

Poly(dimethylsiloxane)/Poly(hexamethylene oxide) Mixed Macrodiol Based Polyurethane Elastomers. I. Synthesis and Properties

PATHIRAJA A. GUNATILLAKE, GORDON F. MEIJS, SIMON J. MCCARTHY, RAJU ADHIKARI

Cooperative Research Centre for Cardiac Technology, CSIRO Molecular Science, Bag 10, Clayton South MDC, Victoria 3169, Australia

Received 19 July 1999; accepted 19 July 1999

ABSTRACT: The compatibilizing effect of poly(hexamethylene oxide) (PHMO) on the synthesis of polyurethanes based on α,ω -bis(6-hydroxyethoxypropyl) poly(dimethylsiloxane) (PDMS) was investigated. The hard segments of the polyurethanes were based on 4,4'-methylenediphenyl diisocyanate (MDI) and 1,4-butanediol. The effects of the PDMS/PHMO composition, method of polyurethane synthesis, hard segment weight percentage, catalyst, and molecular weight of the PDMS on polyurethane synthesis, properties, and morphology were investigated using size exclusion chromatography, tensile testing, and differential scanning calorimetry (DSC). The large difference in the solubility parameters between PDMS and conventional reagents used in polyurethane synthesis was found to be the main problem associated with preparing PDMS-based polyurethanes with good mechanical properties. Incorporation of a polyether macrodiol such as PHMO improved the compatibility and yielded polyurethanes with significantly improved mechanical properties and processability. The optimum PDMS/PHMO composition was 80 : 20 (w/w), which yielded a polyurethane with properties comparable to those of the commercial material Pellethane™ 2363-80A. The one-step polymerization was sensitive to the hard segment weight percentage of the polyurethane and was limited to materials with about a 40 wt % hard segment; higher concentrations yielded materials with poor mechanical properties. A catalyst was essential for the one-step process and tetracoordinated tin catalysts (e.g., dibutyltin dilaurate) were the most effective. Two-step bulk polymerization overcame most of the problems associated with reactant immiscibility by the end capping of the macrodiol and required no catalysts. The DSC results demonstrated that in cases where poor properties were observed, the corresponding polyurethanes were highly phase separated and the hard segments formed were generally longer than the average expected length based on the reactant stoichiometry. Based on these results, we postulated that at low levels (~ 20 wt %) the soft segment component derived from PHMO macrodiol was concentrated mainly in the interfacial regions, strengthening the adhesion between hard and soft domains of PDMS-based polyurethanes. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 2026–2040, 2000

Key words: poly(dimethylsiloxane); poly(hexamethylene oxide); mixed macrodiols; polyurethanes; synthesis; characterization

INTRODUCTION

Polyurethane elastomers represent an important class of segmented copolymers with excellent mechanical properties including high tensile strength, good tear and abrasion resistance, and

Correspondence to: P. A. Gunatillake.
Contract grant sponsor: Commonwealth Government of Australia.

Journal of Applied Polymer Science, Vol. 76, 2026–2040 (2000)
© 2000 John Wiley & Sons, Inc.

relatively good stability in biological environments. Accordingly, polyurethanes have been proposed for use in medical implants such as cardiac pacemakers, catheters, implantable prostheses, cardiac assist devices, heart valves, and vascular grafts. The excellent mechanical properties of segmented polyurethanes are attributed to their two-phase morphology resulting from microphase separation of soft and hard segments. In polyurethanes used for long-term implants the soft segments are typically formed from a polyether macrodiol such as poly(tetramethylene oxide) (PTMO) whereas the hard segments are derived from a diisocyanate such as 4,4'-methylenediphenyl diisocyanate (MDI) and a diol chain extender such as 1,4-butanediol (BDO).¹

Although for many years, PTMO-based polyurethanes were the materials of choice for certain types of medical implants, in some cases the polyurethane degraded and caused malfunction or the failure of the implant. This degradation led to surface or deep cracking, stiffening, erosion, or the deterioration of mechanical properties such as flexural strength.^{2–5} In PTMO-based polyurethanes it is generally accepted^{4,5} that the soft segment ether linkages are the most vulnerable sites for degradation. Furthermore, polyurethanes with a high level of soft segments (softer grades) tend to degrade significantly more than the harder grades. For example, Pellethane™ 80A degrades very severely while Pellethane™ 55D shows no signs of degradation as shown by animal implant experiments.^{6,7}

During the past few years we focused our research on developing degradation resistant polyurethanes for applications in medical implants. We were particularly interested in developing polyurethanes with low durometer hardness (Shore 85 A and lower), high flexibility, good processability, and resistance to degradation. Polyurethanes with such a combination of properties are not currently available. We previously reported⁸ the synthesis of a series of polyurethanes based on novel polyether macrodiols, poly(hexamethylene oxide) (PHMO), poly(octamethylene oxide) (POMO), and poly(decamethylene oxide) (PDMO). These polyurethanes showed improved resistance to stress cracking over that based on PTMO. However, the new polyurethanes exhibited higher hardness and modulus than those of PTMO-based polyurethanes with a comparable weight percentage of the soft segment.⁸ The present article describes the development of a range of polyurethanes containing α,ω -bis(6-hy-

droxyethoxypropyl) poly(dimethylsiloxane) (PDMS) with improved mechanical properties and biostability.

Incorporation of a nonpolar macrodiol such as PDMS into the polyurethane backbone is generally difficult because of its poor compatibility with conventional compounds used in polyurethane synthesis. This was demonstrated by recent studies on the synthesis of polyurethane elastomers based on nonpolar macrodiols such as polyisobutylene,^{9–11} PDMS,^{12–14} and polybutadiene.^{15–17} Because of the incompatibility with the polar hard segment, which largely results from the lack of hydrogen bonding, these materials generally exhibit a high degree of phase separation. Although increased phase separation generally improves mechanical properties, it was reported that the tensile strength and toughness of PDMS-based polyurethanes were inferior to those of conventional polyurethanes. Typically, the tensile strength and elongation at break of PDMS-based polyurethanes are about 7 MPa and 200%, respectively.¹⁷ These poor mechanical properties are attributed to a low glass transition temperature (T_g), the lack of soft segment crystallinity under strain, and compositional heterogeneity resulting from the poor segmental compatibility.

The interest in PDMS-based elastomers is due to their unique properties that include an extremely low T_g (-120°C), good oxidative stability, good blood contacting properties, and excellent insulating properties. However, previous attempts to incorporate PDMS into polyurethanes have not been very successful, particularly with respect to achieving materials with good clarity and mechanical properties. Speckhard and Cooper¹⁷ indicated that as a result of the large differences in solubility parameters between the PDMS and the hard segments, phase separation occurs during synthesis leading to compositional heterogeneity and a low molecular weight, which results in poor mechanical properties. Several techniques were reported in the literature to synthesize PDMS-based polyurethanes with improved mechanical properties, which primarily focused on increasing interfacial adhesion between the PDMS phase and the hard domains. These techniques include mixing with conventional polyether [PTMO, poly(propylene oxide)] or polyester macrodiols,^{13,14,18} the introduction of polar functionality to PDMS,^{19–21} the use of copolymers of PDMS and polyether or polyester,^{12,22,23} and hard segment modifications.²⁴ However, such attempts achieved only limited success.

The main objective of this study was to develop PDMS macrodiol-based polyurethanes with mechanical properties comparable to those of conventional polyurethanes. We investigated the use of PHMO to improve interfacial adhesion by promoting the compatibility of the hard and soft segments.²⁵ It is envisaged that the incorporation of a low level of a polyether macrodiol PHMO would promote segmental compatibility. We studied the effect of PDMS/PHMO composition, the method of polyurethane synthesis, and the PDMS molecular weight in preparing polyurethanes with good mechanical properties, clarity, and processability. Differential scanning calorimetry (DSC) was used as the main tool to examine morphological differences resulting from different polymerization conditions.

EXPERIMENTAL

Materials

The PDMS (X22-160AS, Shin Etsu), was dried at 105°C under a vacuum (0.1 torr) for 15 h to remove any volatile impurities. The MDI (Suprasec MPR, ICI), and BDO (GAF Chemicals) were used as received. The PHMO and PDMO were synthesized by acid-catalyzed condensation polymerization as reported previously.²⁶ The PHMO and PDMO were dried at 130°C under a vacuum (0.01 torr) for 4 h to remove any volatile impurities.

Hydroxyl Number Determination

The hydroxyl numbers of the purified and dried macrodiols were determined by the phthalic anhydride reflux procedure in accordance with ASTM D 2849.²⁷

Two-Step Bulk Polymerization

A series of polyurethanes containing various proportions of PDMS/PHMO was prepared by a two-step bulk polymerization procedure. In all polyurethanes the weight percentage of the hard segment was kept constant at 40 and the [NCO] : [OH] ratio was 1.00.

The following general procedure (PDMS/PHMO 80/20 ratio) describes the two-step method of synthesis used in this study. PDMS (1280 g, MW 940.3) and PHMO (320.0 g, MW 696.1) were placed in a 2-L round-bottom flask and degassed for 2 h at 80°C under a vacuum (0.1 torr). Molten MDI (877.75 g) was placed in a 3-L three-necked

round-bottom flask fitted with a mechanical stirrer, nitrogen inlet, and an addition funnel. The flask was then placed in an oil bath at 70°C. Degassed macrodiol mixture (1540 g) was added from the addition funnel to the MDI while stirring over a period of 30 min. After completing the addition, the mixture was heated at 80°C for 90 min with stirring under nitrogen. The prepolymer after degassing under a vacuum (0.1 torr) was weighed (800.0 g) into a 2-L polypropylene beaker. The BDO (46.27 g) was added quickly to the prepolymer and stirred thoroughly for 1 min. The viscous polymer was then poured onto a Teflon-coated metal pan and cured at 100°C for 4 h in a nitrogen-circulating oven. Other polyurethanes with different ratios of PDMS/PHMO in the series were similarly prepared.

Synthesis of PDMS/PHMO Series of Polyurethanes by One-Step Bulk Polymerization

A series of polyurethanes containing various proportions of PDMS/PHMO was prepared by a one-step bulk polymerization procedure. The weight percentage of the hard segment was kept constant at 40, and the [NCO] : [OH] ratio was 1.00. The following procedure for the preparation of a PDMS/PHMO (80/20 w/w) polyurethane illustrates the general procedure for the one-step bulk polymerization. Other polyurethanes based on different PDMS/PHMO ratios were prepared in a similar manner.

A mixture of predried PDMS (MW 969.6, 120.0 g), PHMO (MW 851.0, 30.00 g), BDO (15.94 g), and dibutyltin dilaurate (DBTD, 0.025 g, 0.01% of total solids) was placed into a 500-mL polypropylene beaker. The mixture was then degassed by placing the beaker in an oven at 80°C for 1.5 h under a vacuum (2 torr). Molten MDI (84.06 g) was quickly added to the macrodiol mixture at 70°C while stirring rapidly with a stainless steel spatula. After stirring for about 15 s the contents were poured onto a Teflon-coated metal tray and cured in a nitrogen-circulating oven at 100°C for 4 h.

One-Step Bulk Polymerization: Synthesis of Polyurethanes to Study Effect of Catalyst

Eight polyurethanes were prepared using a range of common catalysts used in polyurethane synthesis to investigate the catalytic effect in a one-step bulk polymerization procedure. The catalysts investigated included stannous octoate (SO), DBTD,

Table I Effect of Catalyst Type on Reaction Gel Time, Initial Temperature Rise, Sample Clarity, and Molecular Weight in One-Step Polymerization

Expt No.	Catalyst	Reaction Temp. after 12 s (°C)	Reaction Gel Time (s)	Sample Clarity	Number Average Molecular Weight
1	Control (no catalyst)	80	81	Opaque	37,670
2	SO	80	64	Opaque	55,520
3	DBTD	180	7	Transparent	74,850
4	DABU	80	34	Opaque	59,810
5	DTDS	160	6	Transparent	90,730
6	DABCO	85	43	Opaque	37,950
7	TMBD	80	63	Opaque	39,500
8	DMTD	172	6	Transparent	84,860

1,8-diazabicyclo[5,4,0] undec-7-ene (DABU), 1,3-diacetoxy-1,1,3,3-tetrabutyl-distannoxane (DTDS), 1,4-diaza-(2,2,2)-bicyclooctane, (DABCO), *N,N,N',N'*-tetramethylbutanediamine (TMBD), and dimethyltin dilaurate (DMTD).

The PDMS (360.0 g, MW 940.3), PHMO (90.0 g, MW 696.1), and BDO (45.49 g) were degassed in a 1-L round-bottom flask for 1.5 h at 80°C under a vacuum (2 torr). Each catalyst (0.005 g, 0.008 wt % of total weight) was weighed separately into 200-mL polypropylene beakers with 40.0 g of the macrodiol mixture and placed in an oven at 70°C under nitrogen. Molten MDI (20.55 g) at 70°C was weighed into a wet-tarred beaker, added to the macrodiol mixture, and stirred rapidly. The temperature rise in the reaction mixture was monitored by a thermocouple placed in the beaker. The thermocouple was connected to a chart recorder for continuous monitoring. The effectiveness of the catalyst was assessed by measuring the reaction gel time, the rate of initial temperature rise, and the polymer molecular weight, and by the clarity of the final product. The results are summarized in Table I.

Synthesis of Polyurethanes with Varying Hard Segment Percentage by One-Step Polymerization

A polyurethane with a hard segment content of 45 wt % was prepared using the following procedure: PDMS (100.00 g), PHMO (25.00 g), DBTD (0.011 g), and BDO (17.15 g) were degassed in a 500-mL polypropylene beaker by placing the beaker in an oven at 80°C for 60 min under a vacuum (2 torr). Molten MDI (85.12 g) at 60°C was quickly added to the macrodiol mixture in the beaker while stirring with a stainless steel spatula. After about 20 s of mixing, the viscous polymer was poured onto a Teflon-coated tray and cured at 100°C for 4 h in an oven under nitrogen. The cured polymer was opaque. Using a similar procedure but with appropriate quantities, three other polyurethanes with hard segment contents of 50, 55, and 60 wt % were prepared. In all cases the resulting polyurethanes were opaque and materials with a hard segment of 55 wt % and higher were brittle; accordingly, no tensile testing was performed. Table II shows the molecular weights of the prepared polyurethanes.

Table II Molecular Weight and DSC Results of As-Synthesized Polyurethanes with Different Hard Segment Contents Prepared by One-Step Polymerization

Hard Segment (wt %)	\bar{M}_n	\bar{M}_w/\bar{M}_n	Soft Segment (PDMS) T_g (Onset) (°C)	Major Hard Segment Melting Endotherm (°C)	Heat Capacity (J/g)
40	86320	1.9	-110.8	134.5 and 179.0	10.7
45	83950	1.6	-112.9	204.2	10.8
50	63350	1.4	-113.0	212.1	18.7
55	80150	1.5		217.3	23.6
60	73690	1.5		216.0	28.3

Table III Molecular Weights and Tensile Properties of Polyurethanes with Different Hard Segment Contents Prepared by Two-Step Polymerization

Hard Segment (wt %)	\bar{M}_n (\bar{M}_w/\bar{M}_n)	Ultimate Tensile Strength (MPa)	Elongation at Break (%)	Young's Modulus (MPa)	Stress at 100% Elongation (MPa)	Shore Hardness
40	76500 (1.61)	24	415	38	10	83A
45	59810 (1.41)	15	285	58	12	41D
50	52870 (1.43)	24	300	131	18	50D
55	48000 (1.41)	22	175	193	22	57D
60	47070 (1.37)	30	200	220	27	65D

Polyurethanes with Different Hard Segment Content by Two-Step Polymerization

The following procedure illustrates the preparation of a polyurethane with a hard segment weight percentage of 45. A mixture of PDMS (MW 940.3, 80.00 g) and PHMO (MW 696.1, 20.00 g) was degassed at 80°C for 60 min under a vacuum (0.1 torr). MDI (68.09 g) was placed in a 500-mL three-necked round-bottom flask fitted with a mechanical stirrer, a nitrogen inlet, and an addition funnel. The macrodiol mixture (100.00 g) was added to the MDI through the addition funnel over a period of 30 min at 70°C under a slow stream of nitrogen. After the addition was complete, the reaction was continued for 2 h at 80°C with stirring. The prepolymer was then degassed for 15 min at 80°C under a vacuum (0.1 torr). The prepolymer (160.00 g) was weighed into a 500-mL polypropylene beaker and chain extended with BDO (13.06 g), and the polyurethane was cured in a Teflon-coated metal pan at 100°C in a nitrogen-circulating oven for 4 h.

Using a similar procedure, three other polyurethanes were prepared with hard segment contents of 50, 55, and 60 wt %. The molecular weights of the resulting polyurethanes are shown in Table III.

Size-Exclusion Chromatography

The size-exclusion chromatography of the polyurethanes was carried out at 80°C with 0.05M lithium bromide in *N,N*-dimethylformamide (DMF) as the eluent on a Waters Associates chromatograph with three Ultrastyrigel HT columns (10⁵, 10³, and 500 Å). The system was equipped with a refractive index detector and calibrated with narrow distribution polystyrene standards. The results are therefore expressed 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 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. The dumbbells were stored under ambient conditions for 4 weeks before tensile tests and hardness measurements were carried out.

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 six replicates. Hardness measurements were carried out using a Shore A Durometer. The flexural modulus measurements were performed

Table IV Calculated Solubility Parameters

Compound	Calcd Solubility Parameter, δ (cal/mL) ^{1/2}
BDO	13.98 ± 0.05
MDI	9.94 ± 0.08
PTMO, MW 1000	9.55 ± 0.09
PHMO, MW 700	9.34 ± 0.07
PDMO, MW 800	9.03 ± 0.13
PDMS	
MW 1000	6.66 ± 0.20
MW 2180	6.19 ± 0.14
Prepolymer of MDI and PDMS (1000)	7.52 ± 0.17
(MDI-BDO) ₁ hard segment	12.2–12.7 ^a

The parameters were calculated using the MSI Amorphous Cell package with the PCFF2 force field.

^a From Tonelli et al.³⁰

using a three-point bend configuration with 52.8-mm spacing. A 1-kN load cell was used with crosshead speed of 14 mm/min, and the results reported are mean values for three replicates.

DSC

The samples were dried at 45°C for 48 h under a vacuum (0.1 torr) to remove moisture prior to recording the thermograms. The DSC thermograms were recorded over a temperature range of -150 to 250°C on a Mettler DSC 30 heat flux calorimeter that was calibrated for heat flow and temperature. The experiments were carried out at a heating rate of 10°C/min under a nitrogen purge of 20 mL/min. Sample weights were 15–25 mg.

RESULTS AND DISCUSSION

Solubility Parameters of Reactants

The synthesis of polyurethanes based on PDMS macrodiols is generally difficult because of the incompatibility of PDMS with the conventional hard segment forming compounds such as MDI and BDO. Often one needs compatibilizing solvents such as DMF or THF to carry out the polymerization.^{13,28} In a typical one-step bulk polymerization process the polyurethane obtained is usually opaque, compositionally heterogeneous, and low in molecular weight, which is due to premature phase separation. This behavior could be rationalized by considering the calculated solubility parameters of PDMS, BDO, and MDI as shown in Table IV.³⁰ The solubility parameter of the PDMS macrodiol is significantly lower than those of MDI, PTMO, and BDO, which are the components used for preparing conventional poly(ether urethanes). Accordingly, the use of a second macrodiol as a compatibilizer and the polymerization conditions would have a significant effect on the properties and morphology of such polyurethanes.

The miscibility of PDMS with PTMO, PHMO, and PDMO, was examined at 80°C. Mixtures of PDMS with 20, 40, 60, and 80 wt % PHMO were miscible at 80°C whereas PTMO was immiscible. These mixtures stayed cloudy and separated into two layers upon cooling to room temperature. On the other hand, PDMO, which is less polar than PTMO, was miscible with PDMS at 80°C as demonstrated by the clarity of the solution. Although

the calculated solubility parameters (see Table IV) of the three macrodiols do not differ greatly, the trend reflected an increasing hydrophobicity toward PDMO, as expected. The results of miscibility tests with PDMS confirmed this. Based on the solubility differences, we expect PHMO and PDMO to be better compatibilizing macrodiols than PTMO.

Effect of Soft Segment Composition on Properties of PDMS-Based Polyurethanes

A series of polyurethanes was prepared by using different ratios of PDMS/PHMO to establish the optimum macrodiol ratio required for preparing polyurethanes with good mechanical properties and processability. The synthesis was carried out by a two-step bulk polymerization procedure with DBTD as the catalyst.

As the amount of PHMO content was increased, the clarity of the as-synthesized material decreased. Materials with 0, 20, and 100% PHMO were clear and transparent. Figure 1 shows the effect of the PHMO content on the ultimate tensile strength and fail strain. The results clearly demonstrated that the tensile strength significantly increased as the polyether content of the soft segment was increased. The polyurethane with 20% PDMS showed the highest ultimate tensile strength. Generally, all materials were elastomeric with an elongation at break of over 300%, which increased as the polyether content was increased.

The incorporation of only 20% of the PHMO increased the tensile strength by nearly 50%.

Similar trends in tensile properties were observed when the polyurethanes were prepared by a one step-bulk polymerization procedure. Figure 2 shows the change in flexural modulus of the polyurethanes in the series. With only 20% of the PHMO macrodiol, the flexural modulus decreased by 36%. For the intermediate ratios the flexural modulus decreased with increasing PHMO content, but the decrease was only marginal. The decrease in flexural modulus could be attributed to the compatibilizing effect of PHMO. As shown in Figure 2, annealing of the polyurethanes caused the flexural modulus to increase as expected and the increase was more prominent in compositions high in PDMS. This is not surprising because annealing increases phase separation in polyurethanes, and the change is more significant in polyurethanes with high siloxane content.

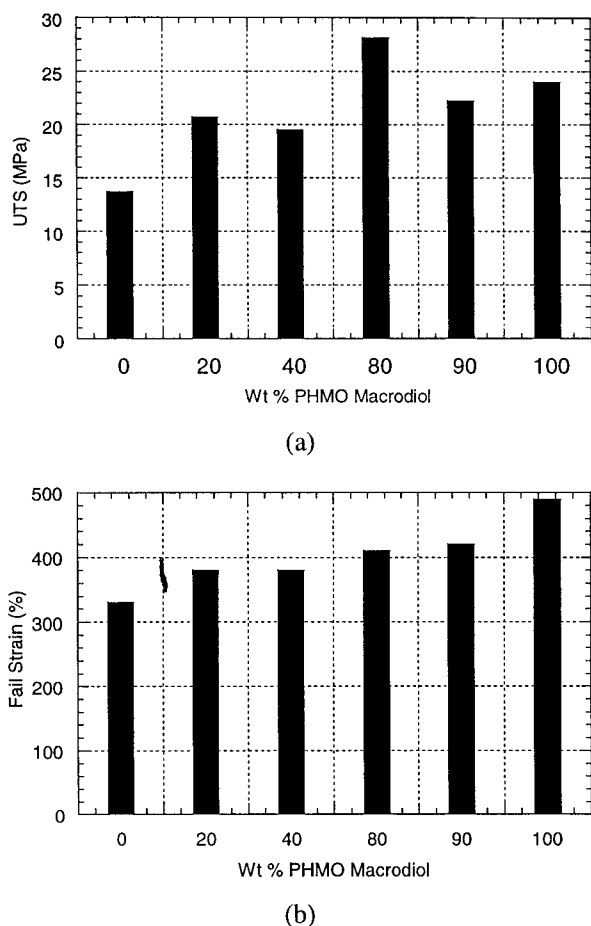


Figure 1 The effect of PHMO content on (a) ultimate tensile strength and (b) fail strain of the PDMS/PHMO series of polyurethanes prepared by a two-step polymerization.

The thermal processability of each of the polyurethanes prepared by the one-step method was evaluated by extrusion into thin films (0.2 mm thick) using a single screw Brabender extruder. The extrudability of the polyurethanes was assessed by observing the clarity of the film, melt strength, postextrusion tackiness, appearance (surface roughness), and sensitivity to variation in processing temperature.

The polyurethane prepared from a macrodiol mixture containing PDMS/PHMO (80/20) was the best in terms of overall processability in that it produced a film with no observable surface defects and it had the best film clarity. The polyurethane based on pure PDMS, although extruded well, showed a high level of surface imperfections and felt rough to the touch. The other polyurethanes based on 20, 40, and 60% PDMS also extruded well but had inferior film clarity.

Thermal Analysis of PDMS/PHMO Series of Materials

DSC was used to understand the morphological effects when varying the soft segment composition in the series of polyurethanes. Figure 3 shows the DSC thermograms of annealed (100°C) polyurethanes.

Polyurethane elastomers typically exhibit multiple DSC endotherms due to short-range order of the hard phase resulting from storage or annealing effects and those associated with long-range order of crystalline hard segments. The interpretation of this multiple endothermic behavior in polyurethanes was thoroughly investigated. The assignment of thermal transitions observed for various materials in this study was made with reference to a system previously reported.^{29,31,32} Primarily based on model compound studies and annealing experiments, melting endotherms are assigned to disordering of structures resulting predominantly from single MDI-derived sequences and MDI₂BDO-, MDI₃BDO₂-, and MDI₄BDO₃-derived hard segments and are labeled as T1 (50–70°C), T2 (100–180°C), T3 (195–210°C), and T4 (211–217°C), respectively. The extent of the use of this approach in our study is limited to polyurethanes with well-resolved high temperature transitions.

In the series all polyurethanes showed a common melting endotherm at around 55°C (see Fig. 3), which was attributed to the order resulting

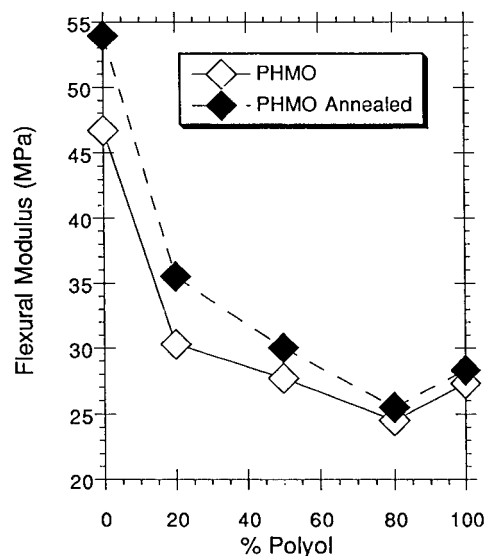


Figure 2 The effect of PDMS/PHMO composition on the flexural modulus of polyurethanes prepared by one-step polymerization.

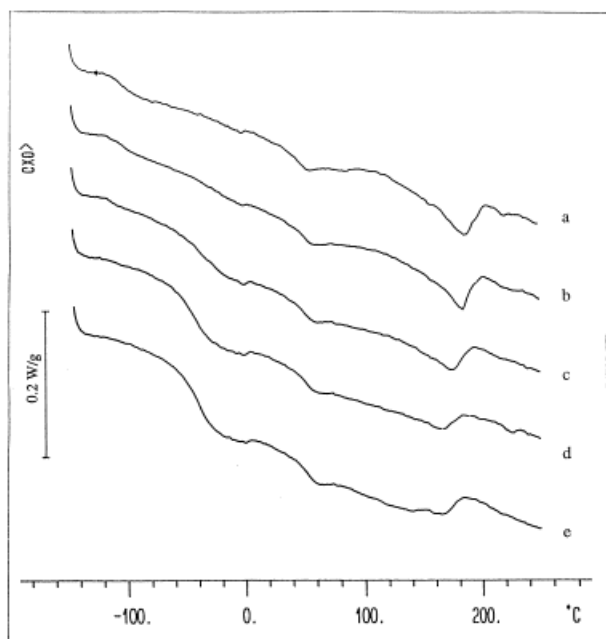


Figure 3 DSC thermograms of annealed polyurethanes based on different PDMS/PHMO compositions: (a) 0, (b) 20, (c) 50, (d) 80, and (e) 100 wt % PHMO in PDMS.

from single MDI units (T1 transition). Material based on pure PDMS exhibited the most phase-separated morphology. This was evidenced by the presence of melting endotherms at 117.5, 184.1, and 219.2°C (Table V), which were respectively assigned to melting of hard segment regions derived predominantly from T2 (MDI-BDO-MDI), T3 (MDI-BDO-MDI-BDO), and T4 (MDI-BDO-MDI-BDO-MDI) type structural units, T3 being the most predominant. Incorporation of 20% PHMO caused the T3 to move lower to 179°C and showed only two major endotherms. This trend continued with increasing PHMO content, and the material based on pure PHMO showed a relatively broad hard segment melting endotherm. It was interesting to note that as the PHMO content was increased the average hard segment size distribution changed more toward T2. The intensity of T2 increased while that of T3 decreased and the peaks moved to lower temperatures, which is indicative of increased phase mixing as the PHMO content was increased. As expected, the soft segment glass transition temperatures of the PDMS and PHMO phases were clearly identifiable only in polyurethanes where the respective macrodiol content was high. The T_g onset temperature of the PHMO phase was highest in the composition with 80% PDMS, indicating that

the PHMO is present in a more phase mixed state than in the other materials. It was interesting to note that this material was the most transparent and produced the clearest film in the processing by extrusion. In polyurethanes with 50 and 20% PDMS the T_g onset was closer to that of the pure PHMO, which is indicative of relatively more phase separated morphology, and these materials produced films with low clarity in extrusion. In all compositions the T_g onset of the PDMS phase remains unchanged, appearing very close to the T_g of the pure PDMS. This result may indicate that the PDMS remains largely immiscible with either PHMO or the hard segment. At low levels of PHMO (about 20%) in the composition, PHMO may be more associated with the hard segment and is probably concentrated more in the interfacial regions. As the PHMO content was increased, it may have formed its own soft segment phases, which may be responsible for the observed opaque appearance. Further work such as SAXS would be required to clearly understand the morphology of these polyurethanes.

These results indicated that siloxane-based polyurethanes with good mechanical properties and processability could be prepared by incorporating a low level of PHMO macrodiol. The optimum level is around 20 wt %, and the DSC results indicated that at this level the PHMO phase is largely associated with the interfacial regions.

Effect of Polymerization Conditions and PDMS Molecular Weight on Properties and Morphology

As discussed previously, the solubility differences of the components (Table IV) can have a significant effect on the morphology of PDMS-based polyurethanes. The more compatible components may react first (e.g., MDI and BDO), particularly in a one-step polymerization, leading to hard do-

Table V DSC Results of PDMS/PHMO Series of Polyurethanes Prepared by One-Step Polymerization

PHMO Macrodiol Content (%)	T_g (Onset)		Peak Temp. (°C)
	PDMS	PHMO	
0	-112.5		117.5, 184.1, 219.2
20	-112.0	-31.8	124.1, 179.0
50	-116.3	-45.8	130.6, 172.3
80		-46.3	120.9, 162.6
100		-40.6	113.9, 162.2

mains rich in segments longer than the expected average length based on reactant stoichiometry. This may eventually lead to materials that are compositionally heterogeneous and/or highly phase separated with poor mechanical properties and clarity. It is also expected that one may achieve materials with significantly different morphologies, depending on the polymerization conditions. We investigated the effect of the method of synthesis, catalyst type, relative amount of the hard segment, and the molecular weight of PDMS macrodiol on the polymerization reaction and the morphology of the resulting polyurethanes. DSC was used to assess the morphological differences of synthesized polyurethanes prepared under different polymerization conditions. Because processing or other thermal treatments (i.e., thermal history) could change the polyurethane morphology, DSC analysis was carried out on as-synthesized polyurethanes, primarily to understand the morphological differences resulting from the method of synthesis and other reaction variables.

One-Step Polymerization: Effect of Type of Catalyst

A polyurethane formulation based on PDMS/PHMO (80/20), MDI, and BDO with a 40 wt % hard segment was used to investigate the catalyst effect. The 80/20 ratio was chosen because this combination, as shown previously, gave polyurethanes that were clear and transparent with good mechanical properties. The effectiveness of various catalysts in the polymerization was assessed by measuring reaction gel time, initial temperature rise during polymerization, and number average molecular weight (M_n) of the cured polymer. The details of the procedure are given in the Experimental section. Table I shows the results observed for the seven different catalysts investigated. The uncatalyzed polymerization yielded an opaque polymer with a low molecular weight, and the gel time was relatively long. Further, the initial rise in reaction temperature was only 10°C. On the other hand, when an effective catalyst such as DBTD (expt 3 in Table I) was used, the reaction was very fast with a gel time of only 7 s, the polymer was transparent and had a molecular weight of 75,000, and the reaction temperature rose to 180°C in 12 s. These results showed that the most effective catalysts for the polymerization were DBTD, DTDS, and DMTD.

It was interesting to note that amines as a class of compounds were ineffective in catalyzing

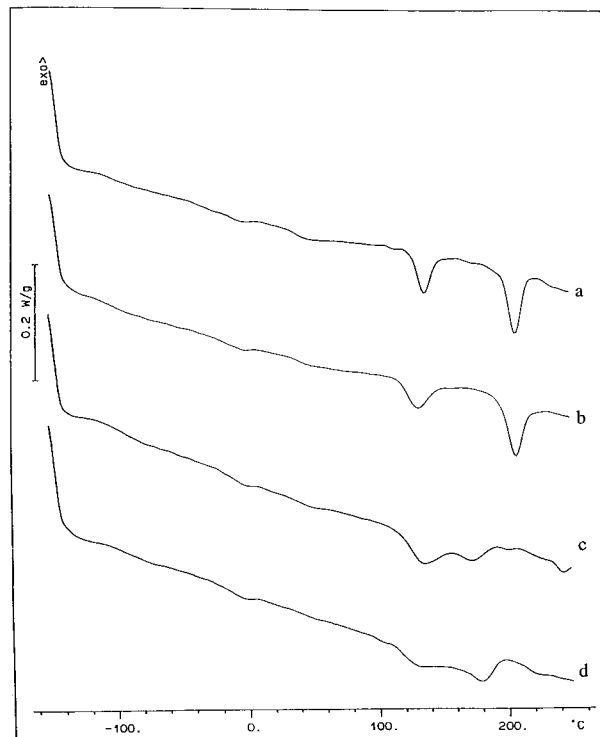


Figure 4 DSC thermograms of as-synthesized PDMS/PHMO (80/20) based polyurethanes (one step): (a) uncatalyzed, (b) stannous octoate, (c) dibutyltin dilaurate, and (d) dimethyltin dilaurate.

the polymerization. Further, we noted that in all of the effective tin catalysts, tin was present in the tetracoordinated form (Sn^{4+}) while those in the dicoordinated state were less effective. This selectivity could be attributed to the difference in miscibility of the catalysts with the reactants, particularly PDMS. Perhaps the presence of four alkyl groups on the Sn may have improved the miscibility of the catalyst with PDMS, enabling its bringing of necessary functional groups to the reaction site and leading to a more homogeneous polymer. Likewise, amines, which are more polar than PDMS, may have poor miscibility with PDMS.

The DSC results confirmed that the uncatalyzed polymerization produced a polyurethane that is highly phase separated. Figure 4 shows the DSC thermograms of as-synthesized polyurethanes obtained in uncatalyzed, and catalyzed polymerizations by SO, DBTD, and DMTD. All polyurethanes showed multiple hard segment melting endotherms. In cases where the catalysts were efficient (expts 3 and 8 in Table I), the resulting polyurethane exhibited a relatively phase

mixed morphology as demonstrated by the presence of broad melting endotherms for the hard segment. The main melting endotherms for these polymers were spread over the 100–200°C temperature range. On the other hand, the material in the uncatalyzed polymerization showed sharp and well-resolved hard segment melting endotherms. This is primarily because of the sensitivity of T1 and T2 type endotherms to annealing and the possible association of disordering of folded, longer hard segments in T2 type endotherms. Accordingly, the material produced in the uncatalyzed polymerization exhibited a high level of order, resulting from predominantly T2 (140°C) and T3 (205°C) type transitions, while the polyurethanes obtained in catalyzed (DBTD or DMTD) polymerizations contained mostly MDI₂BDO (T2) type order (average size based on reactant stoichiometry) along with some mixing of T2 and T3. Some of the minor peaks observed in these thermograms may be due to annealing and storage effects.

The DSC thermogram of the material polymerized with SO (see Fig. 4) and those of others based on less effective catalysts exhibited melting endotherms similar to that observed for the polymer in uncatalyzed polymerization. Their thermograms also showed soft segment T_g values very close to those of the pure macrodiols, indicating highly phase separated morphologies.

Effect of Hard Segment Content on One-Step Polymerization

A one-step polymerization procedure (with effective catalyst) was employed to prepare a series of polyurethanes with hard segment contents in the 45–60 wt % range to explore the range of polyurethanes with different properties that one could synthesize by this method. Unlike the 40 wt % hard segment composition, in all other cases the reaction mixture remained cloudy during mixing, indicating the poor miscibility of the reactants; accordingly, the resulting polyurethanes were not transparent. The polyurethane with a 40% hard segment was easily compression molded and had good mechanical properties. Further, with the exception of the material with the 45% hard segment, the others were all brittle and very weak mechanically and could not be molded into flat sheets for tensile testing. The composition based on the 45% hard segment showed a 12-MPa ultimate tensile strength and 70% elongation at break. The SEC results of the polyurethanes (Ta-

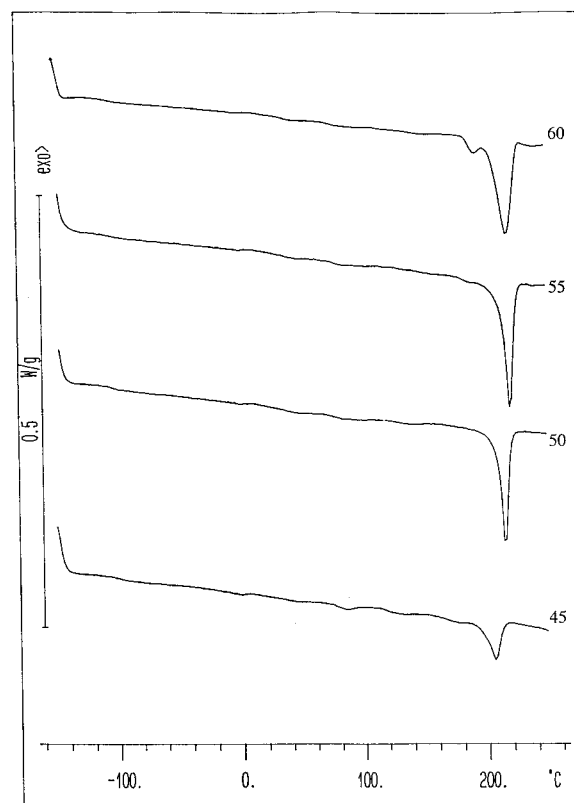


Figure 5 DSC thermograms of as-synthesized PDMS/PHMO (80/20) polyurethanes (one step) based on (a) 45, (b) 50, (c) 55, and (d) 60 wt % hard segments.

ble II) indicated that the molecular weights were generally high with a unimodal distribution, indicating that the polyurethanes produced were compositionally homogeneous. The poor mechanical properties therefore appeared to be due to the very high level of phase separation in these materials, as shown by the DSC results.

The DSC thermograms shown in Figure 5 indicate that all four materials were very highly phase separated, and the consequent lack of interfacial adhesion may have resulted in materials with poor mechanical strength. A sharp hard segment melting endotherm with high heat capacity (Table II) was observed in the 200–220°C temperature range in each of the cases. Further, the T_g of the PDMS component of the soft segment was close to that of pure PDMS. The high temperature melting endotherm could be attributed to the melting of the long-range crystalline order resulting from predominantly T4 type (MDI₄BDO₃) structural units. The other minor melting endotherms observed were perhaps due to predominantly T1, T2, and T3 type transitions and/or

storage annealing effects. The presence of these high temperature melting endotherms makes the materials difficult to process thermally, because one needs to use temperatures over 200°C, above which the polyurethanes generally start to degrade thermally.

Two-Step Polymerization

Two-step polymerization offers advantages over one-step polymerization in polymerizing incompatible monomers. The end capping of the macrodiol to form the prepolymer in the first step of a two-step polymerization changes the solubility parameter of the macrodiol (see Table IV). This enables one to prepare a more homogeneous polymer during chain extension in the second step because all the macrodiol hydroxyls are reacted with the diisocyanate in the first step. A polyurethane based on PDMS/PHMO (80/20) was prepared by a two-step bulk polymerization (with no catalysts) to investigate the effect of the method of synthesis on polyurethane morphology.

During the prepolymer synthesis the reaction mixture stayed cloudy, indicating the poor miscibility of PDMS in MDI. However, as the reaction progressed the solution turned clear and the final prepolymer was a clear, transparent, and viscous liquid. The solution turned slightly cloudy during chain extension, but BDO mixed well with the prepolymer. Unlike the polymer obtained in the catalyzed, one-step polymerization, the cured polymer had a slightly hazy appearance.

Figure 6 shows the DSC thermogram of the as-synthesized polyurethane. The major melting endotherm was centered at 148°C. This could be assigned to a T2 type transition (MDI₂BDO), consistent with the reactant stoichiometry (approximate macrodiol : MDI : BDO molar ratio = 1 : 2 : 1), and the method of polymerization used. This confirms that in the two-step polymerization there is better control over the segment length distribution even when polymerizing incompatible systems.

It is interesting to compare this thermogram (Fig. 6) with that observed for the polyurethane obtained in a one-step uncatalyzed polymerization [see Fig. 4(a)]. The results clearly demonstrated that the two-step method yields materials that are relatively more phase mixed and appeared to be more homogeneous with respect to the distribution of the hard segment size. On the other hand, when compared with the one-step catalyzed polymerization [see Fig. 6(c,d)], the ma-

ior difference was the presence of an endotherm due to segments rich in the T3 (or mixed T2 and T3) type transition (~ 180°C). As seen in Figure 6, there were several other less intense peaks, presumably due to T3 and T4 transitions and/or those due to storage and annealing effects.

The results therefore clearly demonstrated that the two-step method yields polyurethanes that are compositionally more homogeneous even if a catalyst is not present.

Polyurethanes with Different Hard Segment Contents by Two-Step Polymerization

A series of four polyurethanes with hard segment weight percentages of 45, 50, 55, and 60 was prepared by two-step bulk polymerization to investigate whether this method is more suitable to prepare polyurethanes with hard segments higher than 40%. The soft segment was again based on PDMS/PHMO (80/20) while the hard segment was based on MDI and BDO. Unlike the materials obtained in the one-step polymerization, the polyurethanes obtained were not brittle and had good mechanical properties as shown by the tensile properties in Table III.

The DSC results show (Fig. 7) that the polyurethanes were more phase mixed than those prepared by the one-step polymerization. The hard segment melting endotherms were much broader and spread in a very wide temperature range. As expected with an increased hard segment content, these endotherms moved to higher temperature

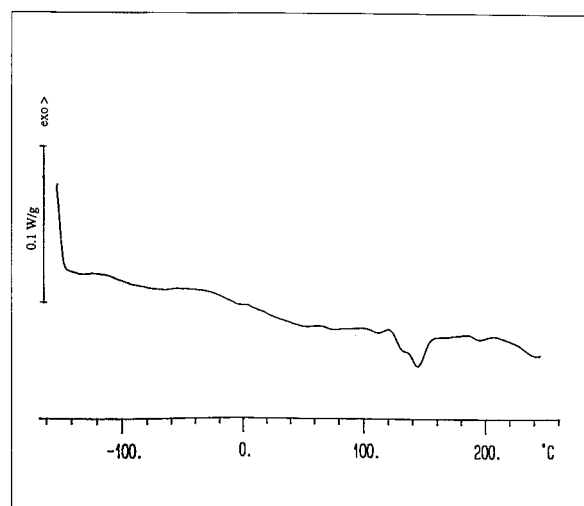


Figure 6 A DSC thermogram of PDMS/PHMO (80/20) as-synthesized polyurethane prepared by two-step polymerization.

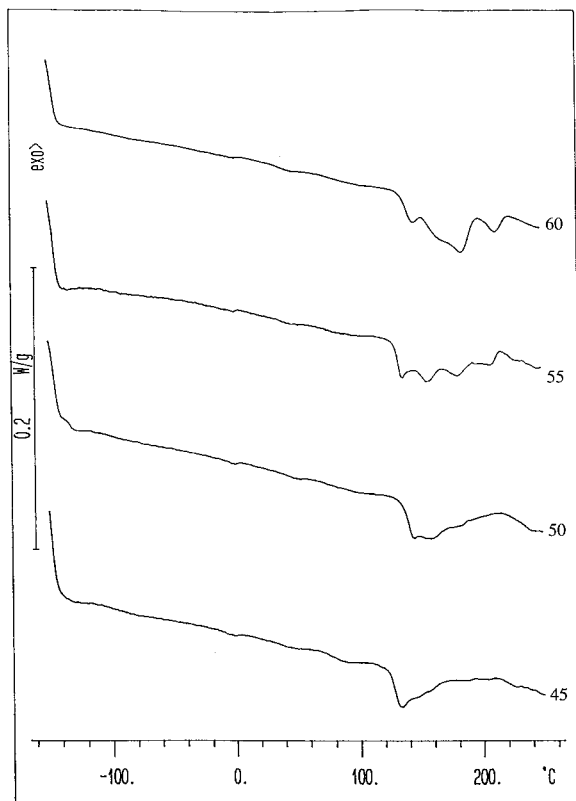


Figure 7 DSC thermograms of as-synthesized PDMS/PHMO (80/20) polyurethanes (two step) based on (a) 45, (b) 50, (c) 55, and (d) 60 wt % hard segments.

ranges and that for the 60% composition appeared in the 130–230°C range.

These results clearly show that the two-step method is preferred over the one-step method in preparing PDMS-based polyurethanes covering a range of hardnesses.

Effect of PDMS Molecular Weight

The hydrophobicity of the PDMS macrodiol is expected to increase with the increase in macrodiol molecular weight (low end-group concentration); in fact, the calculated solubility parameters (see Table IV) supported this. To investigate the effect of the PDMS molecular weight on the polymerization, two polyurethanes based on PDMS (MW 2181)/PHMO (MW 696) (80/20) were prepared by using the one-step and two-step polymerization procedures. The material produced by the one-step method was very opaque and brittle with poor mechanical properties. The tensile strength and elongation at break of this material were only 3.8 MPa and 70%, respectively. In the two-step method the first step produced a white and very

opaque prepolymer in contrast to that obtained in the polymerization with the low molecular weight PDMS. This indicates the greater incompatibility of the reactants with higher molecular weight PDMS, because of its low solubility parameter. The polyurethane produced was again opaque and broke easily during handling, exhibiting extremely poor mechanical strength. By decreasing the hard segment weight percentage to 27 (to keep the molar ratio of macrodiol : MDI : BDO to 1 : 2 : 1 similar to the PDMS-1000), the resulting material was again opaque with poor mechanical properties (tensile strength 2.2 MPa and elongation at break 65%).

The DSC results (Fig. 8) of the two as-synthesized polyurethanes clearly demonstrated that the materials were highly phase separated, as evidenced by the presence of hard segment melting endotherms with high heat capacity and soft segment (PDMS) T_g onset close to -120°C . The poor mechanical properties could be attributed to this. The material from the one-step method ex-

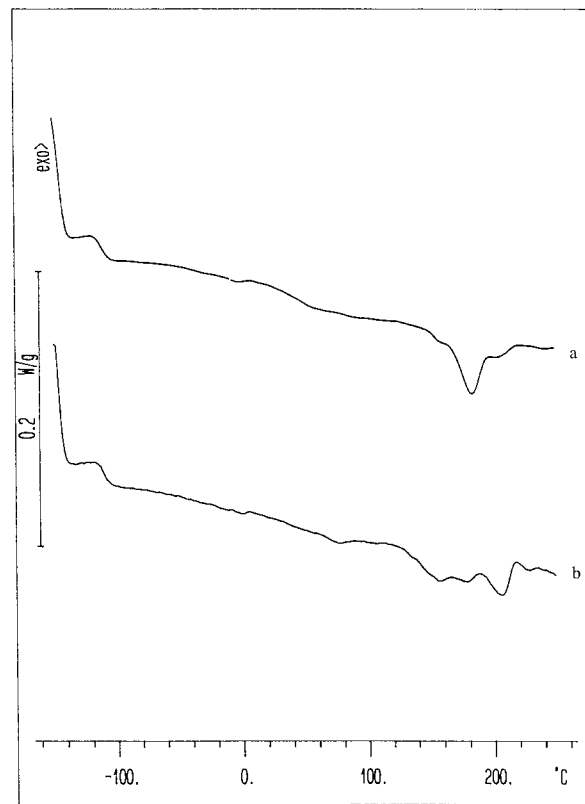


Figure 8 DSC thermograms of as-synthesized polyurethanes based on PDMS (MW 2181)/PHMO (80/20) (a) one-step polymerization or (b) two-step polymerization.

Table VI Comparison of Mechanical Properties of Elast-Eon 2™ with Commercial Polyurethanes Pellethane™ 2363 80A and 55D

Property	Elast-Eon 2™	Pellethane™ 2363-80A	Pellethane™ 2363-55D
Shore hardness	85 A	82 a	55d
Ultimate tensile strength (MPa)	28 ± 0.7	33.7 ± 1.8	40.3 ± 1.8
Elong. at break (%)	580 ± 5	430 ± 20 (550)	328 ± 16 (390)
Young's modulus (MPa)	33 ± 2	13 ± 2 (NA)	87 ± 10 (NA)
Stress at 100% strain (MPa)	10 ± 0.3	8 (60)	20 (17)
Stress at 200% strain (MPa)	13 ± 0.4	11 (NA)	29 (NA)
Tear strength (N mm ⁻¹)	60 ± 2	72 (83)	(115)
Flexural modulus (MPa)	30 ± 1	(NA)	35 ± 2
Abrasion resistance (mg/1000 cycles)	40	10 (20)	(80)

The results shown in parentheses are those reported by the manufacturer. NA, not available.

hibited a melting endotherm peaking at 182.4°C (H 11.8 J/g) and a soft segment T_g onset at -119.3°C. The material in the two-step polymerization showed a relatively broad (120–220°C temperature range) hard segment melting endotherm with a heat capacity of 16.2 J/g and a soft segment T_g onset at -117.3°C, indicating that this material was more phase mixed than that in the one step.

In summary, the results clearly demonstrated that the synthesis of polyurethane elastomers with good clarity and mechanical properties containing a high level of PDMS-based soft segment could be achieved by using a one-step bulk polymerization procedure only under certain conditions. These conditions included a PDMS molecular weight of about 1000 or lower, a hard segment weight percent of about 40, and the presence of a catalyst such as DBTD. On the other hand, the two step-polymerization has a broader applicability, polyurethanes with good properties could be prepared having a range of different hard segment levels, and the presence of a catalyst is not required.

Comparison of Mechanical Properties of New Siloxane-Based Polyurethane (Elast-Eon 2™) with Conventional Polyurethanes

It is preferable, particularly for the fabrication of medical implants, that the synthesis and processing of polymers be carried out free of catalyst residues and other additives. Accordingly, a polyurethane based on PDMS/PHMO (80/20) was prepared by a two-step bulk polymerization. The synthesized polyurethane was subjected to the conventional polyurethane processing steps such as

granulation and pelletization. The processability of the new polyurethane (Elast-Eon 2™) was compared to that of Pellethane™ 80A, which is a commercial material based on PTMO. Despite the absence of any antioxidants and processing waxes, Elast-Eon 2™ was processed without degradation. Particularly, the postextrusion handling of the material was relatively easy compared to Pellethane™ 80A, because of the minimal postextrusion tackiness.

The tensile properties of the polyurethane (Elast-Eon 2™) are presented in Table VI along with those of Pellethane™ 80A and 55D for comparison. The stress-strain curves are shown in Figure 9. The properties of Elast-Eon 2™ are comparable to those of the softer grade P80A.

CONCLUSIONS

The results in this study clearly demonstrated that the problems associated with synthesizing polyurethanes containing soft segments based on a high level of nonpolar macrodiols such as PDMS are due to the incompatibility of PDMS with conventional reactants used in preparing polyurethanes. However, with the use of low molecular weight PDMS (ca. 1000) and a compatible macrodiol such as PHMO one can prepare polyurethanes with good mechanical properties and clarity by the conventional one-step bulk polymerization. The presence of a suitable catalyst was essential for the one-step polymerization, and it was demonstrated that tetracoordinated tin catalysts (e.g., DBTD) were the most effective. The one-step bulk polymerization was limited to pre-

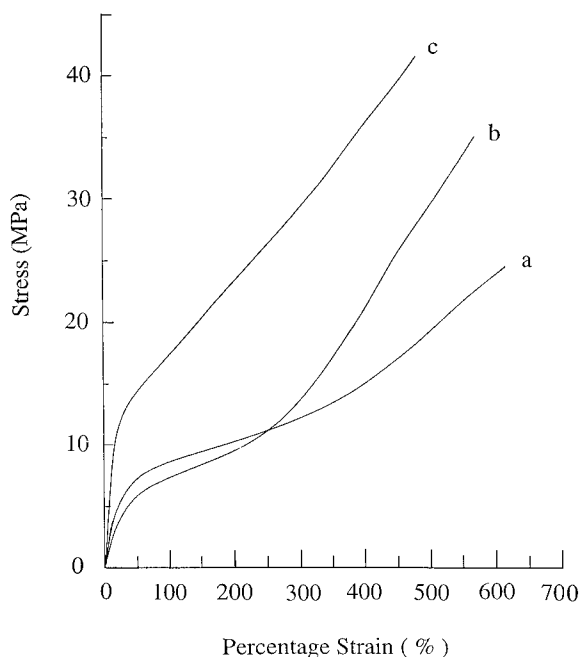


Figure 9 Stress-strain curves of (a) PDMS/PHMO-based polyurethane (Elast-Eon 2™), (b) Pellethane™ 2363-80A, and (c) Pellethane™ 2363-55D.

paring polyurethanes with hard segments of around 40 wt %; higher compositions yielded materials with poor mechanical properties.

The two-step bulk polymerization overcame most of the problems associated with reactant immiscibility by the end capping of the macrodiol and the consequent changes in solubility, resulting in polyurethanes with good mechanical properties. This method is broader in applicability in that polyurethanes with a wide range of properties can be prepared.

The DSC results demonstrated that in cases where poor properties were observed, the corresponding polyurethanes were highly phase separated. It was further demonstrated that in immiscible systems the hard segments formed were generally longer than the average length expected based on reactant stoichiometry. Except for the composition with a 40% hard segment content, the one-step method produced more phase separated materials than the two-step method.

The incorporation of a low level PHMO significantly improved the mechanical properties and processability of the polyurethanes, and the optimum composition of the PDMS and PHMO macrodiol was 80/20 (w/w). Of particular interest was the improvement in flexibility (low flexural mod-

ulus) and increased tensile strength with only 20% PHMO in PDMS, indicating its compatibilizing effect. We postulated that in this composition the polyether phase is largely concentrated in the interfacial regions, resulting in improved adhesion between the soft and hard domains. Further, the polyurethane was easily processable without the presence of conventional processing additives such as antioxidants and processing waxes. The PDMS/PHMO-based polyurethane based on an optimized formulation (Elast-Eon 2™) exhibited properties comparable to those of Pellethane™ 80A. The comparative biostability results will be published elsewhere.

The authors thank Dr. Alfred Uhlherr for carrying out the solubility parameter calculations. The authors also acknowledge the technical support provided by Nicole Sherrif for part of the work.

REFERENCES

1. Lelah, M. D.; Cooper, S. L. *Polyurethanes in Medicine*; CRC Press: Boca Raton, FL, 1986; Chapter 3.
2. Szycher, M. *J Biomater Appl* 1988, 3, 297.
3. Szycher, M.; McArthur, W. A. *Surface Fissuring of Polyurethanes Following In Vivo Exposure, Corrosion and Degradation of Implant Materials*, ASTM STP 859; Fraker, A. C., Griffiths, C. D., Eds.; American Society for Testing and Materials: Philadelphia, PA, 1985; p 308.
4. Pinchuk, L. *J Biomater Sci, Polymer Ed.* 1994, 6, 225.
5. McCarthy, S. J.; Meijs, G. F.; Mitchell, N.; Gunatillake, P. A.; Brandwood, A.; Schindhelm, K. *Biomaterials* 1997, 18, 1387.
6. Brandwood, A.; Meijs, G. F.; Gunatillake, P. A.; Noble, K. R.; Schindhelm, K.; Rizzardo, E. *J Biomater Sci Polym Ed* 1994, 6, 41.
7. Stokes, K.; McNenes, R.; Anderson, J. M. *J Biomater Appl* 1995, 9, 321.
8. Gunatillake, P. A.; Meijs, G. F.; Rizzardo, E.; Chatelier, R. C.; McCarthy, S. J.; Brandwood, A.; Schindhelm, K. *J Appl Polym Sci* 1992, 46, 319.
9. Wirpsza, Z. *Polyurethanes Chemistry, Technology and Applications*; Kemp, T. J., Ed.; Ellis Horwood: New York, 1993; Chapter 4.
10. Speckhard, T. A.; Gibson, P. E.; Cooper, S. L. *Macromolecules* 1971, 4, 452.
11. Mitzner, E.; Goering, H.; Becker, R.; Kennedy, J. P. *J Mater Sci Pure Appl Chem* 1997, A34, 165.
12. Okkema, A. Z.; Fabrizio, D. J.; Grasel, T. G.; Cooper, S. L.; Zdrahala, R. *J Biomater* 1989, 10, 23.
13. Chun, Y. C.; Kim, K. S.; Shin, J. S.; Kim, K. H. *Polym Int* 1992, 27, 177.

14. Phillips, R. A.; Stevenson, J. S.; Nagarajan, M. R.; Cooper, S. L. *J Macromol Sci Phys* 1988, B27, 245.
15. Frisch, K. C.; Sendijarevic, A.; Sendijarevic, V.; Yokelson, H. B.; Nubel, P. O. *Cell Polym* 1996, 15, 395.
16. Zawadski, S. F.; Akcelrud, L. *Polym Int* 1997, 42, 422.
17. Speckhard, T. A.; Cooper, S. L. *Rubber Chem Technol* 1986, 59, 405.
18. Sakurai, S.; Nokuwa, S.; Morimoto, M.; Shibayama, M.; Nomura, S. *Polymer* 1994, 35, 532.
19. Yu, X.; Nagarajan, M. R.; Gibson, P. E.; Cooper, S. L. *J Polym Sci Polym Phys* 1986, 24, 2681.
20. Yang, C. Z.; Li, C.; Cooper, S. L. *J Polym Sci Polym Phys* 1991, 29, 75.
21. Chen, L.; Yu, X. *Gongneng Gaofenzi Xuebao* 1991, 4, 19 [in Chinese].
22. Takamatsu, T.; Tanaka, Y.; Sasabe, H.; Kira, H. *Seitai Zairyo* 1988, 6, 57.
23. Takamatsu, T.; Tanaka, Y.; Sasabe, H.; Kira, H. *Transactions of the Third World Biomaterials Congress*, April 21–25, Vol XI, 1988, Kyoto, p 427.
24. Yu, X.; Nagarajan, M. R.; Grasel, T. G.; Gibson, P. E.; Cooper, S. L. *J Polym Sci Polym Phys* 1985, 23, 2319.
25. Gunatillake, P. A.; Meijs, G. F.; McCarthy, S. J. *Int. Pat. Applic.*, PCT/AU97/00619, 1996.
26. Gunatillake, P. A.; Meijs, G. F.; Chatelier, R. C.; McIntosh, D. M.; Rizzardo, E. *Polym Int* 1992, 27, 275.
27. ASTM D 2849-69 *Standard Methods of Testing Urethane Foam Macrodiol Raw Materials*; American Society for Testing and Materials: Philadelphia, PA, 1969.
28. Grasel, T. G.; Cooper, S. L. *Biomaterials* 1986, 7, 315.
29. Eisenbach, C. D.; Baumgartner, M.; Gunter, C. In *Advances in Elastomers and Rubber Elasticity*; Lal, J., Mark, J. E., Eds.; Plenum: New York, 1986; p 51.
30. Tonelli, C.; Trombetta, T.; Scicchitano, M.; Simeone, G.; Ajroldi, G. *J Appl Polym Sci* 1996, 59, 311.
31. Martin, D. J.; Meijs, G. F.; Gunatillake, P. A.; McCarthy, S. J.; Renwick, G. M. *J Appl Polym Sci* 1997, 64, 803.
32. Martin, D. J.; Meijs, G. F.; Renwick, G. M.; McCarthy, S. J.; Gunatillake, P. A. *J Appl Polym Sci* 1996, 62, 1377.