

Mixed Macrodiol-Based Siloxane Polyurethanes: Effect of the Comacrodiol Structure on Properties and Morphology

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ABSTRACT: Two series of polyurethanes were prepared to investigate the effect of comacrodiol structure on properties and morphology of polyurethanes based on the siloxane macrodiol, α,ω -bis(6-hydroxyethoxypropyl) polydimethylsiloxane (PDMS). All polyurethanes contained a 40 wt % hard segment derived from 4,4'-methylenediphenyl diisocyanate (MDI) and 1,4-butanediol (BDO), and were prepared by a two-step, uncatalyzed bulk polymerization. The soft segments were based on an 80/20 mixture of PDMS (MW 967) and a comacrodiol (MW 700), selected from a series of polyethers and polycarbonates. The polyether series included poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO), poly(tetramethylene oxide) (PTMO), poly(hexamethylene oxide), and poly(decamethylene oxide) (PDMO), whereas the polycarbonate series included poly(hexamethylene carbonate) diol (PHCD), poly[bis(4-hydroxybutyl)-tetramethyldisiloxy carbonate] diol (PSCD), and poly[hexamethylene-co-bis(4-hydroxybutyl)-tetramethyldisiloxy carbonate] diol (COPD). Polyurethanes were characterized by size exclusion chromatography, tensile testing, differential scanning calorimetry (DSC), and dynamic mechanical thermal analysis (DMTA). The results clearly demonstrated that the structure of the comacrodiol influenced the properties and morphology of siloxane-based polyurethanes. All comacrodiols, except PEO, improved the UTS of the polyurethane; PHMO and PTMO were the best polyether comacrodiols, while PSCD was the best polycarbonate comacrodiol. Incorporation of the comacrodiol made polyurethanes more elastomeric with low modulus, but the effect was less significant with polycarbonate comacrodiols. DSC and DMTA results strongly supported that the major morphological change associated with incorporation of a comacrodiol was the significant increase in the interfacial regions, largely through the compatibilization with the hard segment. The extent of compatibilization varied with the comacrodiol structure; hydrophilic polyethers such as PEO were the most compatible, and consequently, had poor mechanical strength. Among the polyethers, PHMO was the best, having an appropriate level of compatibility with the hard segment for substantial improvement in mechanical properties. Siloxy carbonate comacrodiol PSCD was the best among the polycarbonates. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1071–1082, 2000

Key words: polydimethylsiloxane; comacrodiol; polyethers; polycarbonates; synthesis; morphology; characterization; polyurethanes

INTRODUCTION

Siloxane polymers characteristically have unique properties such as oxidative and hydrolytic sta-

bility, good blood contacting properties, a wide service temperature range due to low glass transition temperature (-123°C), low moisture permeability, and low surface energy. The interest in incorporating siloxane segments as part of the polyurethane (PU) structure is to impart such properties to polyurethanes, and to improve some of the inherently poor properties of siloxane polymers such as abrasion, tear, and tensile

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strength.¹ It has been identified that the major problem associated with synthesizing siloxane polyurethanes is the incompatibility of the non-polar siloxane segments with polar urethane hard segments, which resulted in polyurethanes with poor mechanical properties. The poor properties were attributed to weak interfacial adhesion.² We have recently demonstrated that when a relatively small amount of a second macrodiol (comacrodiol) such as poly(hexamethylene oxide) (PHMO) was incorporated as part of the soft segment along with α,ω -bis(6-hydroxyethoxypropyl) polydimethylsiloxane (PDMS), the compatibility of the siloxane soft and urethane hard segments (HS) could be significantly improved, which helps to strengthen the interfacial regions. This key finding has enabled the synthesis of a new family of siloxane polyurethane elastomers with good mechanical properties and biostability.³⁻⁹ The compatibilizing effect of the comacrodiol has been demonstrated using thermo-analytical and mechanical techniques. The optimum compatibility was observed when the comacrodiol was incorporated at a level of about 20 wt % of the soft segment.³⁻⁸

The other main approaches reported in the literature to improve interfacial adhesion were the introduction of polar functionality to PDMS backbone,¹⁰⁻¹² and the use of copolymers of siloxane and polar macrodiols such as polyethers and polyesters.¹³⁻¹⁵ However, these techniques have not been very successful in synthesizing polyurethanes with significant improvement in mechanical properties, particularly for compositions with a high siloxane content.

The chemical structure, molecular weight, and solubility parameter of the comacrodiol should significantly influence its compatibilizing effect in PDMS-based polyurethanes. The aim of this study was to investigate the effect of the comacrodiol structure on properties and morphology of siloxane polyurethanes. A polyether series and a polycarbonate series were included in this study. The polyethers included poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO), poly(tetramethylene oxide) (PTMO), poly(hexamethylene oxide), and poly(decamethylene oxide) (PDMO). This series was chosen because it offers polyethers with different solubility parameters, ranging from hydrophilic (PEO) to hydrophobic (PDMO). The second series (polycarbonate series) included three polycarbonate macrodiols, based on 1,6-hexanediol, 1,3-bis(4-hydroxybutyl)-1,1,3,3-tetramethyldisiloxane and a copolycarbonate based on the two diols. The carbonate and the

siloxane groups are expected to improve compatibility with urethane hard segments and siloxane soft segments, respectively. The number-average molecular weights of all the test comacrodiols were kept constant at 700 ± 10 to eliminate any effects due to molecular weight differences. Selection of above molecular weight was based on earlier results, which provided polyurethanes with good properties.³

EXPERIMENTAL

Materials

Poly(hexamethylene oxide), poly(decamethylene oxide), were synthesized by the acid-catalyzed condensation polymerization of respective diols.¹⁶ PTMO (Terathane™, DuPont), PEO, and PPO (Aldrich), poly(hexamethylene carbonate) diol (PHCD), α,ω -bis(6-hydroxyethoxypropyl) polydimethylsiloxane (PDMS, X22-160AS, Shin-Etsu, Japan) were commercial reagents. Poly [(bis(4-hydroxybutyl)-tetramethyldisiloxy carbonate) diol (PSCD) and poly [hexamethylene-co-bis(4-hydroxybutyl)-tetramethyldisiloxy carbonate] diol (COPD) were synthesized, respectively, from 1,4-bis(4-hydroxybutyl)-1,1,3,3-tetramethyl disiloxane (BHTD) and a 50/50 (w/w) mixture of BHTD and 1,6-hexanediol using a transesterification reaction with ethylenecarbonate^{17,18} and stannous octoate catalyst. 1,4-Butanediol (BDO, GAF) was dried over activated molecular sieves (3 Å), distilled under vacuum, and the middle fraction used for polymerization. All macrodiols were dried thoroughly by heating at 105°C for 12 h under vacuum (0.1 Torr) prior to polymerization. 4,4'-Methylenediphenyldiisocyanate (MDI, ICI product Suprasec MPR™) was used as received. Some properties of macrodiols are listed in Table I.

Macrodiols Molecular Weight Determination

The number-average molecular weights were calculated based on hydroxyl numbers of macrodiols. The hydroxyl numbers of purified and dried macrodiols were determined by a phthalic anhydride reflux procedure in accordance with ASTM method D2849.¹⁹

Synthesis of Polyurethane Elastomers

Both series of polyurethanes were synthesized by a two-step bulk polymerization method without a catalyst. All glassware were dried in an oven

Table I Properties of Macrodiols

Macrodiol	Abbreviation	Solubility Parameter ^a δ (cal/cm ³) ^{1/2}	Glass Transition (Onset, Midpoint, End-Set, °C)
α,ω -Bis(6-hydroxyethoxypropyl) Polydimethylsiloxane	PDMS	6.66	-111.8, -109.5, -107.2,
Poly(ethylene oxide)	PEO		-72.0
Poly(propylene oxide)	PPO		
Poly(tetramethylene oxide)	PTMO	9.55	-96.0
Poly(hexamethylene oxide)	PHMO	9.34	-46.0, -41.5, -37.0
Poly(decamethylene oxide)	PDMO	9.03	-24.0
Poly (hexamethylene carbonate) diol	PHCD		-67.5, -60.1, -52.7
Poly [bis(4-hydroxybutyl)-tetramethyl-disiloxy carbonate]diol	PSCD		-79.1, -75.2, -71.4
Poly [hexamethylene-co-bis(4-hydroxybutyl)-tetramethyl-disiloxy carbonate] diol	COPD		-69.4, -65.1, -60.8

^a Calculated using MSI "Amorphous Cell" package with PCFF2 force field (H. Sun, MSI Polymer Consortium, Del Mon, 1997).

overnight at 105°C. A typical two-step bulk polymerization procedure was performed as follows.

A mixture of predried macrodiols PDMS (40.0 g, MW 966.7) and PHMO (10.0 g, MW 700) was degassed at 80°C for 1 h under vacuum of (0.1 Torr). Molten MDI (28.415 g) was placed in a 500 mL three-necked round-bottom flask fitted with a magnetic stirrer, nitrogen inlet, and an addition funnel. The flask was then placed in an oil bath at 70°C. Macrodiol mixture (50.00 g) was added to MDI dropwise through the addition funnel over a period of 30 min under a slow stream of dry nitrogen. After the addition was over, the reaction mixture was heated to 80°C for a period of 2 h with stirring. The prepolymer obtained was then degassed under vacuum (0.1 Torr) for 30 min. The prepolymer (75.0 g) was then weighed into a 500 mL polypropylene beaker, and chain extended with 1,4-butanediol (4.703 g) and stirred thoroughly for about 1 min. The viscous polymer was then transferred to a Teflon-coated metal pan and cured for 4 h at 100°C in a nitrogen-circulating oven.

Polyurethanes based on PDMS and each of the other comacrodiols were prepared similarly. Polyurethanes are designated as PU-XXXX, where XXXX represents the abbreviation of the comacrodiol; for example, PU-PHMO refers to a PU prepared from a mixture of PDMS/PHMO (80/20) with a hard segment weight percentage of 40. In all polyurethanes the hard segment weight percentage was kept constant at 40 and the PDMS to comacrodiol ratio to 80/20, respectively. The control polyurethane, which contained a soft segment based on PDMS only, was labeled as PU-PDMS.

Size-Exclusion Chromatography

Size-exclusion chromatography of polyurethanes was carried out at 80°C with 0.05 M lithium bromide in *N,N*-dimethylformamide as the eluent on a Waters Associates chromatograph with three μ -Styragel HT columns (10⁵, 10³, and 500 Å), and the flow rate was 1 mL/min. The system was equipped with a refractive index detector, and was calibrated with narrow distribution polystyrene standards. Results are expressed, therefore, as polystyrene-equivalent molecular weights.

Mechanical Properties

After drying for 15 h at 65°C *in vacuo* (0.1 Torr), polyurethane samples were compression-molded into flat sheets at temperatures between 190 and 200°C under a nominal load of 8 tons. The sheets had dimensions of 60 × 100 mm and were 1 mm thick. They were cut into dumbbells of 3 cm in length and 1 cm in width; the narrow section was 1.2 cm in length and 0.4 cm in width. Dumbbells were stored under ambient conditions for 4 weeks before tensile tests and hardness measurements were carried out. For tests where annealed samples were used, the test specimens were annealed by heating at 100°C for 10 h.

Tensile 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 mean values for five replicates. Hardness measurements were carried out using a Shore A Durometer. The flexural modulus measurements were performed using a three-point bend configuration

Table II Molecular Weights of Polyurethanes

Polyurethane	\bar{M}_n	\bar{M}_w	Polydispersity
PU-PDMS	74,522	111,900	1.50
Polyether Series			
PU-PEO	75,596	112,366	1.47
PU-PPO	103,609	166,506	1.60
PU-PTMO	99,827	163,081	1.63
PU-PHMO	100,302	175,897	1.75
PU-PDMO	83,371	136,124	1.63
Polycarbonate Series			
PU-PHCD	81,627	131,139	1.60
PU-PSCD	78,619	114,392	1.45
PU-COPD	84,633	134,340	1.58

with a 52.8 mm spacing. A 1 kN load cell was used with cross head speed of 14 mm/min, and the results reported are mean values for three replicates.

Differential Scanning Calorimetry (DSC)

The samples were dried at 65°C for 48 h under vacuum (0.1 Torr) to remove moisture prior to recording thermograms. DSC thermograms were recorded over the temperature range -150 to 250°C on a Mettler DSC 30 heat flux calorimeter that has been calibrated for heat flow (standard indium) and temperature (Q water and AnalaR *n*-hexane, standard indium, lead and zinc). The experiments were carried out at a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen purge of 20 mL/min. Sample weights were 15–25 mg.

Dynamic Mechanical Thermal Analysis (DMTA)

DMTA was performed on a Rheometrics Scientific Mark IV instrument using rectangular test spec-

imens ($45 \times 10 \times 1.6$ mm) in the dual cantilever mode with a 5-mm free-length frame. The testing was done at a heating rate of $2^\circ\text{C}/\text{min}$ at a frequency of 14 Hz.

RESULTS AND DISCUSSION

The incorporation of a comacrodiol increased the molecular weight of the siloxane-based polyurethane as illustrated by the results in Table II. The increase in molecular weight was dependent on the comacrodiol structure. The increase was modest for PEO, PDMO, and all polycarbonate comacrodiols. The low molecular weight of the control PU-PDMS may be associated with the poor segmental compatibility of nonpolar PDMS with the hard segment. In the polyether series, the most hydrophilic (PEO) and the most hydrophobic (PDMO) macrodiols produced PUs with only marginal improvement in MW. There was no significant difference in MW for the three materials in

Table III Mechanical Properties of Polyurethanes

Polyurethane	Elongation at Break (%)	UTS (MPa)	Young's Modulus (MPa)	Stress at 100% Elong. (MPa)	Flexural Modulus (MPa)	Shore Hardness (A)
PU-PDMS	310 ± 23	10.9 ± 0.5	49.6 ± 4	9.7 ± 0.3	55.6 ± 3	87
Polyether Series						
PU-PEO	471 ± 7	10.4 ± 0.3	23.6 ± 1	7.0 ± 0.6	25.9 ± 2	74
PU-PPO	452 ± 26	15.5 ± 0.9	37.4 ± 4	9.9 ± 0.3	35.0 ± 2	86
PU-PTMO	342 ± 16	22.7 ± 1.1	27.0 ± 2	9.0 ± 0.3	36.5 ± 2	83
PU-PHMO	370 ± 16	22.1 ± 0.6	22.5 ± 3	8.3 ± 0.2	38.9 ± 1	85
PU-PDMO	384 ± 27	14.9 ± 1	39.1 ± 1	10.6 ± 0.1	46.5 ± 3	83
Polycarbonate Series						
PU-PHCD	297 ± 16	17.2 ± 1.4	53.1 ± 7	11.6 ± 0.3	50.0 ± 2	86
PU-PSCD	476 ± 29	19.9 ± 0.9	34.9 ± 1	10.3 ± 0.3	43.8 ± 2	84
PU-COPD	343 ± 73	11.9 ± 1.4	39.3 ± 1	9.8 ± 0.1	40.5 ± 4	86

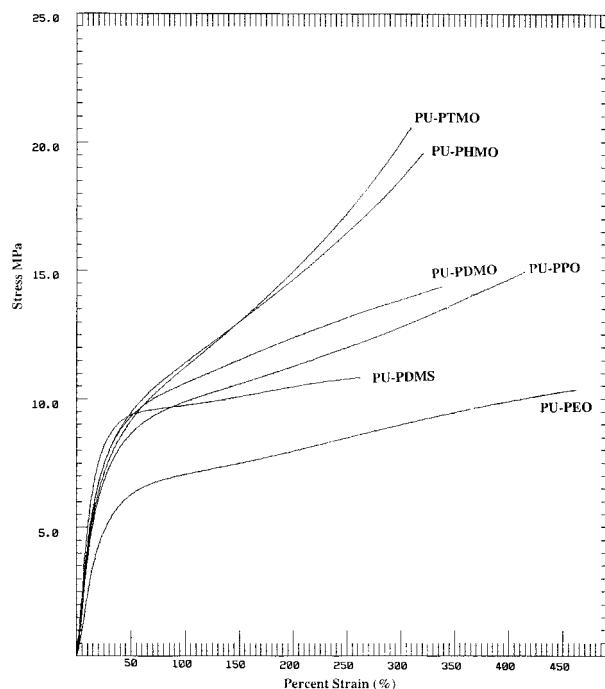


Figure 1 Stress-strain curves of polyether series polyurethanes.

the polycarbonate series. The number-average molecular weights of all polyurethanes were well above 50,000, the limit above which the mechanical properties are not significantly affected by MW differences.²⁰ Accordingly, the effect of MW weight differences on properties of these polyurethanes could be considered to be minor. All polyurethanes produced clear and transparent sheets when compression molded, with the exception of PU-PDMS, PU-PHCD, and PU-PSCD, which were slightly opaque in appearance.

Mechanical Properties

The mechanical properties of the polyurethanes are shown in Table III. PU-PDMS showed low ultimate tensile strength and elongation at break, and was the most stiff material, as shown by the high Young's modulus and flexural modulus. In the polyether series, the properties showed a dependency on the CH_2/O ratio of the macrodiol. The incorporation of PEO made the polyurethane more elastic and soft (low modulus and hardness) than the control PU, and in fact, PU-PEO was the softest of all polyurethanes investigated. However, the tensile strength was poor, almost identical to that of PU-PDMS. Similar results were observed for PU-PPO, except that the ultimate tensile strength (UTS) was higher than the con-

trol. As the CH_2/O ratio of the polyethers was increased from 2 to 6, the UTS gradually increased; the most noteworthy were the PU-PHMO and PU-PTMO where the UTS was nearly doubled. This trend discontinued for PU-PDMS, with a CH_2/O ratio of 10, and was the most hydrophobic polyether in the series (see solubility parameters in Table I, Experimental Section). The incorporation of the comacrodiol improved elasticity of the polyurethanes in all cases, and became softer as evidenced by decrease in Young's modulus, flexural modulus, and Shore hardness. Stress-strain curves shown in Figure 1 clearly illustrated the changes. The observed differences in properties can be attributed to the ability of comacrodiol to interact with both urethane hard segments and siloxane soft segments. PEO because of its hydrophilic nature may preferably associate with the hard segment increasing the size of soft/hard interfacial regions, perhaps to a too large extent, which compromised the mechanical properties. Alternatively, a very hydrophobic polyether such as PDMS would not sufficiently strengthen the interfacial regions, with similar end result, poor tensile strength. PHMO, on the other hand, appears to have the appropriate balance in interacting with both hard and siloxane soft segments, to strengthen the interfacial regions, resulting in very significant improvements in mechanical properties. PTMO also

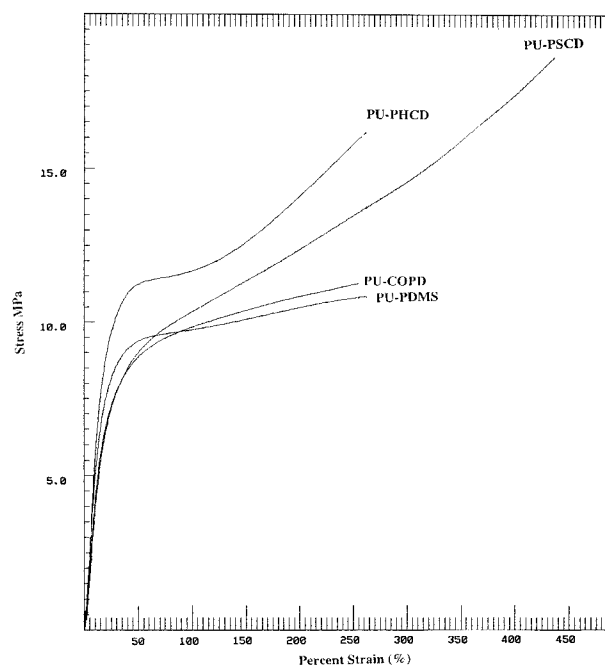


Figure 2 Stress-strain curves of polycarbonate series polyurethanes.

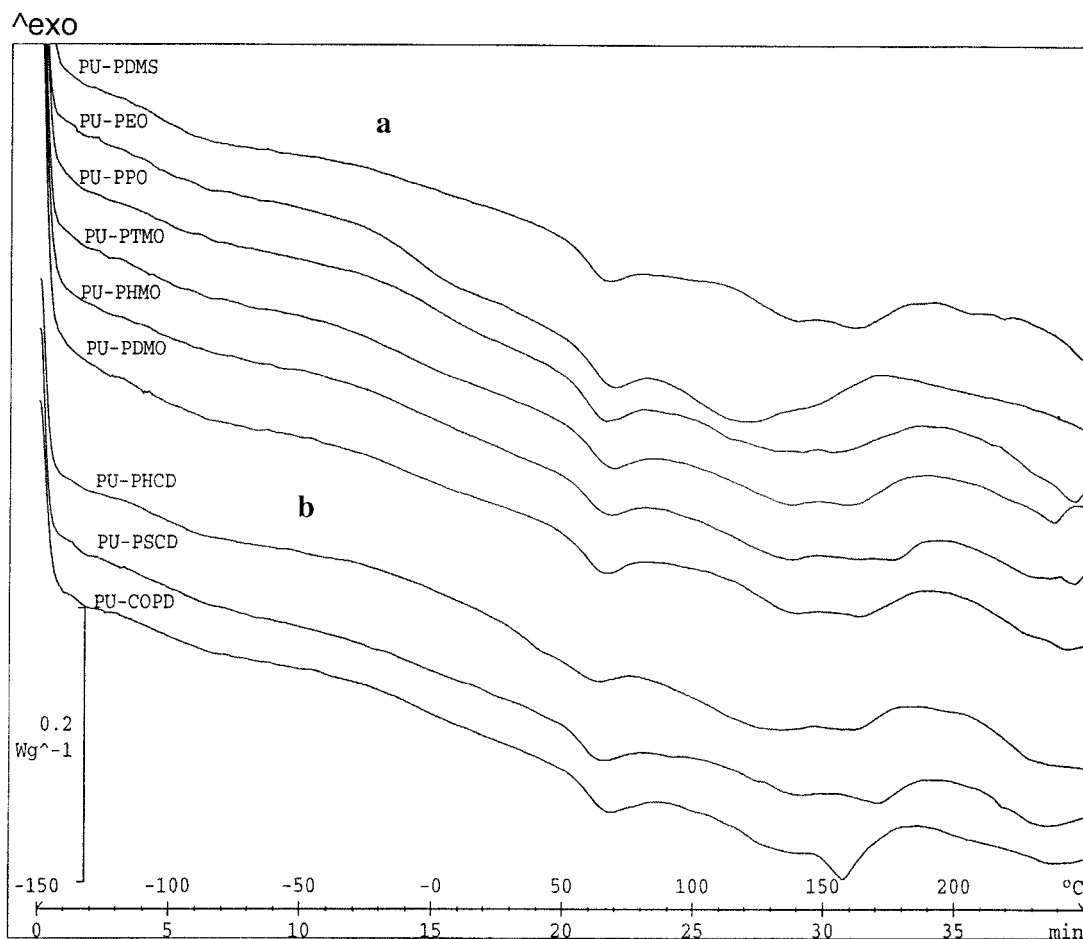


Figure 3 DSC thermograms of polyether (a) and polycarbonate series (b) polyurethanes (unannealed).

appears to show similar effects. The stress strain curves shown in Figure 1 clearly illustrated the effect of the comacrodiol on tensile properties.

In the polycarbonate series, PSCD showed the best compatibilizing effect, judging from the improvements in mechanical properties. Although the incorporation of the commercial polycarbonate diol increased the UTS, there was no significant change to other properties, particularly elongation at break and modulus; the PU in this case was as stiff as the control PU-PDMS. The copoly-carbonate-based polyurethane exhibited intermediate properties. In the polycarbonate series, PSCD was the best compatibilizing macrodiol. In this case, the siloxane and carbonate groups may enhance compatibility with soft and hard segments, respectively, reinforcing the interfacial regions. The stress-strain plots shown in Figure 2 show that, in general, the polycarbonate series polyurethanes were stiffer than those based on polyether comacodiol.

Polyurethane Morphology

Differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) were used to investigate the effect of comacrodiol structure on polyurethane morphology.

The DSC thermograms of the as-molded polyurethanes in the polyether series are shown in Figure 3(a). The main features of the DSC thermograms were the presence of a common transition centred around 60°C, and broad hard segment melting endotherms covering a wide temperature range. The transition centred around 60°C appeared to be a combination of a melting endotherm and a glass transitions, most likely due to single MDI linkages (those linkages where two soft segments are linked by one MDI). In general, the hard segment melting endotherms for all polyether series PUs appeared in a significantly broader temperature range than the control, indicative of improved phase mixing. In the

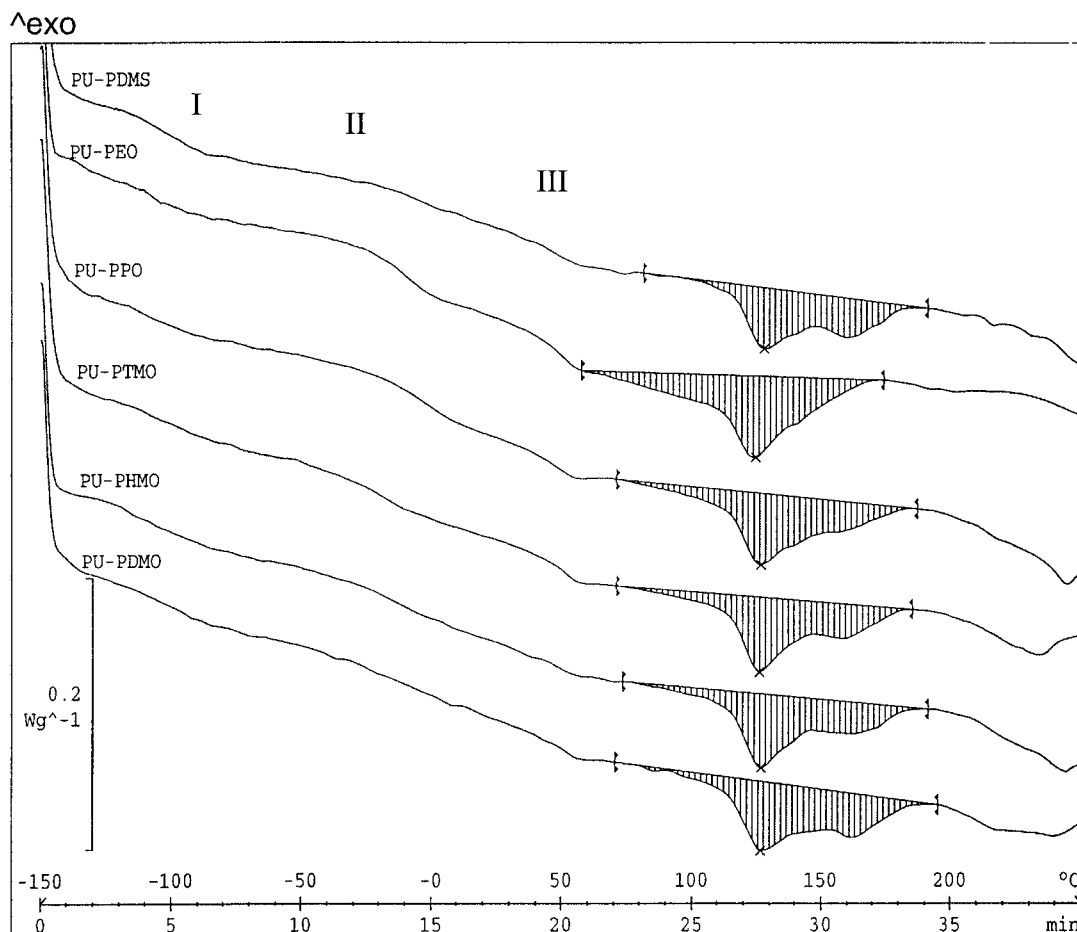


Figure 4 DSC thermograms of annealed (100°C) polyurethanes in the polyether series.

polyether series, PU-PEO and PU-PPO exhibited the largest effect, while PU-PDMS showed the smallest. The assignment of various thermal transitions was difficult due to their poor resolution. The presence of a mixed macrodiol based soft segment, the effect of PDMS end groups (ethoxypropyl), and also the thermal and processing effects may have largely contributed to this. To eliminate thermal and processing effects, all polyurethanes were annealed at 100°C, and then analyzed by DSC. The DSC thermograms of the annealed polyurethanes are shown in Figure 4.

DSC thermograms of the annealed polyurethanes exhibited sharper and fairly well-resolved hard segment melting endotherms, indicative of improved phase separation, as expected. The thermogram of PU-PDMS clearly showed two hard segment melting endotherms centered at 126 and 158.8°C, assigned, respectively, to melting of hard domains derived from MDI₂BDO and MDI₃BDO₂ type segments (see Table IV). These

assignments were made with reference to a literature reported procedure.²¹⁻²³ With the incorporation of a polyether the intensity of the higher temperature endotherm decreased significantly, and the temperature range covering the melting endotherms broadened. The largest changes were observed for PU-PEO and PU-PHMO, while PU-PDMO exhibited the smallest change. The melting endotherm centered around 125°C had a shoulder at the low temperature side, and the size of this varied according to the type of the polyether. PU-PEO exhibited the largest shoulder area, and PU-PDMO the smallest, which was comparable to that of PU-PDMS (see the shaded areas in Fig. 4). The increase in size of the shoulder region may indicate that the polyether segments phase mix with the hard segment to increase the interfacial regions; the driving force for which should be the hydrogen bonding between ether oxygen and urethane N—H groups. This compatibilizing effect of PTMO and PHMO appears to be very similar,

Table IV DSC Results of Polyether Series of Polyurethanes (Annealed at 100°C)

Polyurethane	T_g (PDMS) Onset, Midpoint, End-Set (°C)	T_g (PDMS- End Groups/ <i>co</i> -macrodiol) Onset, Midpoint, End-set (°C)	T_g (HS/SS Interface) Onset, Midpoint, End-set (°C)	HS Heat of Fusion (j/g) (Temp. Range, °C)	HS Melting Endotherm Peak Temperatures (°C)
PU-PDMS	-114.5, -101.8, -89.1	-16.26, -8.34, 0.14	37.6, 45.7, 53.9	10.75 (100 to 190)	126.0,158.8
PU-PEO	-111.5, -98.4, -85.7	-21.0, -11.4, -1.80	41.1, 46.5, 51.9	13.27 (67 to 170)	122.5,140.4
PU-PPO	-116.7, -100.3, -83.9	-18.1, -2.76, 7.09	37.6, 42.5, 47.4	12.35 (57 to 184)	124.7,157.5
PU-PTMO	-111.9, -97.9, -83.9	-24.5, -20.2, -16.0	45.4, 49.5, 53.5	11.75 (80 to 182)	124.4,157.9
PU-PHMO	-109.0, -99.4, -82.0	-24.5, -14.6, -4.82	45.5, 49.6, 53.6	12.42 (64 to 188)	125.3,162.2
PU-PDMO	-114.4, -100.0, -85.7	—	48.1, 51.5,54.8	13.36 (80 to 192)	125.8,160.5

judging by the size of the shoulder region. The heat of fusion of hard-segment melting endotherms are shown in Table IV. It was interesting to note that in all cases the heat of fusion was higher than that of PU-PDMS.

Annealing also caused a significant decrease in intensity of the transition around 60°C. The melting endotherm component of this transition appears to have shifted to higher temperature, leaving a clearly identifiable glass transition (T_g). Some polyurethanes also showed transitions above 220°C, perhaps due to thermal decompositions accordingly, not included in the discussion.

The assignment of various glass transitions was more difficult due to the complex nature of the soft segments in these materials. Three clear regions of glass transitions were observed in all polyurethanes. For the purpose of the discussions, the three regions are designated as I, II, and III, as labeled for PU-PDMS in Figure 4. Region I represents the T_g of PDMS. PU-PDMS showed a very weak transition with an onset of -130°C, assigned to γ transition, but the main PDMS T_g (α) onset was at -114.5°C. The incorporation of a polyether macrodiol caused a broadening of this glass transition region. The onset temperature also had shifted to slightly higher temperatures, except for PU-PDMO and PU-PPO.

The glass transition onset, midpoint, and end point temperatures are shown in Table IV.

In the case of PU-PDMS, the region II transition could be assigned to that of the end groups of PDMS, ethoxypropyl. However, in other polyurethanes the glass transitions of the polyethers (see Table I for T_g s of pure macrodiols) also could interfere, if these were shifted to higher temperatures resulting from phase mixing. In all cases, except PU-PPO and PU-PDMO, the T_g midpoint had shifted to lower temperatures, perhaps indicative of some interactions between ethoxypropyl and polyether soft segments.

The transition in region III is assigned to amorphous hard segment, most likely associated with single MDI linkages. The midpoint temperature of this transition varied in a narrow temperature range for all materials.

In summary, the DSC results showed that the incorporation of a polyether increased the interfacial regions of the polyurethanes, largely through compatibilization with the hard segment. PU-PEO and PU-PPO showed the largest effect, while PDMO had the least effect. The effect of PHMO and PTMO was very similar. Broadening of the PDMS (region I) glass transition as well as the shifting of region II (ethoxypropyl) transition indicated low-order interactions with ethoxypro-

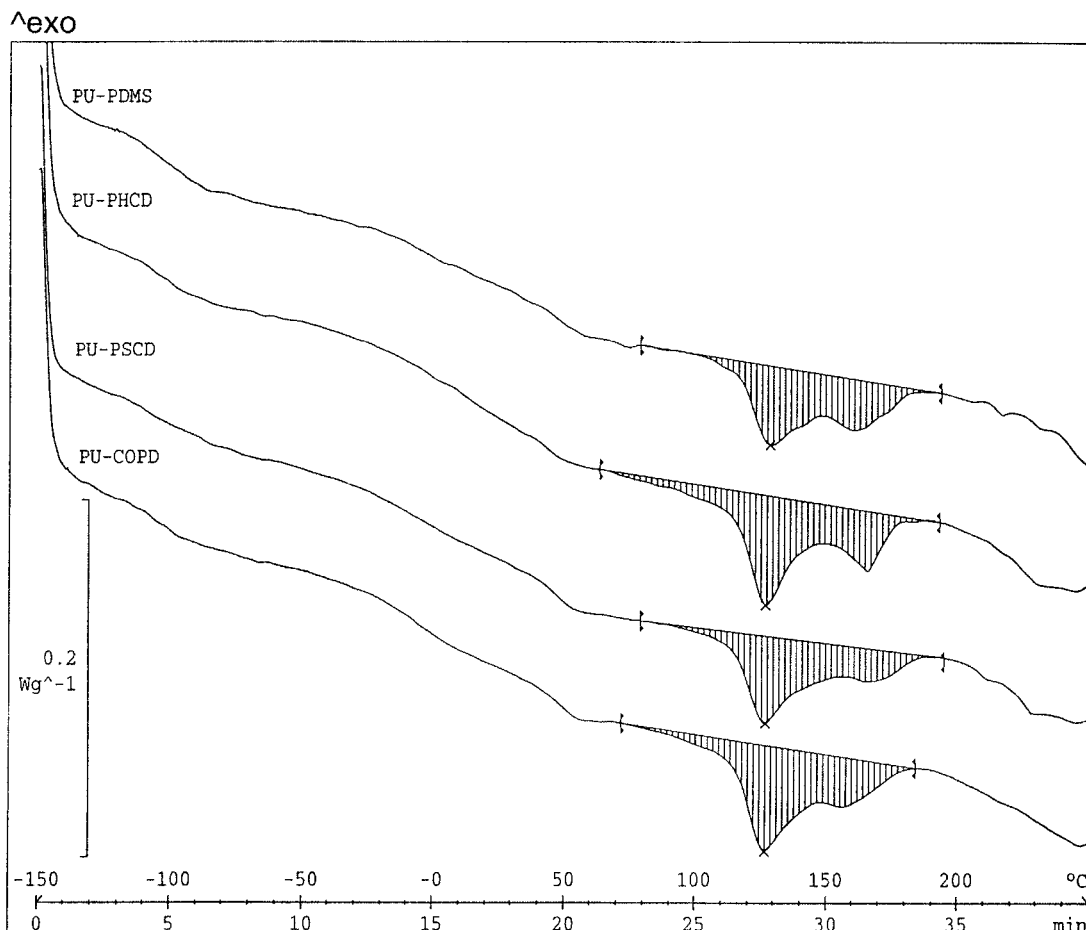


Figure 5 DSC thermograms of annealed (100°C) polyurethanes in the polycarbonate series.

pyl groups of the PDMS soft segment. This interaction appears to be minor compared with interactions with the hard segment.

Figures 3(b) and 5 show DSC thermograms of as-molded and annealed polyurethanes in the polycarbonate series. The thermal transitions and associated heat changes, estimated from DSC thermograms of the annealed polyurethane, are summarized in Table V. In the unannealed state, the DSC features were similar to those observed for the polyether series. Annealing significantly improved resolution of melting endotherm peaks, and glass transitions due to improved phase separation. All three polyurethanes showed a sharp melting endotherm around 125°C. A higher temperature (165°C) melting endotherm was also observed. Similar to that observed for polyether series, the incorporation of a polycarbonate macrodiol caused broadening of the hard-segment melting region as shown by the appearance of a shoulder on the low-temperature side. PU-PHCD

and PU-COPD showed similar effects (comparable heat of fusion), indicating that these two macrodiols compatibilized the hard segment to a similar extent, which was higher than that observed for PSCD.

The PDMS (region I) glass transition regions in all three materials were similar, indicating that the polycarbonate macrodiols did not phase mix with the PDMS soft segments. The region II transitions were also similar to that of the control PU-PDMS, indicating little or no mixing with ethoxypropyl end segments. These results suggest that the polycarbonates largely compatibilized the hard segment increasing the interfacial regions, consistent with their ability to form strong H-bond interactions through the carbonate functional groups. Of the three macrodiols investigated, this effect was lowest for the siloxy-carbonate macrodiol PSCD.

It is interesting to correlate the mechanical properties and morphology differences resulting

Table V DSC Results of Polycarbonate Series of Polyurethanes

Polyurethane	T_g (PDMS) Onset, Midpoint, End-set (°C)	T_g (PDMS End gp/co- macrodiol) Onset, Midpoint, End-set (°C)	T_g (HS/SS Interface) Onset, Midpoint, End-set (°C)	HS Heat of Fusion (j/g) (Temp. Range, °C)	HS Melting Endotherm Peak Temperatures (°C)
PU-PDMS	-114.5, -101.8, -89.1	-16.26, -8.34, 0.14	37.6, 45.7, 53.9	10.75 (100 to 190)	126.0,158.8
PU-PHCD	-111.3, -100.0, -84.1	—	38.5, 42.9, 47.4	13.42 (67 to 187)	125.4,164.6
PU-PSCD	-112.3, -99.1, -85.85	-20.57, -6.77, -7.02	41.33, 46.7, 52.1	10.56 (83 to 190)	124.4,164.6
PU-COPD	-110.4, -105.6, -98.2	-20.84, -8.66, 3.52	40.1, 47.4, 54.6	12.74 (77 to 185)	124.5,154.9

from the incorporation of a comacrodiol. PU-PEO, which showed the highest level of phase mixing, was also the softest as well as the poorest in ultimate tensile strength. PU-PHMO and PU-PTMO were the two materials in the polyether series with the best combination of mechanical properties. However, other studies^{3,9,24} have shown that PHMO was significantly better with respect to polyurethane processability and clarity. In the polycarbonate series, PU-PSCD, which had an intermediate level of phase mixing, exhibited the best combination of properties. These results indicated that macrodiols that can interact with the hard segment to increase the interfacial regions to a moderate level are the best compatibilizing macrodiols, useful in preparing siloxane-based polyurethanes with good mechanical properties.

Dynamic Mechanical Thermal Analysis

DMTA results also provided information on thermal transitions reflecting the morphological changes, corroborating DSC results. The dynamic mechanical properties of the polyurethanes in the polyether series are shown in Figure 6. $\tan \delta$ vs. temperature plots in Figure 6 revealed two main peaks for each polyurethane. The $\tan \delta$ peaks for the control PU-PDMS was broader than those for the other polyurethanes. Incorporation of the comacrodiol caused the higher temperature $\tan \delta$ peak temperatures to shift to lower temperatures,

consistent with the lower modulus observed for these materials. PU-PHMO exhibited the narrowest peak and the lowest peak temperature. The second $\tan \delta$ peak shifted to slightly higher temperatures in all cases, except for PU-PDMS, consistent with DSC results.

The storage modulus (E') vs. temperature plots (Fig. 6) clearly show a “softening” effect of

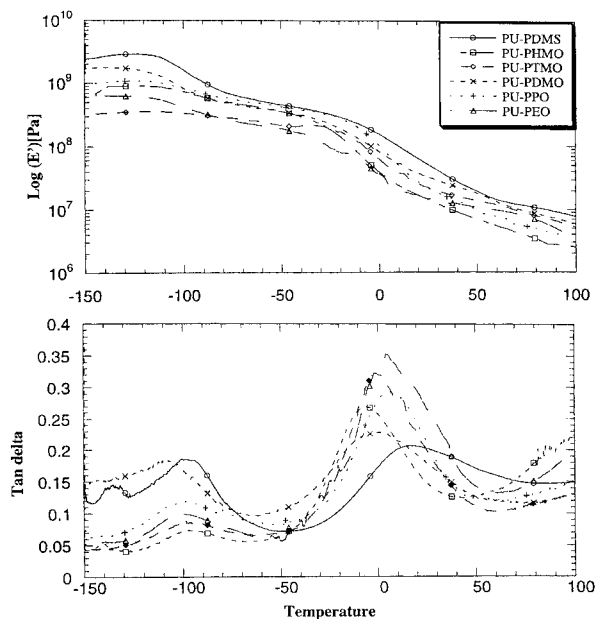


Figure 6 DMTA plots of polyurethanes (unannealed) in the polyether series.

Table VI Thermal Transition Temperatures of as-Molded Polyether and Polycarbonate Polyurethanes Based on DMTA Analysis

Sample	Tan δ Peak Temperatures		T_g (PDMS) ^a	T_g (Soft/Hard Interfacial Regions) ^a
PU-PDMS	-17.41	-100.32	-115.9	-13.6
Polyether Series				
PU-PEO	4.58	-99.56	-108.9	-9.82
PU-PPO	6.33	-99.61	-109.26	-14.43
PU-PTMO	-1.04	-98.61	-98.61	-17.61
PU-PHMO	-6.14	-96.94	-102.3	-25.15
PU-PDMO	-0.33	-108.26	-111.61	-17.93
Polycarbonate Series				
PU-PHCD	20.19, 40.52	-104.25	-107.64	-0.76
PU-PSCD	13.03	-102.81	-106.96	-2.12
PU-COPD	10.73	—	—	0.59

^a Estimated from loss modulus (E'') vs. temperature plots

the comacrodiol, as polyether series polyurethanes showed lower moduli than the control PU. It is noteworthy that the PU-PTMO exhibited the lowest modulus at temperatures below -50°C , but around the ambient temperature PU-PHMO exhibited the lowest modulus. In agreement with tensile test results, PDMO was least effective in lowering the modulus of PU-PDMS.

The glass transition temperatures of the soft segment and soft/hard segment interfaces, estimated from loss modulus vs. temperature plots, are shown in Table VI. The T_g (comparable to the midpoint T_g estimated from DSC results) shifted to lower temperatures in all cases, except for PU-PEO. Interestingly, the highest shift was observed for PU-PHMO. Also, the corresponding tan δ peak showed the highest shift to a lower temperature. Further, the PDMS glass transition showed a shift of about 14°C to a higher temperature, indicating some interaction with the PDMS segment. These results appear to suggest that PHMO was the best compatibilizing macrodiol among those investigated in this study, although such a clear distinction was not possible with the DSC results.

For the polycarbonate series of polyurethanes, the tan δ and storage modulus plots and the transition temperature results are shown in Figure 7 and Table VI, respectively. In this series, PSCD showed the lowest modulus in the temperature range tested. Generally, these polyurethanes were more rigid consistent with ambient temperature modulus results shown in Table III. The shifts in PDMS T_g were lower than those observed for PU-PTMO or PU-PHMO, consistent

with DSC results confirming little or no interaction with PDMS.

CONCLUSIONS

The results in this study clearly demonstrated that the structure of the comacrodiol influenced the properties and morphology of siloxane-based polyurethanes. All comacrodiols, except PEO, improved the UTS of the polyurethane; PHMO and

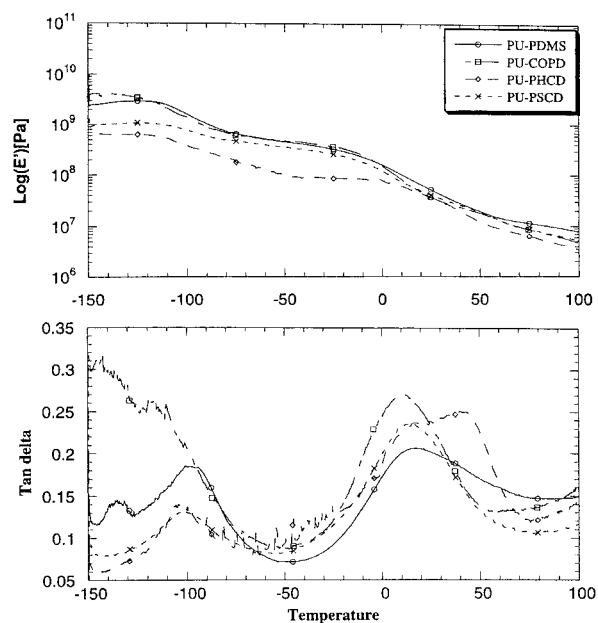


Figure 7 DMTA plots of polyurethanes (unannealed) in the polycarbonate series.

PTMO were the best polyether comacrodials, while PSCD was the best among the polycarbonates. Incorporation of the comacrodial made the polyurethanes more elastomeric with lower flexural modulus, but the effect was less significant with polycarbonates.

DSC and DMTA results strongly supported that the major morphological change associated with the incorporation of a comacrodial was the significant increase in the interfacial regions, largely through the compatibilization with the hard segment. The extent of compatibilization varied with the comacrodial structure; hydrophilic polyethers such as PEO were highly compatible, and consequently, had poor mechanical strength. Among the polyethers, PHMO was the best, having an appropriate level of compatibility with the hard segment for substantial improvement in mechanical properties. Siloxy carbonate comacrodial PSCD was the best among the polycarbonates. Temperature shifts of PDMS glass transition suggested some interactions with the PDMS soft segment, perhaps through the ethoxypropyl end groups, but the contribution from this to the overall compatibility appears to be minor in the 80/20 composition investigated.

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