Polyether-Based Thermoplastic Polyurethanes. I. Effect of the Hard-Segment Content

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Synopsis

A series of polyether-based thermoplastic polyurethanes, varying in hard-segment content between 20 and 80 wt. %, was prepared using an (oxypropylene-oxyethylene) diol of $\overline{M}_n$ = 2000 as the soft segment and 4,4'-diphenylmethane diisocyanate extended with 1,4-butanediol as the hard segment. Physical-mechanical, dynamic-mechanical, and specific heat (DSC) data are used to elucidate the mechanical and morphological behavior of these materials. The polyurethanes varied from soft elastomeric (continuous soft phase) to high-modulus plastic (continuous hard phase) and showed changes in their tensile properties at about 60% hard-segment content, possibly due to phase inversion.

INTRODUCTION

In 1966 Cooper and Tobolsky[1] published a study comparing the viscoelastic properties of linear polyester-based urethanes with a styrene–butadiene–styrene block copolymer. Both systems had an unusually high plateau modulus, generally associated with covalently crosslinked or crystalline polymers. Selective plastifications indicated that the modulus enhancement observed for these polyurethanes could be attributed to the aggregation of the hard segments and to the formation of a segregated structure. Since then, the investigation of the structure/property development of thermoplastic urethane (TPU) elastomers has become a subject of numerous studies.[2–37]

It is now widely accepted that TPUs are multiblock copolymers of $(AB)_n$ general structure. The hard segments are composed of relatively immobile regions containing short polyurethane sequences. The regions are connected by polyether or polyester-based soft segments, providing the flexible character to the polymers. Repulsive interaction between dissimilar segments leads to phase separation and to the formation of hard- and soft-segment domains. The relative ratios of the domains determines the nature of the continuous and dispersed phases and the overall character of the polymers.

In this study, physical-mechanical, thermal, and dynamic-mechanical properties of a series of polyether-based TPUs have been studied as a function of th6 hard-segment content. The concentration of the hard segments based on 4,4'-diphenylmethane diisocyanate (MDI) and 1,4-butanediol (BDO) was varied from 20 to 80 wt. %. A 2000 $\overline{M}_n$ poly(oxypropylene-oxyethylene) diol was used as the soft segment.
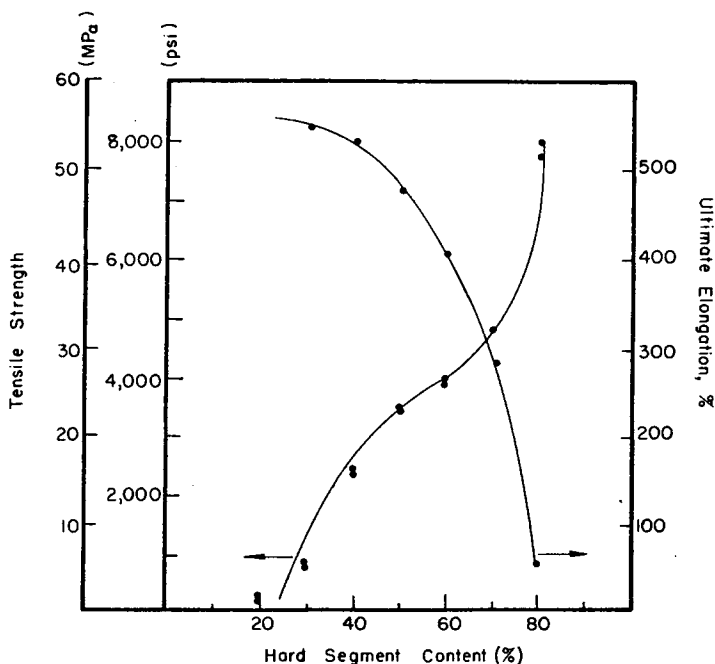
Fig. 1. Dependence of tensile strength and ultimate elongation on the hard segment content of
TPUs.

EXPERIMENTAL

Chemical Preparation and Polymerization

The polyether diol, which contained 30.4 wt. % oxyethylene as an end block
on polyoxypropylene, was dried over molecular sieves prior to use. This material
contained 83% primary hydroxyls and had a functionality of 1.964. Butanediol
was vacuum distilled (5 Torr/95°C) and stored over molecular sieves. Only fresh,
water-white, filtered (~50°C) MDI was used.

The TPUs were prepared by a "hand-casting" technique, described by Gerkin
and Critchfield.[38] Polyether diol, BDO, and catalyst (0.02 wt. % dibutyltin di-
laurate) were charged into a 500-ml, four-neck, round-bottom flask equipped
with a mechanical stirrer, thermometer, and vacuum inlet. This mixture was
degassed by stirring for 30 min under vacuum. Then the stirring was stopped,
the vacuum broken, and 50°C MDI was added to give a 4% excess over the req-
uisite amount. Vacuum was reapplied and stirring continued. After about 30
sec the reacting mixture was poured onto a glass plate (previously treated with
mold-release agent) with a 3.2-mm Teflon spacer around the edges. A second
plate was clamped on top and the entire assembly was placed in a 100°C oven
for 16 hr to complete the cure. The polyurethane was then "demolded" and
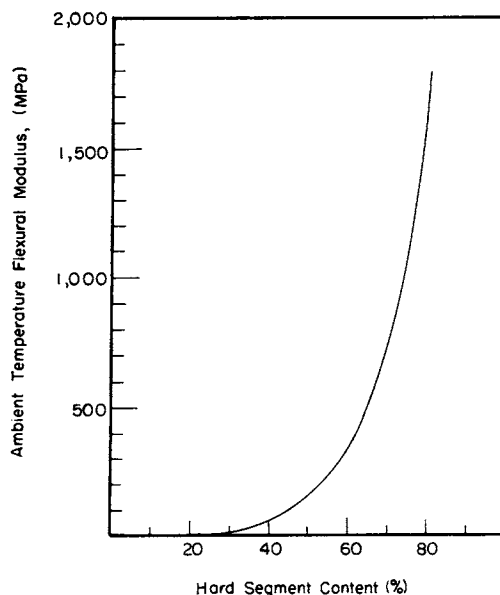allowed to "age" for 1 week at ambient temperatures prior to testing.

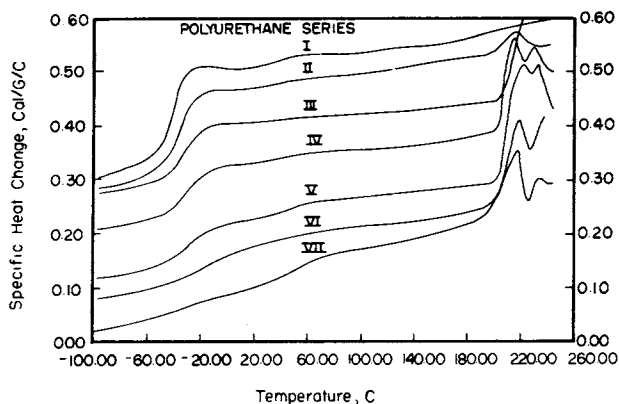Fig. 2. Dependence of the ambient temperature flexural modulus on the hard segment content of the TPUs.

Fig. 3. DSC scans of reheated samples of TPUs containing 20(I), 30(II), 40(III), 50(IV), 60(V), 70(VI), and 80(VII) wt. % of hard segment.

Physical Testing

The standard physical-mechanical properties of the TPUs were measured at ambient temperature with an Instron tensile tester in accordance with prescribed ASTM methods (D638-72). Heat sag, the ability of a polymer specimen to support its own weight, was determined by measuring the deflection of a 100-mm cantilevered bar after 1 hr at 121°C. DSC measurements were performed at 10°C/min heating rates in nitrogen using a DuPont model 990 Thermal Analyzer and model 910 DSC cell base. Relatively large sample sizes (20–60 mg) were used to enhance the signal-to-noise ratio for observing very weak transitions. A Rheovibron, model 200, manufactured by Toyo-Baldwin Company, Ltd., was used for determining the dynamic-mechanical behavior. All measurements were

TABLE I
Properties of Thermoplastic Polyurethanes as a Function of the Hard-Segment Content

Property	Polymer						
	I	II	III	IV	V	VI	VII
Hard-segment content [MDI + BDO (wt. %)]	20	30	40	50	60	70	80
Hardness							
Shore A	54	77	—	—	—	—	—
Shore D	—	—	42	50	64	74	77
100% Tensile stress							
psi	123	379	955	1765	2955	4480	—
MPa	0.85	2.60	6.60	12.20	20.40	31.00	—
300% Tensile stress							
psi	159	787	1505	2460	3300	—	—
MPa	1.10	5.40	10.40	17.00	22.70	—	—
Tensile strength							
psi	277	802	2375	3300	3780	4745	7750
MPa	1.90	5.5	16.40	22.7	26.00	33.00	53.50
Ultimate elongation, %	570	550	535	478	407	287	50
Die "C" tear strength							
pli	84	268	478	605	923	1,240	—
KN/m	14.7	46.9	83.7	106	162	217	—
Flexural Modulii							
−20°F (psi)	Too soft to test	5070	11,800	39,550	139,200	305,000	452,500
−29°C (MPa)		35.0	81.0	273.0	960.0	2100	3100
75°F (psi)		1640	6150	20,300	50,000	109,500	245,000
23°C (MPa)		11.0	42.0	140.0	344.0	755.0	1690
158°F (psi)		1500	5660	15,500	35,000	60,000	102,300
75°C (MPa)		10.0	39.0	107.0	239.0	410.0	705.0
Heat sag							
droop at 250°F, in.	2.70	1.40	0.30	0	0	0	0
droop at 121°C, mm	68.3	35.4	7.6	0	0	0	0

obtained at heating rates of 2°C/min in nitrogen at a frequency of 11 Hz. Modulus measurements with the Rheovibron were corrected for instrument compliance and end effects. The outputs from the DSC and Rheovibron were input during the analyses to a PDP 11/40 minicomputer system, which was used to collect, transform, and plot the data.[39]

RESULTS AND DISCUSSION

Polymer Physical-Mechanical Properties

The polyether diol having an oxypropylene backbone capped on each end with short oxyethylene blocks ($\overline{M}_n$ = 2000; hydroxyl number of 56.2; total primary OH = 83%), was selected as the soft segment for the TPUs. This soft segment is high enough in molecular weight to assure adequate phase separation.[40] Yet the short oxyethylene blocks minimize the formation of higher-order structures through crystallization or chain packing in the soft-segment domains.

The hard segment consisted of MDI extended with BDO. Its concentration (weight fraction of MDI + BDO) in the polymer varied from 20 to 80 wt. % in exactly 10% increments. The physical-mechanical properties of these urethanes are given in Table I.

As the hard-segment concentration of the urethanes increases, the hardness, tensile strength, tear strength, and flexural modulii increase. As expected, the ultimate elongation decreases especially above 60 wt. % hard segment. A very interesting relationship was detected for the dependence of tensile strength on the hard-segment concentration, as illustrated in Figure 1. The S-shaped curve has an inflection point at approximately 60 wt. % hard sement. This probably represents a marked change in domain morphology, which may be related to either inversion of the hard and soft phases or mixing of hard and soft phases.

As expected, the polymer stiffness also increases with increasing hard-segment content (Fig. 2). The ambient temperature flexural modulus increases exponentially as the hard-segment content is increased in a manner typical for filler-reinforced elastomers.

Differential Scanning Calorimeter

Thermal transitions of the TPUs were measured by DSC. In order to study the influence of thermal history, all samples were heated from −100 to 200°C, cooled to −100°C, and then reheated to 250°C at the rate of 10°C/min. Figure 3 illustrates DSC scans for reheated samples, and all the data are summarized in Table II.

The polyurethanes generally exhibited three transition regions detected by DSC. For polymers with hard-segment contents from 20 to 60 wt. %, a sharp increase in specific heat occurs between −50 and −10°C due to the soft-segment glass transition. Above 60 wt. % hard segment, the magnitude of this change drops substantially and is virtually absent at 80 wt. % (curve VII). All of the polymers exhibited a slight increase in specific heat between 10 and 80°C. The magnitude of this transition increased substantially from 60 to 80 wt. % hard segment and became the predominant transition for 80 wt. % hard segment. This occurs in the same hard-segment range as the changes in mechanical properties.
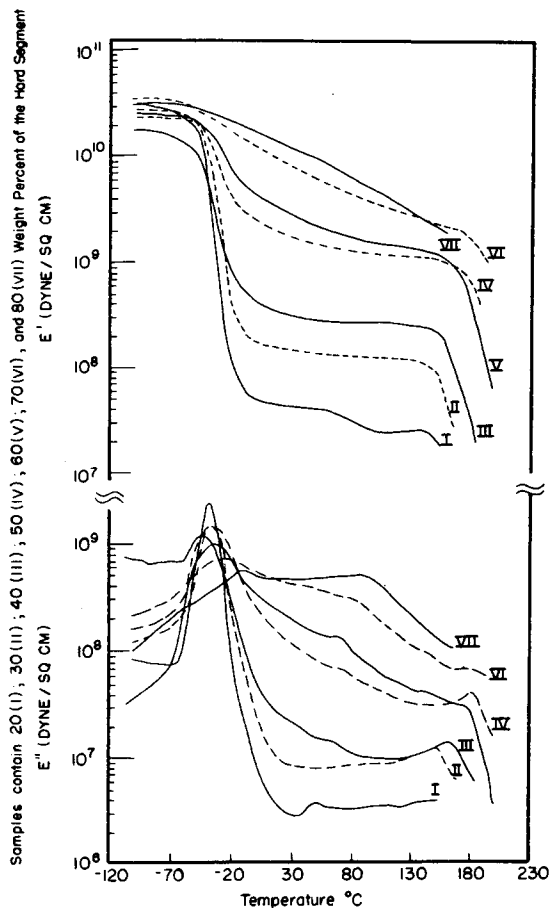
Fig. 4. Temperature dependence of tensile storage (E') and loss (E'') modulii of TPUs determined by Rheovibron measurements for hard-segment contents of 20(I), 30(II), 40(III), 50(IV), 60(V), 70(VI) and 80(VII) wt. %.

Finally, apparent melting peaks are detected for all but one (20 wt. % hard segment) of these polyurethanes. The melting onset temperature for virgin samples ranged from 150 to 170°C, depending on the hard-segment content. The melting-onset temperature shifted up-scale for the reheated samples (195 to 203°C), probably due to melting of low-ordered structures and possible growth of more stable crystallites in the hard phase during the heating/cooling cycle.

Dynamic-Mechanical Measurements

To verify the thermal transitions detected by DSC, and to gain information about the temperature dependence of mechanical properties, Rheovibron analyses were performed on all samples. The temperature dependences of the tensile storage modulus (E') and tensile loss modulus (E'') were determined at a frequency of 11 Hz. The data obtained from those measurements are illustrated on Figures 4–6 and are summarized in Table III.

The transition temperatures, as indicated by the E'' peaks, were 5–10°C higher

TABLE II
DSC and Rheovibron Data for Thermoplastic Polyurethane Series

Sample	Hard Segment, wt. %	Soft-segment transition				Other transitions (DSC)			Modulus data, (E'),[a] (dyn/cm^{-2} × 10^{-8} PA × 10^{-7})	
		DSC		Rheovibron		2nd Order		1st Order		
		T_g, °C	ΔC_p	$\overline{E''PK}$, °C	tan δ, max	Onset T, °C	Approximate ΔC_p	Onset T, °C	30°C	80°C
I	20	−46	0.124	−38	1.5	26	—	None	0.40	0.57
Reheated		−48	0.144	—	—	21	0.023	None	—	—
II	30	−47	0.101	−36	0.6	16	—	149	1.3	1.1
Reheated		−46	0.12	—	—	19	0.022	195	—	—
III	40	−46	0.061	−42	0.33	22	0.023	152	3.1	2.4
Reheated		−45	0.092	—	—	22	0.014	203	—	—
IV	50	−48	0.077	−38	0.17	25	0.036	150	17.0	1.0
Reheated		−44	0.075	—		20	0.028	203	—	—
V	60	−48	0.05	−35	0.095	20	0.048	150	27.0	15.0
Reheated		−44	0.05	—	—	20	0.037	203	—	—
VI	70	−38	~0.03	−30 (80)	0.037 (0.073)	20	~0.05[a]	170	74.0	42.0
Reheated		−45	~0.03	—	—	a	~0.05[a]	203	—	—
VII	80	−46	0.01	−10 (70)	0.033 (0.097)	22	~0.07	170	110.0	60.0
Reheated		−43	0.01	—	—	20	a	190	—	—

[a] Overlapping transitions.
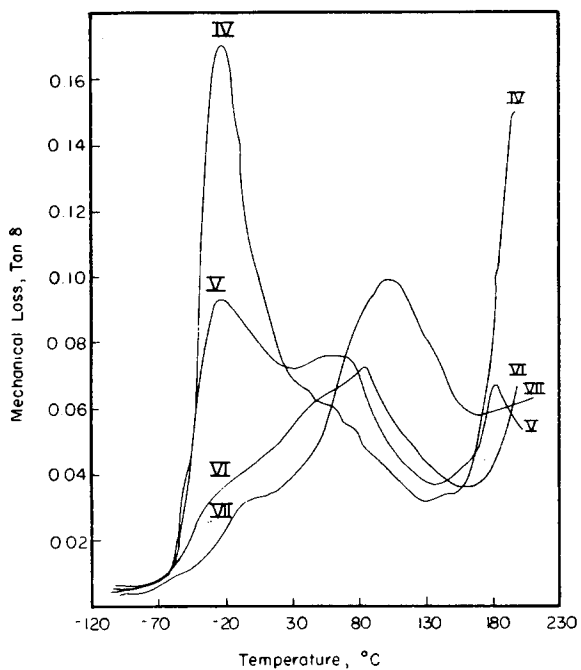
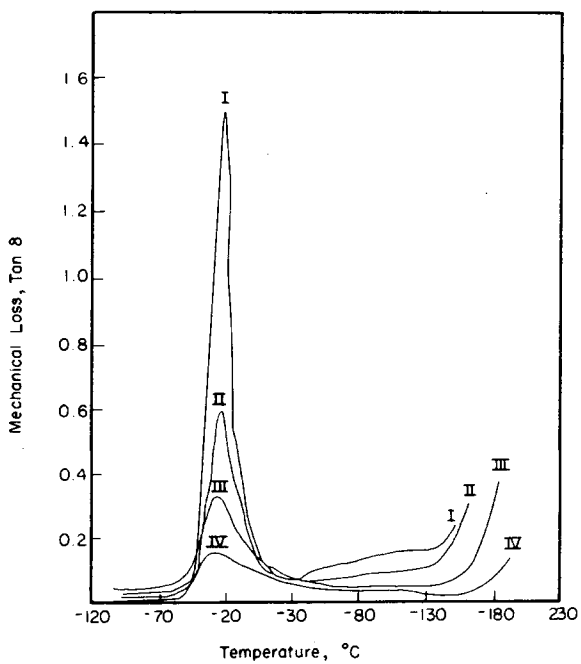Fig. 5. Temperature dependence of tan δ for TPUs containing 20(I), 30(II), 40(III), and 50(IV) wt. % of hard segment.

Fig. 6. Temperature dependence of tan δ for TPUs containing 50(IV), 60(V), 70(VI), and 80(VII) wt. % of hard segment.

than those detected by DSC. This is partially due to the frequency difference and also the use of peak temperatures rather than onset temperatures, as were used in the DSC measurements. The character of the Rheovibron curves (E') and (E'') versus temperature (Fig. 4) clearly illustrates the block copolymer nature of these TPUs. Furthermore, additional evidence for a morphological change due to phase inversion and/or phase mixing (60 and 70 wt. % of hard-segment content) lies in the temperature dependence of the mechanical loss (tan δ) illustrated in Figures 5 and 6. For the polymers having 20–50 wt. % of hard phase, single tan δ peaks associated with the soft-phase T_g are observed which decrease in magnitude and broaden as the hard-phase content increases (Fig. 5). At higher hard-phase contents (60–80 wt. %), the magnitude of tan δ further decreases, the peaks broaden even more, shift to higher temperature, and double peaks are observed (Fig. 6).

CONCLUSIONS

This study demonstrates the influence of the hard-segment content on the development of physical, dynamic-mechanical, and thermal properties of polyether-based TPUs. Within the limits of the hard-segment concentrations studied, two-phase morphology, typical of block copolymers, prevails. Inversion or possibly mixing of the continuous and dispersed phases appears to occur in the system at approximately 60–65 wt. % of hard segment. This changes the nature of the urethane from a tough elastomeric material to a more brittle, high-modulus plastic.

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