crosslinked elastomers (Table 2).

All the onset decomposition temperatures, maximal weight losses, and the final decomposition temperatures

degraded products out of the matrix as indicated by the lower peak degradation rates exhibited at these temperatures. Thus, it is evident that the crosslinking bonds restrict the diffusion of the degradation products from the matrix.

By analysis of the thermograms (Figs. 1–4) cross-linked of poly(ester-urethane) and using the reaction order values by Coats-Redfern method, the activation energy (E_a) curves for degradation as functions of the conversion (α) were derived using the Levi-Reich method. They are presented in Figures 5 and 6.

For $\alpha < 0.2$ a decrease in E_a with increasing α occurs. The conclusion that could be drawn is that in the initial moments, the reaction runs autocatalytically. This is possible due to the weak bonds or oxygen attack. It is well known that in polymer decomposition the presence of oxygen traces has a catalyst or initiator role in thermal or thermoxidative decomposition.

With increasing α values over 0.32, E_a begins to increase, probably because of the primary chemical bond splitting, occurring with an energy consumption. This trend is usually attributed to a decrease in free volume and mobility due to the bonding of soft segments to rigid urethane blocks and to an increase in phase mixing at lower polyester molecular units.

Kinetic parameters of thermal degradation for each degradation step were determined by Coats-Redfern method [19], using a computer program which processed thermogravimetric data up to 600 °C.

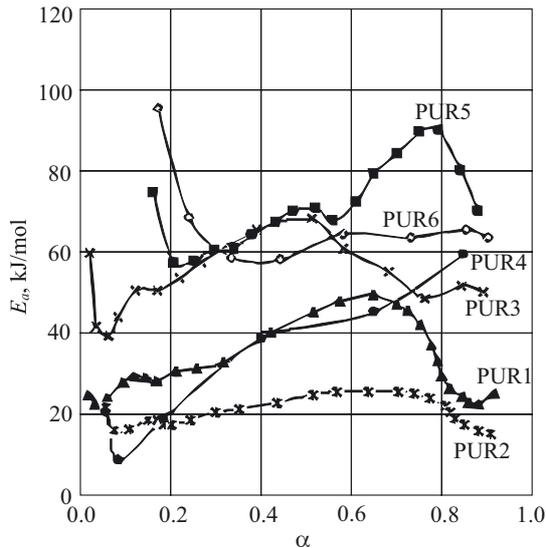


Fig. 5. Activation energy (E_a) versus conversion (α) of PURs with PEA/MDI/(diol and triol) molar ratio equal to 1/2/1

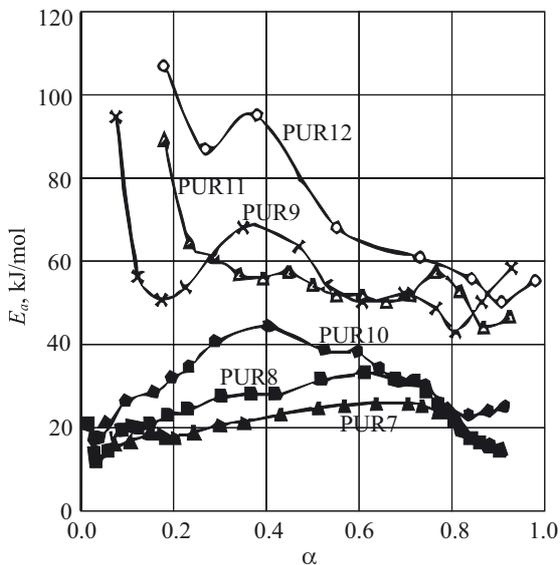


Fig. 6. Activation energy (E_a) versus conversion (α) of PURs with PEA/MDI/(diol and triol) molar ratio equal to 1/3/2

The kinetics of the thermal degradation of PUR elastomers was characterized by E_a which was calculated from experimental data, using Coats-Redfern method. The results obtained show that E_a increases with the increase in hard segment content in the first step of degradation. In the second step of degradation E_a decreases with increasing hard segment content.

This behavior was in agreement with qualitative characterization of the degradation process of these samples. This higher E_a value indicates that the higher hard segment content contributes to the beginning of crosslinking structures which require more energy for the degradation.

The MDI based system can also show more complete microphase separation. The physical crosslinks are im-

portant to providing dimensional stability and to stop cold flow in non-crosslinked materials. The effect of restricting segmental motion in a three dimensional network by chemical crosslinking sites is similar to that of microdomain physical crosslinks except that the former is irreversible. The crystalline polyester domain acts as an additional physical crosslinking site below the melting temperature.

The hard or rigid segments, which are in a glass or semicrystalline state, provide dimensional stability by acting as thermally reversible and multifunctional crosslinks and also as reinforcing fillers. They are formed by urethane groups originating from diisocyanates and also contain chemical crosslinks.

In these cases the differences appear in the first step but also in next step of degradation. Then E_a is higher as the energy necessary for breaking of the bonds among the macromolecular chains formed by polymerization increases.

DSC method was used to determine the thermal degradation pattern and T_g value of polymers. DSC thermograms of prepared PUR samples are presented in Figures 7 and 8.

Glass transition were observed for the polymers in the second heating. A decrease in T_g value for the increased content of methylene groups in the hard segment was observed. This results from a stronger interaction between the molecules in the hard domains.

The samples with higher contents of hard segments showed rather smaller heat of transition, suggesting that more ordered polymer packages were obtained at low contents of hard segments.

The phase separation of the soft and hard segments and good physical properties resulting from that are main reasons of the applications of polyurethanes. On the other hand, both the mechanical and thermal properties of polyurethanes can be affected dramatically by phase mixing. Interaction between the soft and hard segments can increase T_g value of the soft segments and decrease T_g of the hard segments.

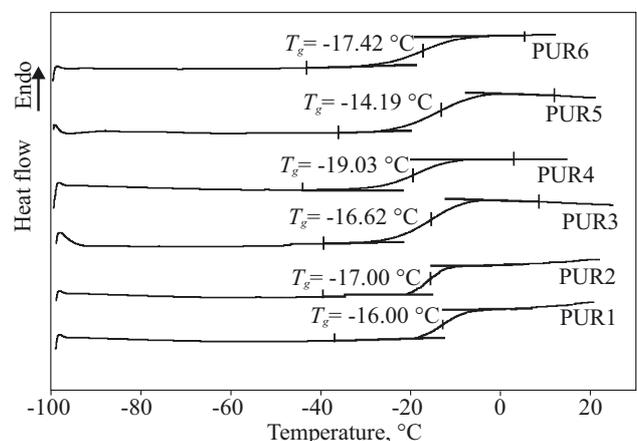


Fig. 7. DSC curves of PURs with PEA/MDI/(diol and triol) molar ratio equal to 1/2/1

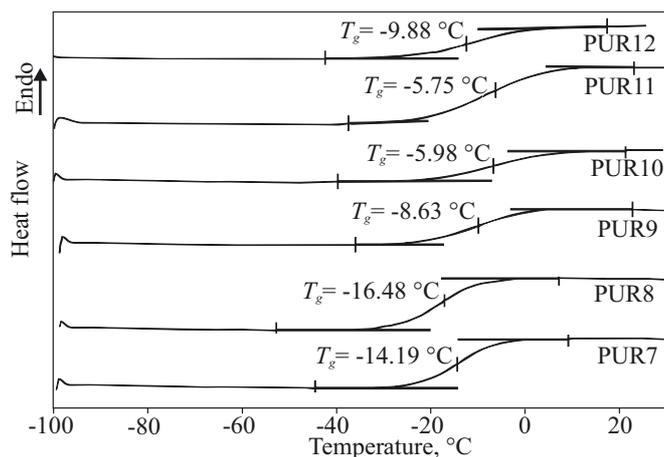


Fig. 8. DSC curves PURs with PEA/MDI/(diol and triol) molar ratio equal to 1/3/2

The DSC scan of HD based PUR exhibit $T_g = -17.42$ °C. Soft segments crystallinity can be compared to BD based PUR. The higher T_g , value in comparison to BD based PUR indicates the phase mixing. The transition at higher temperature corresponds probably, according to Cooper *et al.* [20], to the disruption of ordered segments. Between the completely amorphous and perfectly crystalline states, there exists a continuum of ordered segment morphologies. This has been called an order-disorder transition [21].

CONCLUSIONS

Crosslinked polyurethane materials have been synthesized and effects of hard segment molecular weight and structure of hard segment type have been investigated.

An increase in molecular weight of diol used as extender leads to higher hard segment crystallinity, a longer polymer chain between crosslinking sites in the material. The crosslinking process enhances the urethane domains' rigidity.

The thermal stability of crosslinked polyurethane is a function of the components present in the formulation. The first stage of weight loss was associated with the hard segment degradation and the second one, with the soft segments. Higher length of the hard segment decreased the polyurethane thermal stability.

Analysis of the thermograms leads to determination of E_a dependence on α which evidence a decrease in E_a value for α values below 0.2—0.32 followed by an increase.

The results clearly suggest that the thermal stability of PURs with PEA/MDI/(diol and triol) ratio equal 1/2/1 is better than that for 1/3/2 ratio. It also sug-

gested that the length of hard segments will influence the thermal stability of PUR.

The E_a value increases during the first step of degradation with increasing hard segments' molecular weight but decreases in the second step of degradation. Higher E_a values indicate that the higher thermal stability of these elastomers at the beginning of thermal degradation may be the result of crosslinking.

ACKNOWLEDGMENTS

The author thank to the Ministry of Education and Research for a financial support (CEEX Program — Grant No. X2C29).

REFERENCES

1. Tobushi H. S., Hayashi S., Kojima S.: *J. Soc. Mech. Eng. Int. J.* 1993, **1**, No. 3, 35.
2. Kim B. K., Lee S. Y., Xu M.: *Polymer* 1996, **37**, 5781.
3. Kim B. K., Lee S. Y., Lee J. S., Baek S. H., Choi Y. J., Lee J. O., Xu M.: *Polymer* 1998, **39**, 2803.
4. Takahashi T., Hayashi N., Hayashi S.: *J. Appl. Polym. Sci.* 1996, **60**, 1061.
5. Li F., Zhang X., Hou J., Xu M., Luo X., Ma D., Kim B. K.: *J. Appl. Polym. Sci.* 1997, **64**, 1511.
6. Li F., Zhu W., Zhang X., Zhao C., Xu M.: *J. Appl. Polym. Sci.* 1999, **71**, 1063.
7. Lin J. R., Chen L. W.: *J. Appl. Polym. Sci.* 1999, **73**, 1305.
8. Oprea S., Vlad S.: *J. Opt. Adv. Mater.* 2006, **8**, 675.
9. Takahashi T., Hayashi N., Hayashi S.: *J. Appl. Polym. Sci.* 1996, **60**, 1061.
10. Lai Y. C., Quinn E. T., Valint P. L.: *J. Polym. Sci., Part A: Polym. Chem.* 1995, **33**, 1767.
11. Janik H., Vancso J.: *Polimery* 2005, **2**, 139.
12. Jasińska L., Masiulonis B.: *Polimery* 2006, **51**, 12.
13. Zulfiqar S., Zulfiqar M., Kausar T.: *Polym. Degrad. Stab.* 1987, **17**, 327.
14. Gupta T., Adhikari B.: *Thermochim. Acta* 2003, **402**, 169.
15. Oprea S.: *Polym. Degrad. Stab.* 2002, **75**, 9.
16. Chang T. C., Chiu Y. S., Chen H. B., Ho S. Y.: *Polym. Degrad. Stab.* 1995, **47**, 375.
17. Świerz-Motysia B., Pielichowski K.: *Polimery* 2005, **50**, 601.
18. Coats A. W., Redfern J. P.: *Nature* 1964, **201**, 68.
19. Reich L., Levi D. W.: *Macromol. Chem.* 1963, **66**, 102; *Polymer Letters* 1964, **2**, 621.
20. Bogart J. W. C., Bluemke D. A., Cooper S. L.: *Polymer* 1981, **22**, 1428.
21. Ryan A. J., Macosko C. W., Bras W.: *Macromolecules* 1992, **25**, 6277.

Received 27 XII 2007.