Thermoplastic Polyurethane Elastomers— Thermostability in Relation to Composition

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Synopsis

The dependence of thermal stability of poly(ester–urethane) elastomers on their composition was investigated. For polyurethanes of hard segment content above 30%, hydroquinone di(β-hydroxyethyl) ether (HQEE) is the choice for good thermomechanical stability while the stability of bisphenol-A-based polymers is rather poor. The temperature sensitivity of modulus was essential in the range of −30–24°C, while in the range of 24–70°C it is moderate. The modulus in the low temperature region depends on the nature of polyesterdiol. Its drop with temperature is lower for poly(hexamethylene carbonate) glycol (PHC)-based polyurethanes than poly(ethylene–adipate) glycol (PEAd)-based ones. In the high temperature region it also depends on the nature and amount of hard segments. The thermal stability of 4,4′-dicyclohexylmethane diisocyanate (SMDI)-based polyurethanes is inferior to the one for 4,4′-diphenylmethanediisocyanate (MDI)-derived polymers.

INTRODUCTION

The thermal stability of polyurethanes depends on the chemical composition of the materials used in polyurethane formulations. It is true not only for the thermal stability in the physical meaning of the term, i.e., the stability that is reflected in such reversible transitions as melting or softening, but also in the chemical stability that is connected with the dissociation of urethane linkages which takes place in the range of 200–250°C. To a certain degree the nature of the soft segment (ether or ester groups) also effects the chemical stability of these polymers.

The melting point of linear polyurethanes can in some cases exceed 200°C. It depends not only on the nature and molar ratios of the components, but also on the way in which the synthesis is carried out since the existence and magnitude of microcrystalline domains formed by hard segments is influenced by the synthesis conditions.[2,3] The degree of crystallinity of polyurethanes and the melting point thereof are also determined by the processing parameters, e.g., the higher the processing temperature is, the lower the ultimate properties.[3,4]

In this work, however, the attention is focused mainly on the chemical composition and on how the composition effects the ultimate properties and thermal stability.

EXPERIMENTAL

Materials. The materials used in this study are listed in Table I. Hydroxy-terminated polyesters were dried at 100–110°C under vacuum of about

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TABLE I
Materials Used in Polyurethane Formulations

Material	Designation	Chemical formula	Molar mass $(g \cdot mol^{-1})$	Supplier
Polyesterdiols				
Poles 60/20	PEAd	$HO{-}[(CH_2)_2{-}O{-}\overset{O}{C}{-}(CH_2)_4{-}\overset{O}{C}{-}O]_n{-}H$	2140	ZaChem, Poland
Desmophen 2020	PHC	$HO{-}[(CH_2)_6{-}O{-}\overset{O}{C}{-}O]_n{-}H$	2000	Bayer
Diisocyanates				
Desmodur 44MS	MDI	$OCN{-}C_6H_4{-}CH_2{-}C_6H_4{-}NCO$	250	Bayer
Hylene W	SMDI	$OCN{-}C_6H_{10}{-}CH_2{-}C_6H_{10}{-}NCO$	262.3	DuPont
Chain extenders				
1,4-butanediol	1,4-BD	$HO{-}(CH_2)_4{-}OH$	90.1	BASF
Hydroquinone di(β-hydroxyethyl)ether	HQEE	$HO{-}(CH_2)_2{-}O{-}C_6H_4{-}O{-}(CH_2)_2{-}OH$	198	Bayer
2,2-bis(4-Hydroxyphenyl)propane	Bisphenol A	$HO{-}C_6H_4{-}\underset{CH_3}{\overset{CH_3}{C}}{-}C_6H_4{-}OH$	228.3	Merck-Schuchardt
Catalyst				
Stannous heptanocarboxylate-3	Stannous octoate	$Sn[O{-}CO{-}CH(C_2H_5)(C_4H_9)]_2$		Akzo Chemie

0.6 kPa for 3 h. Butanediol was dried by azeotropic distillation with benzene.

Synthesis. All syntheses were carried out by the one-step method. The temperatures of the starting materials were 125°C for the diol mixtures and 65°C for MDI, and the catalyst concentration was kept at 0.01–0.05% (by weight). The polyurethanes obtained in this way are denoted as PUT.

In the case of bisphenol A as a chain extender the temperature of the diol mixture was 150°C. The volatility of SMDI made it necessary to keep the temperature of diols and diisocyanate at 85°C. It was also necessary to increase the catalyst concentration up to 0.05%.

To complete these reactions, the obtained polymers were heated at 100°C for 14 h. Only in the case of SMDI-based polyurethanes did reaction occur by heating for 1 h at 85°C.

The ratio of isocyanate to hydroxyl groups was kept as 1.1:1.0 in all these preparations.

Measurements. The samples for the thermomechanical and tensile strength measurement were injection-molded (Monomat 80, F0200/80 machine). The tensile strength measurements at room temperature were obtained with the ZE400 (VEB Thuringer Ind.) Dynamometer with the crosshead speed of 0.83 cm/s. For the temperature dependence of the strength of the investigated polyurethanes an Instron instrument was used and the data were taken at -30°C, 24°C, and 70°C with the crosshead speed of 0.33 cm/s.

Differential thermal analysis (DTA) and thermogravimetry (TGA) data were obtained by means of a Derivatograph 0D104 MOM, Budapest, apparatus on nonprocesed sample. The heating rate was 12 deg/min for DTA and 6 deg/min for TGA.

Thermomechanical analysis was carried out in tension with a TMA-Politechnika Lodz analyzer. The samples of dimensions $1 \times 10 \times 25$ mm were loaded with a force of 1 N and the heating rates were 2.5 deg/min.

The softening temperature was determined on a Vicat's Analyzer according to the Polish Standard 69/C-89024.

RESULTS AND DISCUSSION

At room temperature the stress at 100% elongation (σ_{100}) is greater for polyurethanes with higher hard segment concentration and depends on the nature of chain extenders and diisocyanates (Table II).

From among the polyurethanes of hardness of 85–90°Sh the highest value of σ_{100} is noticed for PUT V (HQEE extended), although the hard segment content is, in this case, lower than for 1,4-BD or bisphenol A extended polymers (PUT's III and IV). The results for PUT's VII and VIII indicate, however, that at lower segment concentration the beneficial effect of HQEE is not evident.

The SMDI-based elastomer of the highest hard segment content (PUT VI) shows lower values of σ_{100} and ϵ_r in relation to PUT derived from MDI (PUT III).

The stress–strain relations taken from the Instron dynamometer (Fig. 1 and Table III) indicate that σ_{100} in the temperature range of 24–70°C is less sensitive to temperature than in the range of -30°C–24°C. The ratio of σ_{100} at -30°C to σ_{100} at 70°C that can be taken as a measure of thermomechanical stability of

TABLE II
Composition and Properties of the Investigated Polyurethanes at Room Temperature (Crosshead Speed 0.83 cm/s)

PUT	Materials	Catalyst content (%)	Hard segment (%)[a]	Hardness (°Sh A)	σ_{100} (MPa)	σ_r[c] (MPa)	E_r[c] (%)
I	PEAd, MDI, 1,4-BD	0.01	36.9	85	7.1	35.5	650
II	PEAd, MDI, 1,4-BD	—	36.9	85	8.3	36.9	580
III	PHC, MDI, 1,4-BD	—	37.9	90	13.7	41.5	420
IV	PHC, MDI, bisphenol A	0.02	34.6	90–80[b]	9.2	35.2	310
V	PHC, MDI, HQEE	0.01	33.6	86	14.1	40	390
VI	PHC, SMDI, 1,4-BD	0.05	38.7	94	13.3	39	440
VII	PEAd, MDI, 1,4-BD	0.01	31	76	4.8	42	660
VIII	PEAd, MDI, HQEE	0.01	26.8	76	4.4	28	650

[a] Weight percent of diisocyanate with chain extender in polyurethane formulations.
[b] Stable values are not accessible with this sample.
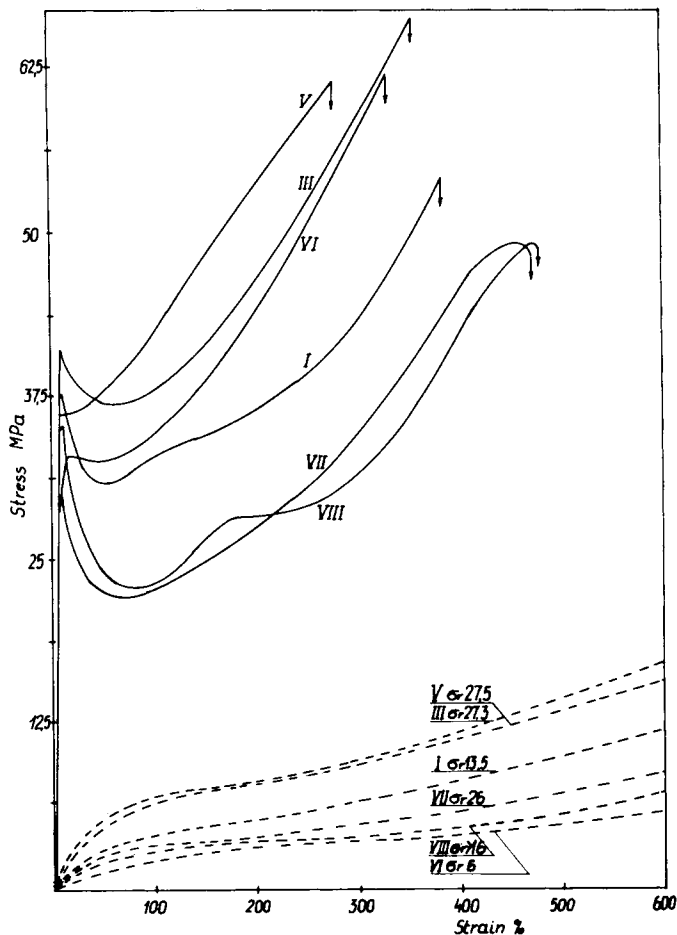[c] σ_r = tensile strength; E_r = relative elongation at break.

Fig. 1. Stress–strain relations for investigated polyurethanes at −30°C (——) and at +70°C (- - -).

polyurethanes[5] is the highest (the least beneficial) for polyurethanes obtained from SMDI. In the case of MDI-based elastomers, the ratio is better for PHC than for PEAd polymers. It must be added, however, that σ_{100} for the latter polymers in the range of 24–70°C shows a little smaller change.

For polyurethanes of similar hard segment concentration obtained in similar conditions the decrease in mechanical properties in the low temperature region is determined by the nature and regularity of the structure of polyesterdiols, i.e., by the glass transition of the soft phase.

The stress–strain curves for the polyurethanes investigated at −30°C exhibit the characteristic yield point typical of plastics. On the other hand, the stress–strain curves taken at 24°C or 70°C show transitions typical of elastic properties.[6]

The HQEE extended polyurethan (PUT V) exhibits the higher σ_r and the lowest ϵ_r value at −30°C and the maximum value of σ_r and ϵ_r at 70°C when compared with other polymers based on MDI or SMDI of greater hard segment concentration.

TABLE III
Effect of Composition Investigated Polyurethanes on σ_{100} at Various Temperatures

PUT		I	III	V	VI	VII	VIII
Polydiols, hard segment content		PE Ad MDI–BD 36.9	PHC MDI–BD 37.9	PHC MDI–HQEE 33.6	PHC SMDI–BD 38.7	PE Ad MDI–BD 31	PE Ad MDI–HQEE 26.8
σ_{100}	(MPa)						
Temp	−30°C	33.5	38.8	39.8	36	23.5	24
	24°C	5.5	9.9	10.5	9.5	3.8	3.6
	70°C	4.1	7.0	6.7	2.5	3.4	2.8
$\sigma_{100-30°C}/\sigma_{100 24°C}$		6.1	3.9	3.8	3.8	6.1	6.6
$\sigma_{100 24°C}/\sigma_{100 70°C}$		1.3	1.4	1.5	3.8	1.1	1.3
$\sigma_{100-30°C}/\sigma_{100 70°C}$		8.1	5.5	5.9	14.4	6.9	8.5

At 24°C there were no remarkable differences between PUT III, V, VI as far as the tensile strength was concerned. Application of SMDI is not recommended as far as stability of mechanical properties at elevated temperature is concerned based on data collected at 70°C. PEAd based polyurethanes of lower hard segment concentration exhibit higher σ_r values when 1,4-BD was used as a chain extender: HQEE-extended polyurethanes are of lower strength (Fig. 1, PUT's VII, VIII).

From DTA measurements, the melting point of hard segments strongly depends on the nature of diisocyanate and chain extender and on their concentration in the reaction mixture (Table IV).

The lowest softening point (TMA) exists for PUT extended with bisphenol A (PUT IV). At room temperature, its properties are leatherlike and at temperatures about 80°C the elongation is rapidly increased. This is due to the chain extender structure. The methyl groups in bisphenol A provide steric hindrance and, as a consequence, do not allow for ordering of the hard segments and for an increase in molecular interactions.

The best thermomechanical stability is observed for HQEE extended elastomers (Fig. 2). An increase in elongation with temperature for this polymer occurs in temperature as high as 70°C, while the increase reflecting the region of flow of viscoelasticity occurs at 170°C. For comparison, 1,4-BD extended PUT's (I, II, III; Fig. 2, Table IV) show the region of flow in temperatures about 145–154. However, the beneficial effect of HQEE on the thermomechanical stability is not observed if the hard segment concentration is lower than 30% (Table IV; PUT's VII, VIII).

PUT derived from SMDI shows a lower softening point in comparison with MDI-based polymers (shown with both TMA and Vicat's measurements (Table IV; Fig. 2)). The cyclohexane ring in the structure of the diisocyanate is responsible for the increased mobility within the hard segments leading to easier deformability of the polymers. SMDI has three isomers,[9] does not crystalize, and the polymers formed from this diisocyanate are of low modulus and softening temperature. Polymers based on SMDI show the greatest elongation at 70°C. Thus, the thermomechanical stability of the SMDI based polyurethanes is lower than MDI-derived elastomers.

TABLE IV
Temperature Transitions in Investigated Polyurethanes[a]

Technique	PUT							
	I	II	III	IV	V	VI	VII	VIII
DTA (°C) up to 300°C	50 (T'_m)	75 (T_g)	54 (T'_m)	43 (T'_m)	95 (T_g)	50 (T'_m)	50 (T'_m)	85 (T_g)
	74 (T_g)	162	157	57	170	125	91 (T_g)	148
	166	208 (T''_m)	226 (T''_m)	153	228 (T''_m)	160	140	205 (T''_m)
	218 (T''_m)			208 (T''_m)		210 (T''_m)	220 (T''_m)	
TMA (°C) $\sigma = 0.1$ MPa	72	98	65	57	150	66	76	66
	145	149	154	79	170	115	137	102
				108		138		
Vicat's softening temp (°C)	134	115	162	40	153	62	120	100

[a] For DTA data T'_m stands for the melting point of crystalline phase within the soft segment matrix; T''_m corresponds to the melting of crystalline hard segment phase; T_g is the glass transition of the hard segment phase while the unspecified transitions most probably are due to disruption of lower levels of order. The above-given assignment of the transitions is according to Seefried et al.[7] and Redman.[8] The samples investigated by TMA and Vicat's methods were processed prior to the measurements so the data do not correspond to the DTA data.
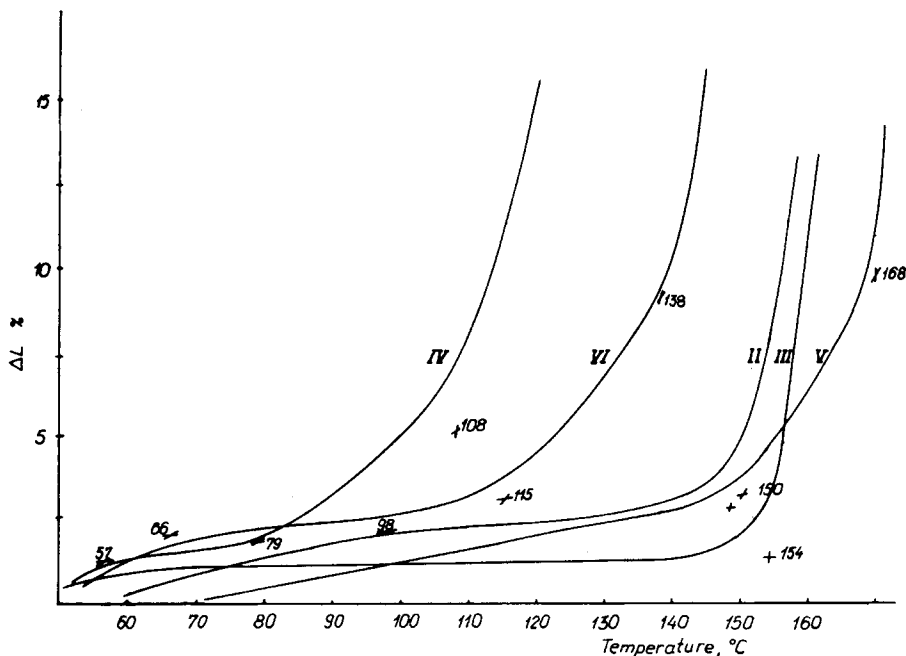
Fig. 2. Thermomechanical curves for the investigated polyurethanes (load 0.1 MPa).

Injection molding of PUT VI requires higher temperatures (170–185°C, screw speed 80–100 rpm) than PUT III (155–170°C, screw speed 140 rpm). The samples for TMA molded in this way are transparent in the case of PUT VI while PUT III samples exhibit a milky appearance, indicating the presence of pseudocrystalline ordering that is responsible for the observed good thermomechanical stability of the polyurethane in question. In addition to PUT III, HQEE-extended polymers (PUT V) show, to an extent, the presence of crystalline phase which can be noticed even on samples that were processed twice (165–180°C, screw speed 80–100 rpm) before measurements.

The catalyzed reactions favor formation of longer hard segments that are more stable. Thus, the presence of the catalysts results in an elevation of the softening temperature as measured by TMA or Vicat's method in the comparison between PUT I and PUT II. The data obtained from the Vicat's instrument confirms the ones from TMA. The unusually high softening temperature of PUT III most probably stems from the higher hard segment concentrations and the best developed crystallinity of PUT III as compared to other polymers studied.

TG measurements (up to 600°C; Fig. 3) show that the decomposition temperatures of the investigated polymers are rather close, because the decomposition results from the disruption of urethane groups that are the least thermally stable chemical groups in these systems.[1] From the TGA curves taken at the same heating rate one can extract some information on the decomposition kinetics as well. The 50% weight loss is for PHC polyurethanes observed at 360–370°C, while in the case of PEAd-based polymers at 405–420°C it depends on soft segment content. It should not be surprising since PHC polyols were developed not for thermal, but for hydrolytic stability. The above given data show, however, to what extent the thermal stability is diminished if PHC is used.
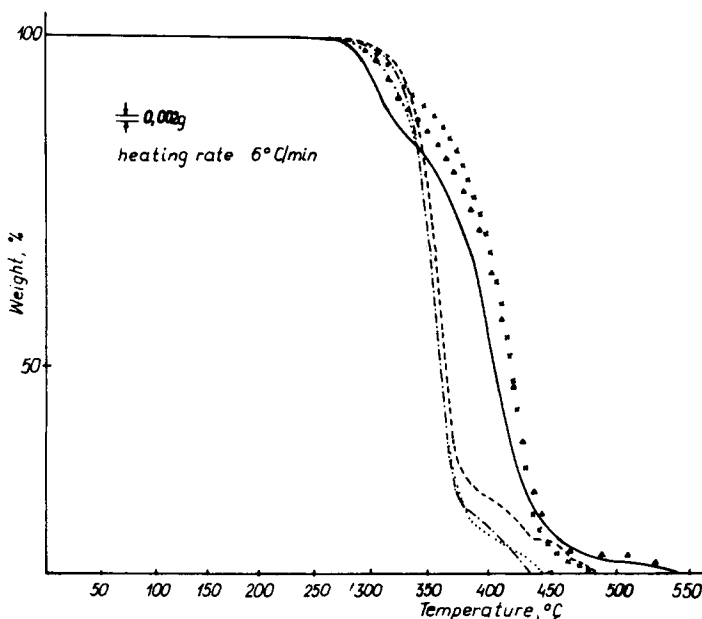
Fig. 3. Thermogravimetric traces for the investigated polymers. (———) II; (- - -) III; (–··–) V; (·· ·) VI; (▲) VII; (x) VIII.

The rate of the decomposition and the decomposition temperatures are not essentially influenced by the nature of chain extenders (PUT's, VII, VIII; Fig. 3).

CONCLUSIONS

Application of HQEE instead of an aliphatic glycol chain extender results in better strength of the obtained polyurethanes and good thermal stability. This effect operates only for polymers of hard segment concentrations above 30%.

Bisphenol A and SMDI are not recommended for applications requiring dimensional stability and stability of mechanical properties at elevated temperatures.

Polyurethanes based on PHC undergo easier thermal decomposition than those based on PEAd, but their thermomechanical stability in the range of −30–24°C is better.

The observed drop in mechanical properties of the polyurethanes based on MDI is more pronounced in the range of −30–24°C than in the range of 24–70°C.

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