New thermoplastic polyurethane elastomers based on sulfur-containing chain extenders

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New thermoplastic polyurethane elastomers (TPUs) were synthesized by a one-step melt polyaddition from poly(oxytetramethylene) diol of $\overline{M}_n$ = 2000 g/mol as the soft segment, 1,1'-methanediylbis(4-isocyanatocyclohexane) (HMDI, Desmodur $W^{®}$), and 2,2'-[methanediylbis(benzene-4,1-diylmethanediylsulfanediyl)]diethanol (diol E) or 6,6'-[methanediylbis(benzene-4,1-diylmethanediylsulfanediyl)]dihexane-1-ol (diol H) as unconventional chain extenders. The effects of the kind and amount of the polymer diol and chain extender used on the structure and properties of the polymers were studied. The polymers were examined by Fourier transform infrared spectroscopy, gel permeation chromatography, thermogravimetric analysis, differential scanning calorimetry, Shore hardness and tensile testing. Both the adhesive and optical properties were determinated for a selected polymer. The obtained TPUs were amorphous, colorless, high-molar-mass materials. It was observed that the polymers with the diol E showed higher hardness and tensile strengths but smaller elongations at break than diol H-based ones. All of the polymers exhibited a relatively good thermal stability. Their temperatures of 5% mass loss were in the range 312–338°C.

Keywords: sulfur-containing thermoplastic elastomers, amorphous polymers, polyether soft segments, melt polyaddition, thermal and mechanical properties, adhesion to copper, optical properties.

INTRODUCTION

Thermoplastic polyurethane elastomers (TPUs) are an important class of thermoplastic elastomers with wide applications as coatings, binder resins, fibers and high-performance elastomeric products. Typical TPUs are multiblock copolymers comprised of alternating flexible "soft" segments derived from aliphatic polyether or polyester diols and "hard" segments formed from diisocyanates and short-chain diols. The thermodynamic incompatibility of these segments, often combined with crystallization of either or both segments, drives their microphase separation into hard and soft phases that are respectively below and above their glass transition temperatures. This microphase separation is responsible for the excellent elastomeric properties of these polymers[1–4]. TPUs with excellent tensile strength are usually prepared from aromatic diisocyanates, mostly 1,1'-methanediylbis(4-isocyanatobenzene) (MDI)[1–4],polyether, polyester or polycarbonate diols, and short aliphatic diols as chain extenders, mostly butane-1,4-diol. Aromatic diisocyanate-based TPUs generally bear superior mechanical properties due to a strong cohesion force between the hard segment chains. However, the aromatic diisocyanate-based TPUs possess serious defects such as change of color, decrease in thermal and mechanical properties against ultraviolet and visible light and heat[3–5]. In contrast, the aliphatic diisocyanate-based TPUs do not show the change of color under the same condition[4]. TPUs with polyether soft segments and aliphatic diisocyanates are characterized by better low-temperature properties and hydrolytic resistance than TPUs with polyester soft segments and aromatic diisocyanates[4].

In this work, we present the synthesis and characterization of 1,1'-methanediylbis(4-isocyanatocyclohexane) (HMDI, *Desmodur W*®)-based TPUs with polyether soft segments (poly(oxytetramethylene) diol of $\overline{M}_n$ = 2000 g/mol) and unconventional chain extenders *i.e.* 2,2'-[methanediylbis(benzene-4,1-diylmethanediylsulfanediyl)]diethanol (diol E) or 6,6'-[methanediylbis(benzene-4,1-diylmethanediylsulfanediyl)]dihexane-1-ol (diol H). TPUs were synthesized with 30–60 wt% hard segments. Because the newly obtained TPUs incorporate sulfur atoms in their structure, they can exhibit improved antibacterial activity, optical and adhesive properties[7–9].This paper, additionally, discusses the influence of sulfur atoms in polymer on the refractive index, transparency and adhesive properties in comparison with conventional TPU based on HMDI, PTMO and butane-1,4-diol. Moreover, herein we include a characterization of the newly obtained nonsegmented polyurethanes (NPTUs) based on diol E or H and HMDI, building the hard segment in these TPUs.

In our previous papers[10–13] we described the synthesis and basic properties (physicochemical, thermal and mechanical) of several series of segmented polyurethanes (including TPUs) derived from the above mentioned chain extenders (diol E and diol H), 1,6-diisocynatohexane (HDI) or MDI and PTMO of $\overline{M}_n$ = 1000 g/mol or poly(hexane-1,6-diyl carbonate) diols (PHCDs) of $\overline{M}_n$ = 860 or 2000 g/mol. The content of hard segments was contained within 30–70 wt.%.

The PHCDs yielded polymers with a significantly higher tensile strength than PTMO (up to 59.6 MPa vs. up to 36.5 MPa). Unfortunately, the PHCD-based polymers, exhibited higher glass transition (T_g), less advantageous for elastomers. In the case of each of the oligomer diols used, polymers from MDI showed a higher tensile strength, a lower degree of microphase separation (a higher T_g) and a smaller tendency of the hard-segments to form ordering structures. In most cases, polymers from diol H showed a higher tensile strength, elongation at break and lower T_g than their anlogs from diol E. All the polymers showed relatively good thermal stability, while in the case of HDI derivatives it was somewhat better.

EXPERIMENTAL

Materials

The diols E (mp = 77–78°C) and H (mp = 67–68°C) were obtained by the condensation reaction of (methanediyldibenzene-4,1-diyl)dimethanethiol with 2-chloroethanol and 6-chlorohexan-1-ol in 10% aqueous solution of sodium hydroxide, respectively.[14] PTMO of $\overline{M}_n$ = 2000 g/mol were purchased from Sigma-Aldrich (St. Louis, USA). Before being used, the PTMO were heated at 90°C *in vacuo* for 10 h. HMDI (*Desmodur W®*) kindly supplied by Bayer (Leverkusen, Germany). Dibutyltin dilaurate (DBTDL) from MerckSchuchardt (Hohenbrunn, Germany) was used as received. The polymerization solvent, *N,N*-dimethylformamide (DMF), with a water content of less than 0.01%, was purchased from Sigma-Aldrich (Steinheim, Germany) and was used as received.

Measurements

Elemental analysis was performed with a Perkin-Elmer CHN 2400 analyzer (Norwalk, USA). Reduced viscosities (η_{red}'s; dL/g) of 0.5% polymer solution in 1,1,2,2-tetra-chloroethane (TChE) were measured in an Ubbelohde viscometer (Gliwice, Poland) at 25°C. Number ($\overline{M}_n$) and mass ($\overline{M}_w$) average molar-mass, and the molar-mass dispersity ($Đ_M$, $Đ_M = \overline{M}_w/\overline{M}_n$) of the polymers were determined by gel permeation chromatography (GPC) performed on a Viscotek GPCMax (USA) equipped with Triple Detector Array TDA305. The eluent was tetra-hydrofurane, the flow rate was 1mL/min, the operation temperature was set at 35°C, and the molar-mass was calibrated with polystyrene standards. Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra were obtained with a FTIR TENSOR 27 (Bruker) spectrophotometer using thin films. Spectra were recorded from 4000 to 600 cm^{-1} averaging 32 scans with a resolution of 4 cm^{-1}. The thermogravimetric analysis (TGA) was performed on a MOM 3427 derivatograph (Paulik, Paulik and Erdey, Budapest, Hungary) at the heating rate of 10°C/min in air; Al_2O_3 was used as a standard substance. Differential scanning calorimetry (DSC) thermograms were obtained with a Netzsch 204 calorimeter (Günzburg, Germany) in the range of –100 to 200°C. The reported transitions were taken from the first and second heating scans. The scans were performed at the heating/cooling rate of 10°C/min under nitrogen atmosphere (flow = 30 cm^3/min). Sample weights about 10 mg were used. Glass-transition temperatures (T_gs) for the polymer samples were taken as the inflection point on the curves of the heatcapacity changes. The hardness of the TPUs was measured by the Shore A/D method on a Zwick 7206/H04 hardness tester (Germany) at 23°C. The values were taken after 15 s. Tensile testing was performed on a Zwick/Roell Z010 tensile-testing machine according to Polish Standard PN-81/C-89034 at the speed of 100 mm/min at 23°C; the tensile test pieces 1 mm thick and 6 mm wide (for the section measured) were cut from the pressed sheet. Molding was done with a Carver hydraulic press at 50–110°C under the pressure of about 10–30 MPa. The single lap-shear strength of the polymers to copper plate, 100 mm x 25 mm x 1.5 mm,

was measured in accordance with Polish Standard PNEN 1465:2009 by using a Zwick/Roell Z010 (Germany). The adhesive joint, 12.5 mm x 25 mm x 0.2 mm, was prepared by pressing the polymer between the ends of two copper plates (prepared according to PN-EN-13887:2005), and then leaving them under the pressure of 30 MPa to cool to room temperature. Next, plates were fixed by tensile-testing machine clips and underwent tensile testing at 2 mm/min speed at 23°C. Refractive index was measured at 23°C by using an Conbest Abbe's Refractometer Type 325 instrument according to method A of European Standard EN ISO 489:1999. 1-Bromon-aphtalene was applied between the sample film and the prism shield. The ultraviolet-visible (UV-VIS) spectra of the compression-molded sheetes of the selected polymer were determined by a UV-2550 (Shimadzu, Kioto, Japonia) UV spectrophotometer at a scanning rate of 200 nm/min in the range of 200–900 nm.

Polymer synthesis

NPURs

NPURs was prepared by the solution polymerization of an equimolar amount (0.01 mol) of diol E or diol H and HMDI (DMF, concentration ~ 20 wt.%); this was carried out under dry nitrogen for 4 h at 85°C in the presence of a catalytic amount of DBTDL. The polymer precipitated and then washed with distilled water was dried at 100°C *in vacuo*.

FTIR (cm^{-1}) of the NPURs: 1697–1694 (C=O stretching), 1509–1507 (N–H bending) and 3328–3327 (NH stretching) of the urethane group; 2921–2919 and 2851–2849 (asymmetric and symmetric C–H stretching of CH_2, respectively); 1448–1447 (C–H bending of cyclohexane ring); 976 (C–C asymmetric cyclohexane ring stretching); 776–772 (cyclohexane ring breathing); 3022 (C–H stretching of benzene ring); 815 (C–H bending of *p*-disubstituted benzene ring).

Elemental analysis

NPUR from diol E: Calcd for $C_{34}H_{46}N_2O_4S_2$: C, 66.85%; H, 7.47%; N, 4.58%. Found: C, 66.59%; H, 7.38%; N, 4.79%.

NPUR from diol H: Calcd for $C_{42}H_{62}N_2O_4S_2$: C, 69.76%; H, 8.57%; N, 3.87%. Found: C, 69.67%; H, 8.41%; N, 4.15%.

TPU

TPUs with hard-segment contents of ~30, 40, 50 and 60 wt.% were prepared, according to Scheme 1, by a one-step melt polyaddition process from HMDI, diol E or diol H and PTMO, at the NCO/OH molar ratio of 1.05. The general procedure for the synthesis of TPUs by this method was as follows. PTMO and diol E or diol H (0.01 mol together) and HMDI (0.0105 mol) were heated with stirring under dry nitrogen to 90°C in an oil bath. A catalytic amount of DBTDL (about 0.03 g) was added to the formed clear melt and polymerization rapidly began at vigorous stirring. The reaction temperature was gradually raised to 130°C and the formed colorless rubber-like product was additionally heated at this temperature for 2 h.
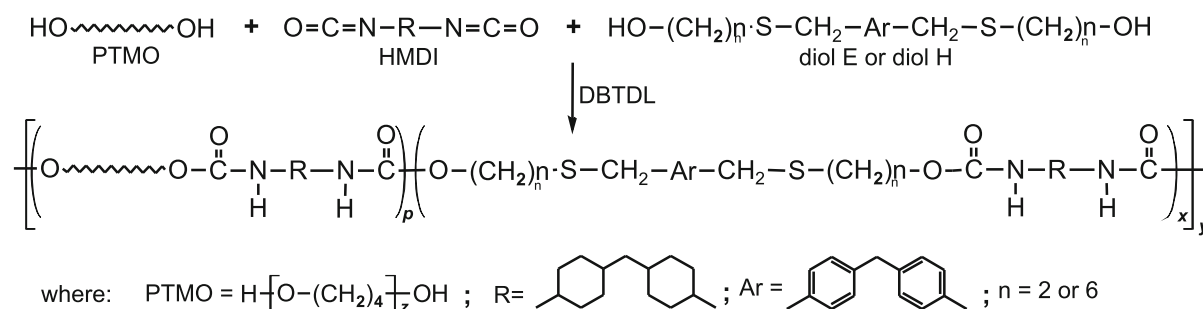
Scheme 1. Synthesis of TPUs.

FTIR (cm^{-1}) of the polymers: 1718–1715 and 1701–1683 (nonbonded and H-bonded C=O stretching of the urethane group, respectively); 3334–3324 (N–H stretching) and 1507–1506 (N–H bending) of the urethane group; 1105–1099 (C–O stretching of the ether group); 2928–2919 and 2853–2850 (asymmetric and symmetric C–H stretching of CH$_2$, respectively); 1448–1447 (C–H bending of cyclohexane ring); 981–973 (C–C asymmetric ring stretching (cyclohexane)); 778–776 (cyclohexane ring breathing); 816 (C–H bending of *p*-disubstituted benzene ring).

RESULTS AND DISCUSSION

Polymer characterization

The new TPUs were colorless, mostly transparent solids. They were soluble in *N*-methyl-2-pyrrolidone, *N,N*-dimethylacetamide and DMF at room or higher temperature, soluble or partially soluble in TChE and tetrahydrofurane and insoluble in dimethyl sulfoxide. The designations, η_{red} values and GPC data of the TPUs and NPURs are listed in Table 1. As can be seen in Table 1, the η_{red} values (in the range of 1.45–3.94 dL/g) determined for polymers soluble in TChE, suggest their high molar mass. It was veryfied by GPC measurements. The increased hard segment content resulted in decreased $\overline{M}_n$ (just as η_{red}'s) for the TPUs soluble in THF. These polymers exhibited relatively low molar-mass dispersity included in the range of 1.21–1.38, however for NPURs these values are several times higher.

The chemical structures of the polymers were examined by elemental analysis (only for NPURs) and FTIR spectroscopy. All the spectra exhibited significant absorptions of the urethane group, cyclohexane ring and methylene group. Moreover, in the TPUs spectra there is also a significant absorption of the ether group. The

appearance of absorptions peaks of the carbonyl bands of urethane groups at the low frequency in the range of 1701–1683 cm^{-1} indicates forming a physical network both in NPURs and TPUs. Figure 1 presents the typical FTIR spectra of TPUs (E40 and H40) and NPURs.

Thermal properties

The thermal behavior for all of the synthesized polymers was investigated by means of DSC and TGA, and the numerical data are shown in Table 2. The DSC curves of the NPURs and selected TPUs are presented in Figure 2.
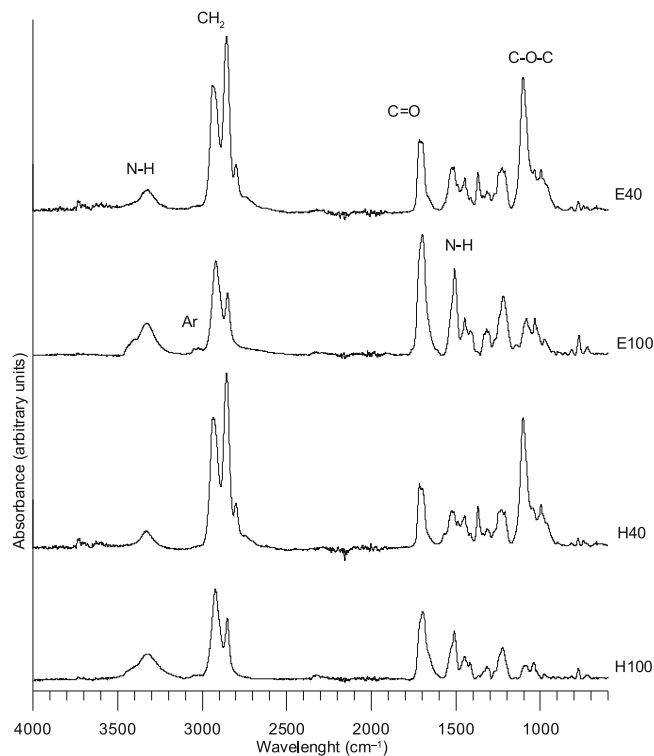

Figure 1. ATR-FTIR spectra of the NPURs and selected TPUs (E40 and H40)

Table 1. Designations, η_{red} values and GPC[b] data of the TPUs and NPURs

Polymer	Chain extender	Hard-segment content (wt.%)	η_{red} (dL/g)	GPC[b] data (g/mol)		
				$\overline{M}_n$	$\overline{M}_w$	$Đ_M$
E30	diol E	30.1	0.57[a]	–	–	–
E40		40.3	0.54[a]	–	–	–
E50		50.0	1.50[a]	–	–	–
E60		59.9	0.44[a]	–	–	–
E100		100	0.34	12662	80544	6.36
H30	diol H	29.9	3.94	190496	230274	1.21
H40		39.8	2.02	161997	224286	1.38
H50		49.9	1.45	28823	35091	1.22
H60		59.9	1.01[a]	–	–	–
H100		100	0.48	21490	65143	3.03

[a] η_{red} values of the soluble fraction.
[b] GPC measurements were performed for the polymers soluble in THF.

Table 2. DSC and TGA data of the polymers

Polymer	T_g (°C)		TGA data (°C)			
	I[a]	II[a]	T_5[b]	T_{10}[c]	T_{50}[d]	T_{max}[e]
E30	−75	−72	338	358	408	412; 550
E40	−71	−66	330	352	402	405; 558
E50	−37	−35	322	345	410	413; 582
E60	46	45	312	345	408	415; 578
E100	73	75	308	332	390	370; 470; 585
H30	−68	−71	335	358	405	410; 552
H40	−68	−69	330	353	405	410; 578
H50	−33	−35	330	350	405	410; 590
H60	−1	−1	328	343	402	410; 570
H100	48	42	322	337	390	375; 445; 600

[a] I and II – first and second heating scans, respectively.
[b,c,d] The temperature of 5%, 10% and 50% mass loss from the TG curve, respectively.
[e] The temperature of the maximum rate of mass loss from the DTG curve.
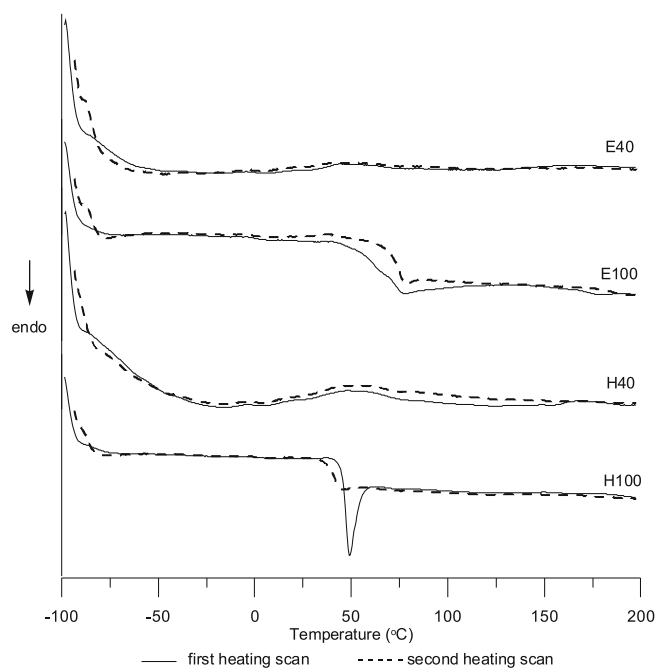
Figure 2. DSC curves of NPURs and selected TPUs (E40 and H40)

TGA

The decomposition of the NPURs was a three-stage process, whereas the decomposition of the TPUs occurred in two stages. The DTG curve of the NPURs showed, in turn: sharp and high peak with maximum at 370–375°C, which may be ascribed to the decomposition of the sulfide and urethane bonds, second, smaller peak with maximum at 445–470°C associated with the aromatic content in the polymer and third, small and broad peak with maximum at 585–600°C connected with the oxidation of the char formed in the previous stages[11]. In the case of the TPUs in the region 370–470°C only one high but broader peak may be observed with the maximum at 405–415°C connected with decomposition of both ether bonds from PTMO and the hard segments[15]. The second stage of decomposition of TPUs (small and broad peak at 550–590°C) relates to the third stage of decomposition of NPURs. All the synthesized TPUs exhibited a relatively good thermal stability. Their 5% and 10% mass loss took place in the temperature range of 308–338°C and 332–358°C, respectively. The increase of the hard-segment content in the polymers caused some reduction in T_5 and T_{10}.

DSC

The DSC curves of the all polymers (both NPURs and TPUs) exhibited only a glass transition; this pointed to the amorphous structure of these polymers. In the case of NPUR from diol H (see Fig. 2), the first heating scan shows a significant relaxation peak superimposed on the glass transition. However, the second heating scan of this NPUR exhibits the glass transition in a normal shape. This endothermic peak resulted from the relaxation of the enthalpy occurring during the storage of amorphous polymesr in a temperature not much lower than the temperature of the glass-transition region. From a comparison of the values of the T_g of PTMO (−79°C)[15] and those of the obtained segmented polymers (−75 to 46°C), it appeared that in both series an increase in the hard-segment content causes an increase in T_g, indicating deterioration of the degree of microphase separation. The polymer with hard-segment content of 60 wt.% and based on diol E (E60) indicates the T_g value over room temperature characteristics for plastomers, thus we cannot ranking it as TPUs. Generally, the somewhat better degree of microphase separation was exibited by TPUs based on diol E than the analogous diol H-based ones.

Mechanical properties

The Shore A/D hardness and tensile properties were determined for all of the segmented polymers (TPUs and E60), and the results are shown in Table 3 and Figures 3 and 4. These polymers showed tensile strength in the range of 2.6–17.0 MPa and elongation at break in the range of 325–1200%. Analyses of the hardness and tensile test results indicate that in both series increased hard segment content resulted in increased hardness, modulus of elasticity and tensile strength, whereas elongation
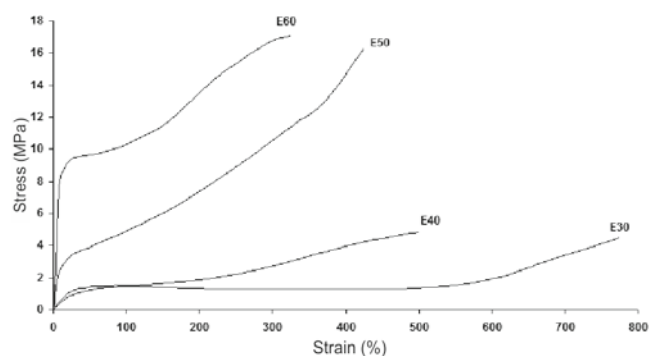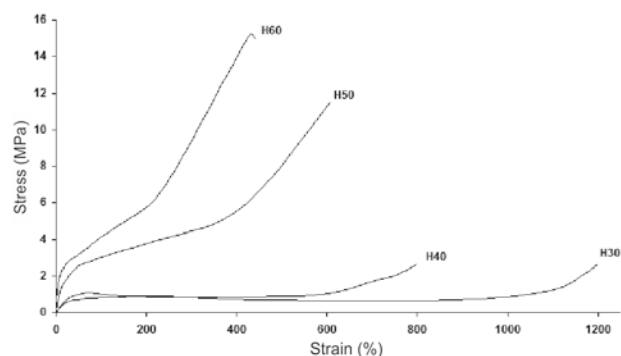

Figure 3. Stress-strain curves of the polymers obtained from diol E

Table 3. Mechanical properties of the polymers

Polymer	Hardness (Shore A/D)	Tensile strength (MPa)	Elongation at break [%]	Modulus of elasticity [MPa]
E30	49/12	4.49 ± 0.67	775 ± 14.4	2.14 ± 0.12
E40	54/15	4.83 ± 0.45	500 ± 14.4	4.88 ± 0.46
E50	68/21	16.30 ± 0.56	425 ± 0	14.10 ± 1.30
E60	91/34	17.00 ± 0.78	325 ± 28.9	47.17 ± 4.10
H30	39/–	2.62 ± 0.69	1200 ± 28.9	1.25 ± 0.03
H40	39/–	2.65 ± 0.56	800 ± 14.4	1.70 ± 0.09
H50	37/–	11.50 ± 0.23	800 ± 28.9	1.62 ± 0.12
H60	55/15	15.20 ± 0.13	450 ± 14.4	2.80 ± 0.17

**Figure 4.** Stress-strain curves of the TPUs obtained from diol H

at break increased. As it can be seen from the data in Table 3, the polymers based on diol E showed much higher hardness, tensile strength, modulus of elasticity but smaller elongation at break.

Adhesive and optical properties

The influence of sulfur-containing chain extender on the above mentioned properties of TPUs was investigated by comparing the lap shear strengths to copper (adhesion), refractive index and transparency between the newly synthesized TPU E50 (T_g, = –37°C) and its analog obtained from butane-1,4-diol as a chain extender and containing the same of hard segment content, B50 (T_g, = –68°C)[16]. As it can be seen from the data in Table 4 polymer with sulfur atoms caused increased adhesion to copper and refractive index in comparison to B50 (up to 2.97 vs. 2.41 and 1.5255 vs. 1.4910, respectively). However, B50 exhibits somewhat better transparency (up to 87.9% vs. 86.5%) than E50. Considering T_g values as miscibility criterion one may suppose that not the miscibility between the soft segment and the hard segment but rather the difference in their refractive indices plays the decisive role in determining the transparency of the compared polymers[17].

CONCLUSIONS

One step catalyzed melt polyaddition of HMDI, PTMO of $\overline{M}_n$ = 2000 and sufur-containing diols (diol E or H) used as unconvetional chain extenders give high-molar-mass amorphous segmented polyurethanes. Two series of polymers with various hard segment contents (30–60 wt%) were obtained. Apart from polymer E60 (from
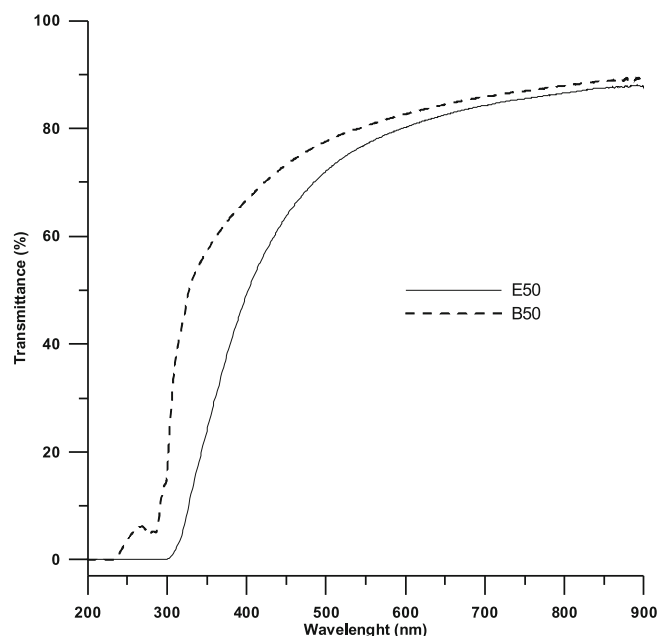
Figure 5. UV-VIS spectra of the E50 and B50

diol E and with 60 wt.% hard segments, T_g = 46°C) the remaining were TPUs. The T_g values of TPUs were contained within (–75 to –1°C) range. These polymers showed tensile strength in the range of 2.6–16.3 MPa and elongation at break in the range of 425–1200%. It was found that the TPUs properties depended largely on the molar ratio of chain extender to PTMO and less on the kind of the used extender. In both series, the increased hard-segment content resulted in increased T_g, hardness, modulus of elasticity and tensile strength, whereas elongation at break decreased. The polymers based on diol E compared with those based on diol H showed much higher hardness, tensile strength, modulus of elasticity but smaller elongation at break. Generally, the slightly better degree of microphase separation was exibited by TPUs based on diol E than the analogous diol H-based ones. All the synthesized TPUs exhibited a relatively good thermal stability. The increase of hard-segment content in the polymers caused some reduction in T_5 and T_{10}. The study of adhesive and optical properties for selected TPU E50 showed its enhanced copper adhesion (2.97 MPa vs. 2.41 MPa), increased the refractive index (1.5255 vs. 1.4910) but somewhat worse transparency

Table 4. Adhesion, refractive index and transparency of the E50 and B50[a]

Polymer	Lap-shear strength (MPa)	Refractive index	Transparency	
			T_{500}[b]	T_{800}[c]
E50	2.97 ± 0.20	1.5255 ± 0.07	72.1	86.5
B50	2.41 ± 0.17	1.4910 ± 0.02	77.6	87.9

[a] polymer based on HMDI, PTMO and butane-1,4-diol.
[b,c] Transmittance data at 500 and 800 nm, respectively.

(86.5% vs. 87.9% at 800 nm) close to conventional TPU based on butane-1,4-diol as chain extender.

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