# Low-Modulus Siloxane-Based Polyurethanes. I. Effect of the Chain Extender 1,3-Bis(4-hydroxybutyl)1,1,3,3-tetramethyldisiloxane (BHTD) on Properties and Morphology

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**ABSTRACT:** A series of eight polyurethane elastomers was prepared using a two-step bulk polymerization procedure to investigate the effect of the siloxane chain extender 1,3-bis(4-hydroxybutyl)1,1,3,3-tetramethyldisiloxane (BHTD) on polyurethane properties and morphology. All polyurethanes were based on 40 wt % hard segment derived from 4,4′-methylenediphenyl diisocyanate (MDI) and a mixture of 1,4-butanediol (BDO) and BHTD in varying molar ratios. The soft segment was based on an 80 : 20 (w/w) mixture of the macrodiols $\alpha,\omega$-bis(6-hydroxyethoxypropyl)polydimethylsiloxane (PDMS, MW 965) and poly(hexamethylene oxide) (PHMO, MW 714). Polyurethanes were characterized by size-exclusion chromatography, tensile testing, differential scanning calorimetry, dynamic mechanical thermal analysis, and FTIR spectroscopy. Clear and transparent polymers were produced in all cases with number-average molecular weights in the range of 90,000 to 111,000. The ultimate tensile strength decreased only slightly (15%), but Young's modulus and flexural modulus decreased by 76 and 72%, respectively, compared with that of the pure BDO extended polyurethanes as the amount of BHTD was increased to 40 mol %. This change resulted in "softer" and more elastic polyurethanes. Polyurethanes with BHTD contents above 40 mol % were more elastic but had poor tensile and tear strengths. A 60 : 40 molar ratio of BDO : BHTD produced a "soft" polyurethane, which combined good tensile strength and flexibility. The DSC and DMTA results confirmed that the incorporation of BHTD as part of the hard segment yielded polyurethanes with improved compatibility between hard and soft segments. IR data indicated that the amount of hard segments soluble in the soft-segment phase increased with increasing BHTD, contributing to the improved phase mixing. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 736–746, 2002

**Key words:** siloxane macrodiol; siloxane chain extender; polyurethanes; morphology; mixed macrodiols; low modulus

## INTRODUCTION

Incorporation of a high level of siloxane segments into the backbone of polyurethanes significantly im-

proves their biostability.[1–7] Earlier attempts[8–17] to synthesize siloxane-rich polyurethanes with good mechanical properties have met with only limited success. We previously reported[1–7] that siloxane-rich polyurethanes (Elast-Eon™ 2 and 3) with improved biostability and good mechanical properties could be synthesized when a low level (20 wt %) of a comacrodiol such as poly(hexamethylene oxide) (PHMO) was incorporated with bis(6-hydroxyeth-

oxypropyl)-polydimethylsiloxane (PDMS) as part of the soft segment. The comacrodiol promotes adhesion between polar urethane hard segments and nonpolar siloxane soft segments. This finding enabled us to synthesize a range of polyurethanes with siloxane-rich polymer backbones, which have shown good biostability[4,6] and mechanical properties.[5]

Further improvements in segmental compatibility could be achieved by incorporating siloxane-based chain extenders such as 1,3-bis(4-hydroxybutyl)1,1,3,3-tetramethyldisiloxane (BHTD) along with common chain extenders like 1,4-butanediol (BDO) as part of the hard segment. This strategy has enabled the synthesis of soft and low-modulus polyurethanes without a significant compromise in tensile strength or elasticity.[18] The morphology of mixed chain extender polyurethanes, however, is not well understood. It would be useful to ascertain the morphological consequences as well as the effect on mechanical properties when the chain extender compositions are varied.

The main objective of this study, therefore, was to investigate the effect of mixed chain extenders on polyurethane properties and morphology. The study examined the effect of varying the ratio of BHTD and BDO. A series of eight different polyurethanes with a constant weight fraction of hard segment (40%) was prepared using a two-step bulk polymerization procedure by varying the BHTD and BDO molar ratio. The soft segment in all polyurethanes was based on 80 wt % PDMS (MW 965.6) and 20 wt % of PHMO (MW 714.8).

## EXPERIMENTAL

### Materials

$\alpha,\omega$-Bis(6-hydroxyethoxypropyl)-polydimethylsiloxane (PDMS; Shin-Etsu X22160AS, Japan) was a commercial reagent, whereas poly(hexamethylene oxide) (PHMO) was synthesized by a previously reported method.[19] 1,4-Butanediol (BDO; GAF, Australia) was dried over activated molecular sieves and distilled under vacuum, and the middle fraction was used for polymerization; 1,3-bis(4-hydroxybutyl)tetramethyldisiloxane (BHTD; Silar Labs, Scotia, NY) was degassed at room temperature for about 6 h to remove cyclic impurities. PDMS and PHMO were dried under vacuum (13 Pa) at 105°C for at least 12 h prior to polymerization. 4,4′-Methylenediphenyldiisocyanate (MDI; Orica, Australia) was used as received.

### Molecular Weight Determination of Macrodiols by Hydroxyl Number

The number-average molecular weights were calculated based on hydroxyl numbers of macrodiols. The hydroxyl numbers of the purified and dried macrodiols were determined by a phthalic anhydride reflux procedure in accordance with ASTM method D2849.

### Synthesis of Polyurethane Elastomers

Polyurethanes were synthesized by two-step bulk polymerization without catalyst and additives. All glassware was dried in an oven overnight at 105°C. A typical polymerization for a polyurethane with 60 : 40 mol fraction of BDO : BHTD (PU-40) was carried out as follows.

A mixture of the predried macrodiols PDMS (240.0 g, MW 965.6) and PHMO (60.0 g, MW 714.8) was degassed at 80°C for 1 h under vacuum (0.1 Torr). Molten MDI (155.31 g) was placed in a three-necked flask fitted with a magnetic stirrer, nitrogen inlet, and an addition funnel. The macrodiol mixture (300 g) was added dropwise to MDI from the addition funnel over a period of 30 min under a slow stream of dry nitrogen. After the addition, the reaction mixture was heated at 80°C for a period of 2 h with stirring. The prepolymer thus obtained was then degassed under vacuum (0.1 Torr). The prepolymer (440 g) was weighed into a 500-mL polypropylene beaker. A mixture of BDO (14.10 g) and BHTD (29.078 g) was then added to the prepolymer and stirred rapidly for about 3 min. It was then quickly poured onto a Teflon-coated metal pan and cured for 4 h at 100°C in a nitrogen-circulating oven. Other polyurethanes in the series were similarly prepared.

Polyurethanes are designated as PU-X, where X denotes the molar percentage of BHTD in the chain extender mixture. For example, PU-10 refers to a PU prepared from a mixture of PDMS–PHMO (80/20) containing 10 mol % BHTD, whereas PU-0 refers to the control without any BHTD. An 80 : 20 composition of the PDMS–PHMO macrodiols was chosen because previous studies have shown that this composition provides the optimum PHMO level to obtain polyurethanes with clarity and good properties.[1,5] (See Table I.)

### Size-Exclusion Chromatography

Size-exclusion chromatography (SEC) of polyurethane materials was carried out on a Waters chro-

**Table I   Molar Ratios of Reagents Used for Polyurethanes in the Series**

| Polyurethane | Polyols : MDI : (BDO–BHTD) (molar ratio) | BDO : BHTD (molar ratio) |
|---|---|---|
| PU-0 | 1 : 2.04 : 0.988 | 100 : 0 |
| PU-10 | 1 : 1.99 : 0.937 | 90 : 20 |
| PU-20 | 1 : 1.94 : 0.891 | 80 : 20 |
| PU-30 | 1 : 1.90 : 0.850 | 70 : 30 |
| PU-40 | 1 : 1.86 : 0.812 | 60 : 40 |
| PU-60 | 1 : 1.79 : 0.745 | 40 : 60 |
| PU-80 | 1 : 1.74 : 0.689 | 20 : 80 |
| PU-100 | 1 : 1.69 : 0.640 | 0 : 100 |

matograph (Waters & Associates, Milford, MA) using $0.05M$ lithium bromide in $N,N'$-dimethylformamide as the mobile phase at 80°C. The flow rate was 1.0 mL/min. The stationary phase consisted of a set of three $\mu$-Styragel HT columns ($10^5$, $10^3$, and 500 Å) column. The system was calibrated with polystyrene standards. Results are expressed, therefore, as polystyrene-equivalent molecular weights.

### Sample Preparation

After drying for 15 h *in vacuo* (0.1 Torr), polyurethane samples were compression-molded into flat sheets at a temperature between 180 and 200°C under a nominal load of 8 tons. The sheets had dimensions of $60 \times 100$ mm and were 1 mm thick. They were cut into dumbbell-shaped specimens of 3 cm length and 1 cm width; the narrow section was 1.2 cm in length and 0.4 cm in width for the tensile test. A rectangular bar of dimension $12.7 \times 3$ mm was used for flexural tests, whereas a trouser leg–shaped specimen (ASTM D-624) was used for tear tests. All samples were inspected under cross-polarizers and were stress free, given that they exhibited no birefringence under cross-polarizers. All samples were stored under ambient conditions for at least 1 week before tensile tests and hardness measurements were performed.

### Mechanical Properties

Mechanical testing was carried out with an Instron Model 4032 Universal Testing machine. A 1-kN load cell was used and the crosshead speed was 500 mm/min. The results reported are the median values for five replicates. Hardness measurement was carried out using a calibrated Shore A durometer. The flexural modulus measurements were performed using a three-point bend configuration with 52.8-mm spacing. A 1-kN load cell was used with a crosshead speed of 14 mm/min, and the results reported are mean values for three replicates. The tear test was performed with a crosshead speed of 200 mm/min and the results reported are mean values of three replicates.

### Thermal Analysis

DSC analysis over the temperature ranges $-150$ to 220°C was carried out using a Mettler DSC 30. The experiments were carried out at a heating rate of 10°C/min under nitrogen. Sample weights ranged between 20 and 25 mg. The samples were dried at 65°C for 48 h under vacuum (0.1 Torr) prior to analysis. Annealing was carried out on predried samples in a nitrogen-circulating oven at 100°C for 10 h and samples were allowed to cool to room temperature in the oven. Dynamic mechanical analysis was performed using a Rheometric dynamic thermal mechanical analyzer DMTA IV (Rheometric Scientific) equipped with bending head and reducing force option. The analysis was carried out using predried as-molded materials with a heating rate of 2°C/min at 14 Hz.

## RESULTS AND DISCUSSION

The chain extender composition did not affect the clarity and transparency of the resulting polyurethanes. Table II shows the molecular weights of the eight polyurethanes as determined by SEC. The number-average molecular weights varied between 90,000 and 138,000, whereas the poly-

**Table II   Molecular Weights (by SEC) of Polyurethanes**

| Polyurethane | $\bar{M}_n$ | $\bar{M}_w$ | Polydispersity $(\bar{M}_w/\bar{M}_n)$ |
|---|---|---|---|
| PU-0 | 118,612 | 307,475 | 2.5 |
| PU-10 | 90,318 | 236,938 | 2.6 |
| PU-20 | 102,450 | 279,214 | 2.7 |
| PU-30 | 108,772 | 228,085 | 2.0 |
| PU-40 | 116,490 | 340,645 | 2.9 |
| PU-60 | 138,300 | 453,347 | 3.2 |
| PU-80 | 108,676 | 351,477 | 3.2 |
| PU-100 | 115,241 | 453,279 | 3.9 |

dispersity ranged from 2.0 to 3.9; both values showed a dependency on the chain extender composition. The amount of BHTD did not show a direct correlation to polyurethane molecular weight because, at low molar percentage, there was a moderate decrease compared to that of the control PU-0, followed by an increase with 60 mol % BHTD, yielding the highest molecular weight in the series. In general, an increase in the amount of BHTD increased the polydispersity, the exception being PU-30. Given that all the polyurethanes had molecular weights well above the level at which mechanical properties would be affected, any difference in mechanical properties would likely be attributed to structural and morphological differences.[18] All polyurethanes were easily compression moldable at temperatures between 180 and 200°C to produce clear and transparent sheets.

## Mechanical Properties

The incorporation of BHTD resulted in a significant decrease in the modulus of polyurethanes as illustrated by the stress–strain curves in Figure 1 (representative plots) and by the mechanical properties in Table III. It is noteworthy that the Young's modulus, flexural modulus, stress at 100% elongation, and the Shore hardness decreased with increasing amounts of BHTD up to 40 mol %, yet the ultimate tensile strength (UTS) did not significantly decrease. This is graphically illustrated in Figure 2. The UTS remained largely unchanged up to 20 mol % of BHTD, but the flexural modulus halved. The results clearly showed that about 40 mol % of BHTD could be incorporated without significantly reducing the ultimate tensile strength. At 40 mol %, the flex-

ural modulus of the polyurethane was about a third that of the control PU-0 and the polyurethane had a Shore hardness of 70A. Increasing BHTD above 60 mol % made the polyurethanes mechanically weaker than the PU based on BDO, with PU-100 showing the lowest UTS of the series. However, the modulus (see Table III), which gradually decreased up to the 60 mol % of the BHTD level, started to increase with PU-100, exhibiting a modulus similar to that of PU-20. The tear strength of the polyurethane gradually decreased with increasing BHTD content (see Table III), whereas elongation at break increased.

As seen from the stress–strain curves in Figure 1, the polyurethanes with BHTD greater than 60 mol % exhibited a high level of plastic deformation. PU-100 exhibited the highest deformation in the series.

The results demonstrate that by incorporating BHTD up to 40 mol % in this series, polyurethanes with a range of Shore hardness and flexibility could be prepared without significant compromise in tensile strength and elasticity. A 60 : 40 molar ratio of BDO : BHTD yields a "soft" polyurethane that combines good tensile strength and flexibility.

## Polyurethane Morphology

It is envisaged that the siloxane chain extender BHTD could influence the morphology of the resulting polyurethanes because it could alter the ordering of the hard segments attributed to its steric and solubilities properties. To understand such morphological changes the polyurethanes were analyzed using differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), and infrared (IR) spectroscopy. DSC, DMTA, and FTIR spectroscopy provided strong evidence to suggest that this siloxane chain extender caused a considerable change in the ordering of the hard domains.

## Differential Scanning Calorimetry

Figure 3(a) and (b) show the DSC thermograms of compression-molded films in as-molded and annealed states (100°C), respectively. Annealing resulted in improved phase separation, as evidenced by the upward shift in melting endotherm peak temperatures as well as improved peak resolution. Because annealing also removes any differences resulting from thermal effects, for comparison purposes, the results of annealed samples
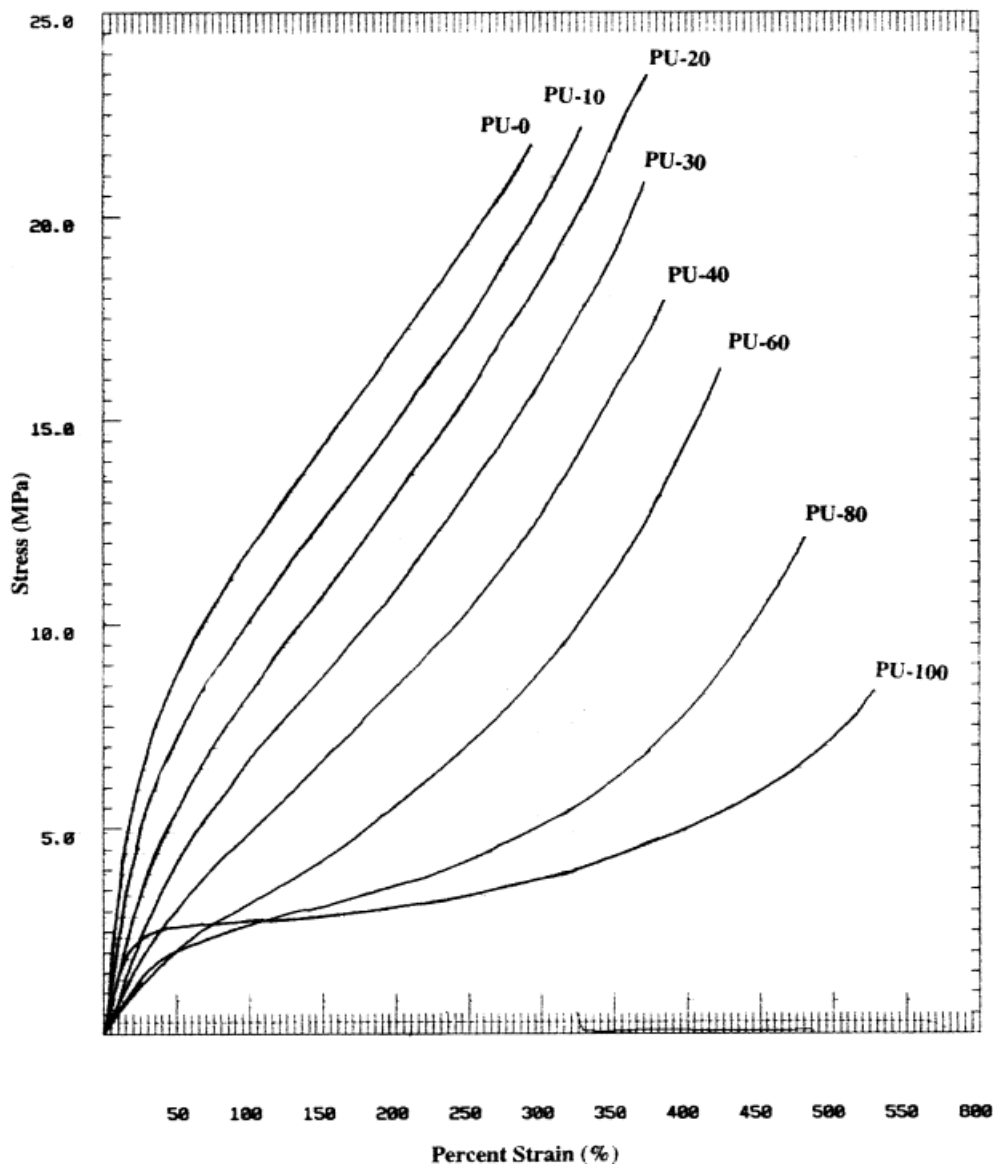
**Figure 1** Representative stress–strain curves of the polyurethanes.

in Figure 3(b) were used. The control PU-0 based on BDO exhibited a melting endotherm centered at 140°C. The most notable change resulting from the incorporation of BHTD was the appearance of two additional peaks centered around 50 and 80°C along with a downward shift in the main melting endotherm accompanying a decrease in peak area. With the increasing amount of BHTD, the two low-temperature melting endotherms increased in intensity up to about 60 mol % level, whereas the main peak nearly disappeared.

A further increase in BHTD resulted in the disappearance of the peak at 80°C, with PU-100 exhibiting only one melting endotherm at 50°C. The hard segment melting endotherm of PU-0 was assigned to hard segments of the type $MDI_2$–BDO, consistent with the average MDI : BDO molar ratio of 2 : 1 based on formulation details shown in Table I. In mixed chain extender–based polyurethanes, the hard segments of the type $MDI_2$–BHTD and $MDI_3$–BHTD–BDO could be expected. Some single MDI linkages would also be expected. The melting endotherm at around 50°C was assigned to melting of hard domains based on $MDI_2$–BHTD segments and the one around 80°C observed for mixed chain extender–based PUs to $MDI_3$–BHTD–BDO.

**Table III   Mechanical Properties of Polyurethanes in the Series**

| Sample | Elongation at Break (%) | UTS (MPa) | | YM (MPa) | | Stress at 100% | Tear S (N/mm) | F. M (MPa) | | Shore Hardness (A) |
|---|---|---|---|---|---|---|---|---|---|---|
| PU-0 | 317 ± 4 | 23 | ± 0.9 | 32 | ± 3 | 11.6 ± 0.4 | 61 ± 4 | 36 | ± 2 | 85 |
| PU-10 | 356 ± 16 | 24 | ± 1.5 | 22 | ± 1 | 9.9 ± 0.1 | 58 ± 2 | 27 | ± 1.4 | 79 |
| PU-20 | 381 ± 6 | 24 | ± 0.9 | 14 | ± 0.5 | 8.3 ± .07 | 52 ± 0.5 | 16 | ± 3 | 75 |
| PU-30 | 378 ± 18 | 21 | ± 1.6 | 9.3 ± 1.1 | | 6.5 ± 0.1 | 44 ± 3 | 12 | ± 2 | 73 |
| PU-40 | 391 ± 5 | 20 | ± 0.4 | 7.8 ± 0.4 | | 5.1 ± 0.1 | 43 ± 0.6 | 10 | ± 0.5 | 70 |
| PU-60 | 420 ± 10 | 16 | ± 1.3 | 7.4 ± 1.1 | | 3.1 ± 0.05 | 31 ± 0.9 | 7.9 ± 0.4 | | 63 |
| PU-80 | 489 ± 15 | 13 | ± 0.8 | 7.3 ± 1.2 | | 2.6 ± 0.1 | 23 ± 0.4 | 9 | ± 0.1 | 64 |
| PU-100 | 547 ± 10 | 9.2 ± 0.4 | | 13 | ± 0.9 | 2.7 ± 0.04 | 19 ± 0.3 | 17 | ± 0.3 | 71 |

The heats of fusion associated with melting endotherms for the two control polyurethanes PU-0 and PU-100 were very similar and close to 10 J g$^{-1}$, indicating a high level of phase separation in both materials. The hard segment melting endotherm $\Delta H$ showed a dependency on the chain extender composition. The combined $\Delta H$ for all hard segment melting endotherms decreased with increasing BHTD up to 60 mol % and then increased. The results strongly suggested that BHTD enhanced the phase mixing between hard and soft segments at moderate levels, but the behavior reversed upon reaching 60 mol % BHTD. The change in soft segment glass-transition temperatures (see Table IV) supported this. Figure 3(b) shows two major glass transitions, as expected, given that the soft segment is based on an 80/20 mixture of PDMS and PHMO. The first low-temperature $T_g$ around −110°C is assigned to PDMS, whereas the second around −20°C is assigned to the PHMO/PDMS end group (ethoxypropyl). The $T_g$ onset at −20.6°C observed

for PU-0 gradually moved to higher temperatures with increasing the BHTD content, reaching −13.4°C for PU-40, and then started to shift downward, reaching −21.5°C for PU-100. However, such a clear trend was not observed with the $T_g$ of the PDMS soft segment, perhaps indicating that it is largely PHMO and the ethoxypropyl end groups that are involved in phase mixing with the hard segment to form interfacial regions.

In summary, the DSC results provided evidence to indicate that the major morphology change associated with the incorporation of BHTD as part of the hard segment was the improved phase mixing, which depended on the amount of BHTD. The phase mixing gradually increased up to 60 mol % BHTD, and the trend reversed above that level.

## Dynamic Mechanical Thermal Analysis

DMTA results supported DSC results with respect to morphological changes as well as the corresponding modulus changes discussed earlier. Figure 4(a) shows the change of storage modulus ($E'$) as a function of temperature. The polyurethanes based on mixed chain extenders showed significantly lower modulus compared to those of the two control materials at ambient temperature, in agreement with the measured modulus (see Table III). The largest difference was observed in the 19–35°C temperature range, and above 35°C PU-100 exhibited a very sharp decrease in $E'$, whereas PU-0 exhibited only a modest decrease. Below ambient temperature the modulus difference between the materials in the series was not very large and, interestingly, PU-20 showed the lowest modulus in the low-temperature range, illustrating that with a rela-
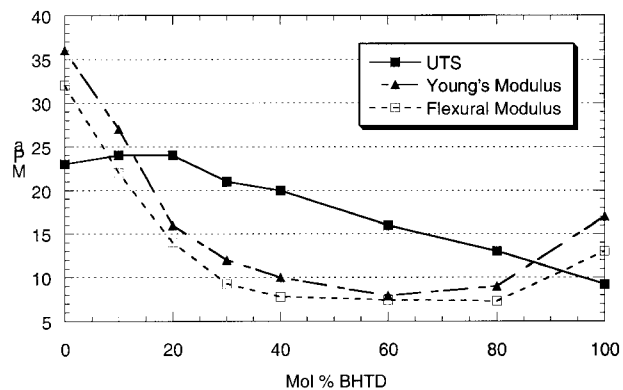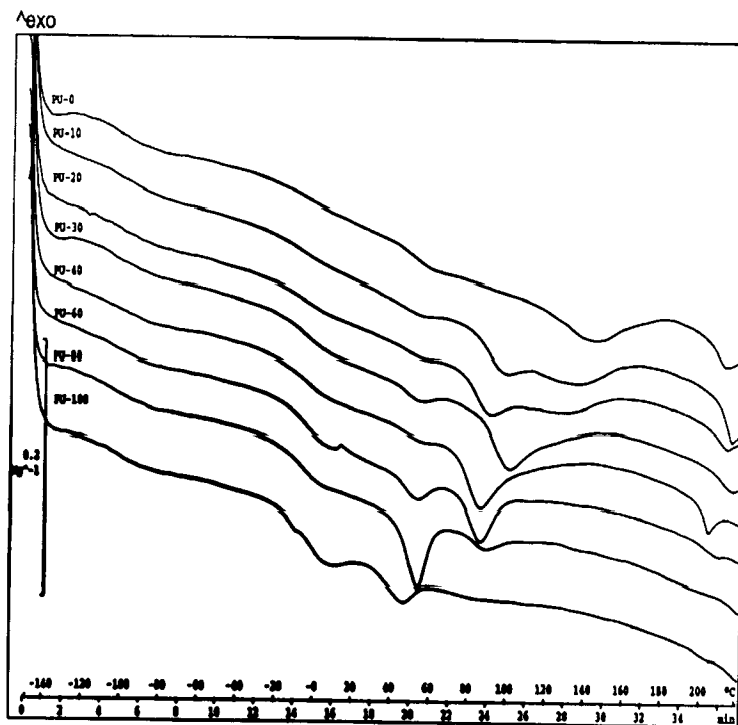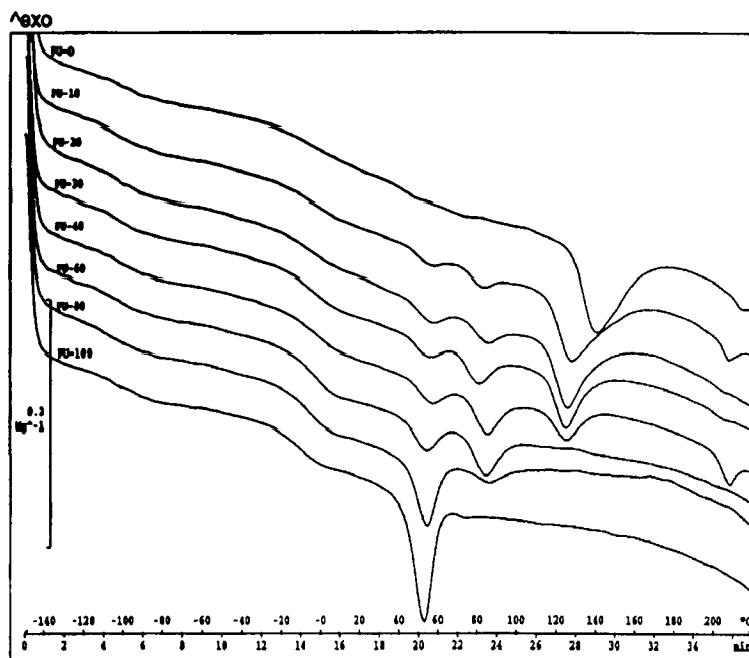


**Figure 2**   Effect of BHTD mol % on UTS, Young's modulus, and flexural modulus.

(a)



(b)

**Figure 3**   DSC thermograms of the polyurethanes: (a) as molded; (b) annealed.

**Table IV   DSC Thermal Transitions and Melting Endotherm Heats of Fusion of Polyurethanes (Annealed)**

| Sample | $T_g$ (PDMS) Onset, Midpoint, and Endset (°C) | $T_g$ (PDMS end group/comacrodiol) Onset, Midpoint, and Endset (°C/$\Delta C_p$, J g$^{-1}$ k) | Hard Segment Melting Endotherms Peak Temperatures (°C) and Heat of Fusion ($\Delta H$/J g$^{-1}$) |
|---|---|---|---|
| PU-0 | −107.2, −107.2, −93.2 | −20.6, −7.4, 10.19 (0.18) | 138.3 (9.95) |
| PU-10 | −112.7, −105.8, −98.3 | −16.8, −10.0, 2.25 (0.13) | 53.7 (0.64), 80.6 (0.78), 125.64 (7.84) |
| PU-20 | −106, −104, −101.9 | −16.3, −9.8, 3.34 | 54.5 (1.01), 83.7 (1.04), 124.3 (5.78) |
| PU-30 | −108.8, −104.4, −98.6 | −16.5, −6.7, 3.8 (0.17) | 52.8 (0.86), 78.9 (1.67), 123.17 (4.21) |
| PU-40 | −113.8, −112.2, −110.5 | −13.4, −5.3, 3.7 (0.15) | 55.2 (1.17), 83.6 (2.26), 123.7 (1.94) |
| PU-60 | −112.6, −104.1, −94.5 | −14.8, −4.9, 4.3 (0.22) | 52.5 (1.76), 83.2 (2.55) |
| PU-80 | −115.1, −115.6, −112 | −17.6, −7.8, 1.66 (0.21) | 53.1 (7.69), 84.2 |
| PU-100 | −110.5, −107.3, −103.7 | −21.5, −15.2, −4.9 (0.15) | 51.6 (9.82) |

tively small amount of BHTD, there was a significant decrease in modulus.

The position and intensity of the tan δ peak [see Fig. 4(b) and Table V] were dependent on the chain extender composition. With the exception of PU-60 (because of a sample holder problem) all samples showed two tan δ peaks. The low-temperature, low-intensity peak was assigned to PDMS and the other was assigned to amorphous hard segment/interfacial regions. The two controls PU-0 and PU-100 showed peak temperatures of 29.7 and 6.37°C, respectively, for the latter peak. The PUs with mixed chain extenders showed intermediate values. The most noticeable shift in temperature was observed for PU-60, consistent with DSC results. The tan δ peak for polyurethane with higher BHTD contents was generally narrower.

As we previously observed with other systems,[18] the $T_g$ midpoints estimated from $E''$ were slightly higher than those determined by DSC. However, the general trend was similar; the PDMS $T_g$ midpoint shifted to higher temperatures with increasing BHTD up to about 40 mol %, indicating improved phase mixing. At higher levels (above 40 mol %) of BHTD, PDMS appears to exists in a largely phase-separated state. Similarly, the amorphous soft/hard interfacial region $T_g$ midpoint shifted to higher temperatures with the incorporation of BHTD, and the largest shift was observed for PU-60.

Overall, DMTA results corroborated DSC results. Incorporation of BHTD up to about 60 mol % results in significant increase in phase mixing largely associated with amorphous hard segments, ethoxypropyl groups of PDMS, and PHMO segments.

## Infrared Spectroscopy

FTIR spectroscopy of all polyurethanes was carried out to provide further supportive evidence on morphology changes ascertained from DSC and DMTA results. The relative intensities of bonded and nonbonded IR carbonyl absorptions could be used to obtain semiquantitative data on the level of phase mixed hard segments. The transmission IR spectra were obtained from uniform thin films (2.5 μm) sectioned from compression-molded films after similar thermal treatments as for DSC and DMTA test specimens. The heights of carbonyl peaks were normalized against the urethane N—H bending and C—N stretching bands near 1532 cm$^{-1}$ as the main reference peak.[20] As shown in Figure 5, the relative intensities (peak heights) of nonbonded carbonyl groups $CO_{nb}$ (1730 cm$^{-1}$) increased with a corresponding decrease in bonded carbonyl $CO_b$ (1702 cm$^{-1}$) intensity up to 60 mol % BHTD, and the trend reversed thereafter. This indicated that the incorporation of BHTD decreased the level of interurethane hydrogen bonding of the hard segments, whereas a reverse trend was observed above 60 mol % BHTD, perhaps indicating that above this level the BHTD-based hard segments form ordered structures, consistent with DSC results.

The nonbonded carbonyls are largely associated with urethane linkages formed by the reaction of MDI with two macrodiol molecules (referred to as "single MDI links") and those with phase mixed hard segment; the IR data were used to calculate the percentage of such links dissolved in the soft-segment phase. Figure 6 shows the change of the percentage of soluble single MDI links [calculated from peak heights of $CO_{nb}$ (1732
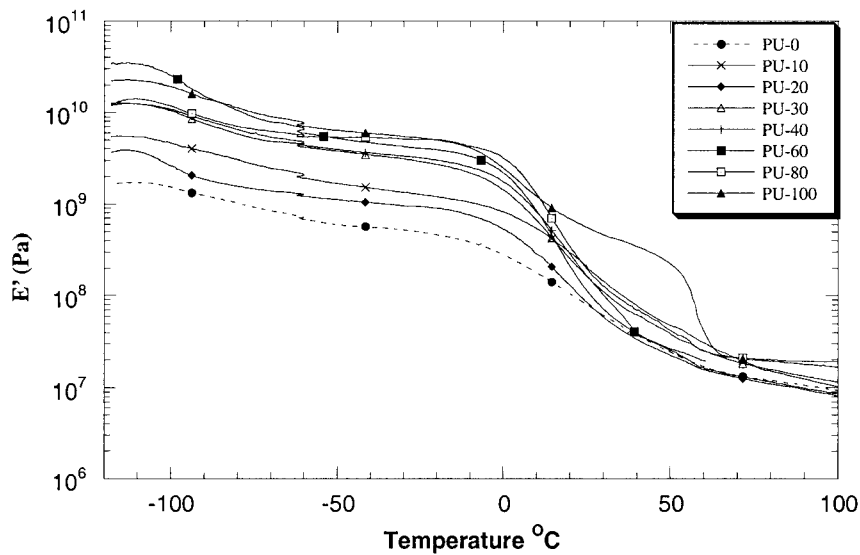
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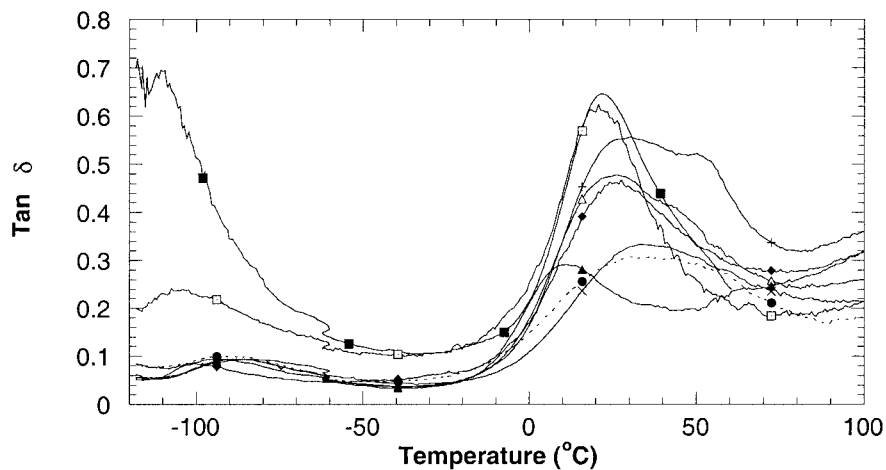


(b)

**Figure 4** Dynamic mechanical spectra of polyurethanes: (a) $E'$ versus temperature; (b) tan $\delta$ versus temperature.

cm$^{-1}$) and urethane amide absorptions (1532 cm$^{-1}$) and adjusted to the hard segment weight percentage] as a function of BHTD mol %. The amount of such links increased with increasing BHTD, exhibiting a maximum of 15.6% for PU-60, and decreased for other compositions above 60 mol % BHTD. It should be noted here that the percentage of single MDI links in all polyurethanes was found to increase with increasing BHTD because of the use of less than two moles of MDI per mole of macrodiol (see Table I) as the weight percentage of hard segment was kept constant at 40. On this basis one would expect the percentage of such links to increase if those links

**Table V    DMTA Thermal Transition Temperatures of Polyurethanes**

| Sample | Tan δ Peak Temperatures | $T_g$ (PDMS) Midpoint (°C) from $E''$ | $T_g$ (Soft/Hard Interfacial Regions) Midpoint (°C) from $E''$ |
|---|---|---|---|
| PU-0 | −93.0, 29.66 | −100.86 | 2.17 |
| PU-10 | −101.0 | −104.49 | −1.88 |
| PU-20 | −78.86, 25.73 | −89.66 | 3.23 |
| PU-30 | −93.59, 25.44 | −95.69 | 2.30 |
| PU-40 | −95.94, 24.46 | −101.84 | 2.46 |
| PU-60 | 12.39 | — | 10.83 |
| PU-80 | −106.12, 20.12 | 106.12 | −0.14 |
| PU-100 | −94.31, 6.37 | −101.94 | −6.68 |

were not associated with hydrogen bonding. Despite this, the results in Figure 6 clearly indicate that at higher levels of BHTD (60 mol % and above) the amount of such links significantly decreased, suggesting that in polyurethanes with BHTD 80% or above, the single MDI links may exist in the hard domain phase. Both PU-0 and PU-100 showed similar levels of soluble hard segments. This is consistent with DSC results in which both these materials showed similar $\Delta H$ for melting of hard segments.

The relatively high level of compatibilized hard segments in mixed chain extender –based polyurethanes appears to be the main reason for the polyurethanes to have low modulus.

## CONCLUSIONS

This study demonstrated that in this system, by incorporating BHTD up to 40 mol % polyurethanes with a range of Shore hardness values and flexibilit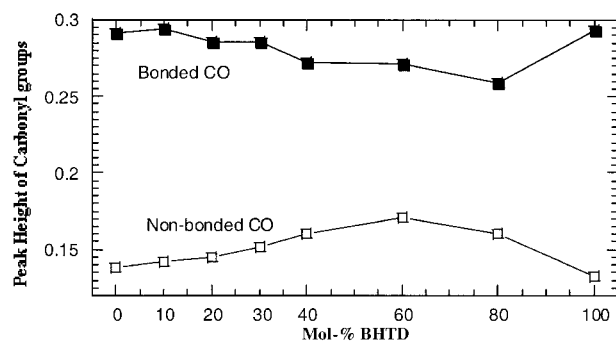y could be prepared without significant compromise in tensile strength and elasticity. A 60 : 40 molar ratio of BDO : BHTD yielded a "soft" (Elast-Eon™ 3-0070A) polyurethane, which combines good tensile strength and flexibility. DSC and DMTA results confirmed that the incorporation of BHTD as part of the hard segment resulted in improved phase mixing between hard and soft segments. IR data indicated that the amount of solubilized hard segments increased with increasing BHTD, which improved the phase mixing.

In a separate study, the biostability of a soft-grade (Shore hardness 70A, Elast-Eon™ 3) polyurethane was assessed[3,6] by a 3-month *in vivo* implant study. SEM examination of explanted Elast-Eon test specimens showed no signs of degradation.

**Figure 5**    Change of peak heights of bonded ($CO_b$) and nonbonded carbonyl ($CO_{nb}$) absorptions with mol % of BHTD.
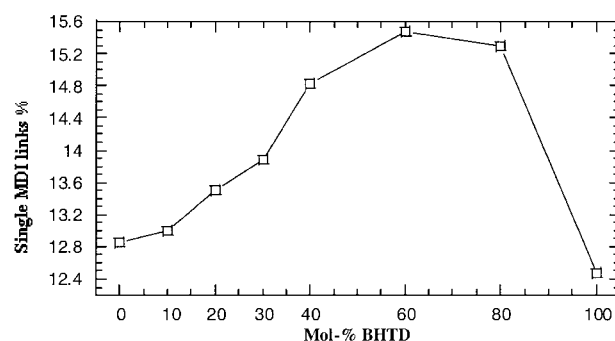


**Figure 6**    Percentage of soluble "single MDI links" based on the relative intensities of bonded ($CO_b$) and nonbonded carbonyl ($CO_{nb}$) absorption.

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