The Effect of Diisocyanate Isomer Composition on Properties and Morphology of Polyurethanes Based on 4,4′-Dicyclohexyl Methane Diisocyanate and Mixed Macrodiols (PDMS–PHMO)

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ABSTRACT: Three series of polyurethanes were prepared having 42 wt % hard segments based on 4,4′-dicyclohexyl methane diisocyanate (H_{12}MDI) with trans,trans isomer contents in the 13 to 95 mol % range and 1,4-butanediol chain extender. The soft segments were based on macrodiols poly(hexamethylene oxide) (PHMO, MW 696), α,ω-bishydroxyethoxypropyl polydimethylsiloxane (PDMS, MW 940), and two mixed macrodiol compositions consisting of 80 and 20% (w/w) PDMS. H_{12}MDI with 35, 85, and 95% trans,trans isomer contents were obtained from commercial H_{12}MDI (13% trans, trans) by fractional crystallization, and all polyurethanes were prepared by a one-step bulk polymerization procedure. The polyurethanes based on the commercial diisocyanate-produced materials soluble in DMF with molecular weights in the 53,655–75,300 range and generally yielded clear and transparent materials. The polyurethanes based on H_{12}MDI with trans,trans contents of 35% or higher yielded materials insoluble in *N,N*-dimethylformamide (DMF) and were generally opaque. Mechanical properties, such as tensile strength and elongation at break, decreased with increasing trans,trans content, while the Young's modulus and Shore hardness increased. The polyurethanes based on mixed macrodiols yielded higher tensile properties than those of materials based on individual macrodiols. The best mechanical properties were observed for a polyurethane consisting of a soft segment based on PDMS–PHMO (80/20) and a hard segment based on commercial H_{12}MDI and BDO. Differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR) were employed to characterize the polyurethane morphology. DSC results confirmed that the polyurethanes based on H_{12}MDI with high trans,trans isomer were very highly phase separated, exhibiting characteristic hard segment melting endotherms as high as 255°C. The other materials were generally phase mixed. FTIR spectroscopy results corroborated DSC results. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 573–582, 1999

Key words: polyurethane; dicyclohexyl methane diisocyanate; mixed macrodiols; polydimethylsiloxane; mechanical properties; morphology

INTRODUCTION

Polyurethane elastomers are linear alternating block copolymers. Typically, these materials con-

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sist of a continuous amorphous soft domain and a discrete glassy or crystalline hard domain. Due to the incompatibility of the two domains, these materials generally exhibit a two phase morphology. The soft segment domains impart elastomeric properties, whereas the hard segment domains provide rigidity and mechanical strength. Hard and soft segment structure, molecular weight, polydispersity, and crosslinking in either phase

influence microphase separation in these copolymers. Phase separation is primarily responsible for their good mechanical properties. Most previous investigations have concentrated on polyurethanes based on hard segments derived from aromatic diisocyanates[1–6] with relatively few studies based on aliphatic diisocyanates.[7–18]

The aliphatic diisocyanate 4,4′-dicyclohexyl methane diisocyanate (H_{12}MDI) is commercially available and used as a building block for polyurethane elastomers that require light stability and resistance to hydrolysis. This diisocyanate is supplied as a mixture of three geometrical isomers (trans,trans, cis,trans, and cis,cis isomer) and generally has 10–30% of trans-trans isomer in the mixture. In this composition, the diisocyanate remains liquid at room temperature and is easy to handle industrially.[19–20] Isomeric mixtures of H_{12}MDI with a wide range of trans,trans isomer contents (10–100%) can be obtained by various techniques.[21–24] Crystallization from melt or solution is reported to be the best technique to obtain H_{12}MDI with high level of trans-trans isomer.[25,26] The elastomers prepared directly from the commercial H_{12}MDI are reported to have little or no crystallinity in the hard segment microdomains, resulting in transparent polymers with good flexibility and bend recovery. The properties of these polyurethanes show a strong dependency on the isomeric ratio, with increasing trans,trans isomer content resulting in polyurethanes having improved mechanical properties.[14]

There have been only a few studies in the past on polyurethanes based on H_{12}MDI and nonpolar macrodiols, such as PDMS.[27–30] These studies have reported a high degree of phase separation in the materials due to decreased compatibility of the soft and hard segments. Although the increase in phase separation is generally thought to improve mechanical properties,[31–35] PDMS-based polyurethanes have shown inferior tensile strength, extensibility, and toughness, which was attributed to the inability of the soft segment to crystallize under strain and to poor interfacial adhesion between the hard and soft microdomains.[36]

Recent studies in our laboratory have shown that polyurethanes with good mechanical properties, clarity, processability, and resistance to degradation induced by hydrolytic, oxidative, and *in vivo* can be obtained from nonpolar macrodiols, such as PDMS.[37,38] This has been achieved by using a mixture of PDMS and a polyether macrodiol, which introduces a controlled level of phase

mixing between hard and soft segments while broadening the interfacial region. Further, these studies have shown that a low level (~ 20%) of either polyol in the mixture has a significant effect on properties, such as ultimate tensile strength and flexural modulus. A particularly useful combination involves PDMS and poly(hexamethylene oxide) (PHMO)-based soft segment, and MDI–BDO-based hard segment. As an extension of this work, we investigated polyurethanes based on H_{12}MDI. Polyurethanes based on mixed macrodiols PDMS–PHMO and H_{12}MDI have not been reported previously. Since properties of polyurethanes based on H_{12}MDI are sensitive to it's isomer composition, this study was focused on understanding the effect of trans,trans isomer content of H_{12}MDI on the morphology and physicomechanical properties of three series of PHMO- and PDMS-based polyurethanes. The three series of polyurethanes were based on soft segments derived from pure macrodiols PDMS and PHMO, and two mixed macrodiol compositions consisting of 20 and 80 wt % PDMS, respectively. All the polyurethanes in this study were formulated with an [NCO]/[OH] molar ratio of 1.00 at a 42 wt % hard segment content.

EXPERIMENTAL

Materials

Diisocyanates having different percentages of trans,trans isomer were obtained from commercially available H_{12}MDI (Aldrich) by repeated fractional crystallizations at different temperatures.[21,22] The actual composition of geometrical isomers in the commercial sample was 13 trans, trans, 85 cis, trans, and 2% cis, cis, as determined by gas chromatography–mass spectroscopy (GC–MS). H_{12}MDI containing 35, 85, and 95% trans, trans isomer were prepared by fractional crystallization of commercial diisocyanate and used in various experiments.

Poly(hexamethylene oxide) was synthesized by the acid-catalyzed condensation polymerization of 1,6-hexanediol according to the procedures reported.[39] The BDO (BASF) was dried over molecular sieves 3Å and distilled under vacuum, and middle fraction used for polymerization. α,ω-Bishydroxyethoxypropyl polydimethylsiloxane (product no. X-22-160AS) was obtained from Shin Etsu (Japan). PDMS was dried thoroughly under a vacuum of 0.1 torr at 105°C for at least 12 h prior to polymerization. PHMO was dried at

130°C for 4 h under vacuum (0.1 torr) to remove cyclic oligomers. The catalyst dibutyltin dilaurate (Eastman Kodak) was used as received.

Synthesis of Polyurethane Elastomers

All polyetherurethane elastomers were synthesized by a one-step bulk polymerization procedure. The glassware was dried in an oven at 105°C overnight. A typical one-step polymerization procedure is described below.

In the one-step procedure, predried macrodiols PDMS (40.00 g) and PHMO (10.00 g), 1,4-butanediol (5.594 g), and dibutyltin dilaurate (0.01 wt % of total solids) were placed in a 250-mL polypropylene beaker and degassed at 80°C in an oven under a vacuum of 2 mmHg for 1.5 h. H_{12}MDI (30.61 g) was weighed into a wet-tarred 50-mL polypropylene beaker and quickly poured into the macrodiol mixture while rapidly stirring with a stainless steel spatula, under a nitrogen blanket. After stirring for about 1 min, the viscous polymer was poured onto a Teflon-coated metal pan and cured for 12 h in an oven at 100°C under dry nitrogen.

In all polyurethanes, the hard segment weight percentage and isocyanate index ([NCO]/[OH]) were kept constant at 42 and 1.00, respectively. Three series of polyurethanes, designated as PU1, PU2, and PU3, were prepared in this study. In the PU1 series, the weight ratio of macrodiols PDMS and PHMO was kept constant at 80 : 20 (w/w), and the chain extender was 1,4-butanediol, while varying the content of trans,trans isomer of H_{12}MDI. Accordingly, a material designated as PU1-35 was made using PDMS–PHMO (80/20 w/w), BDO, and H_{12}MDI containing 35% trans, trans isomer. In the PU2 series, the PDMS–PHMO ratio was 20 : 80, and the chain extender was BDO, while H_{12}MDI with different trans, trans isomer contents were used for different materials. For example, PU2-35 denotes a polyurethane-based on PDMS–PHMO (20 : 80), BDO, and H_{12}MDI with 35% trans,trans isomer. In the PU3 series, four materials based on individual macrodiols, PDMS and PHMO, each with 13 and 95% trans,trans-H_{12}MDI and BDO, were prepared. Accordingly, a material designated as PU3–PDMS-13 was prepared from PDMS, 13% trans,trans-H_{12}MDI, and BDO.

Size-Exclusion Chromatography

Size exclusion chromatography (SEC) of polyurethane materials was carried out on a Waters Associates Chromatograph using 0.05M lithium bromide in N,N-dimethylformamide (DMF) as the mobile phase at 80°C. The flow rate was 1.0 mL/min. The stationary phase consisted of a set of two μ-Styragel HT columns (10^5 and 10^3 Å and one PLgel (100 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 200 and 250°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. All samples were inspected under cross-polarizers to determine if internal stress was present. Dumbbells were stored under ambient conditions for at least 1 week before tensile tests and hardness measurements were carried out.

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 result reported are the median values for five replicates. Hardness measurements were carried out using Shore A and D durometers.

Differential Scanning Calorimetry

DSC thermograms of the samples from the compression-molded sheets over the temperature range of -150 to 300°C were recorded on a Mettler DSC 30 calorimeter linked to a Mettler TC 10A thermal analysis processor. The experiments were carried out at a heating rate of 10°C/min under nitrogen purge. Sample weights were 20–25 mg. All samples were dried at 48°C for 48 h under vacuum (0.1 torr) to subject them to uniform thermal conditions prior to DSC analysis.

RESULTS AND DISCUSSION

Synthesis and Mechanical Properties of Polyurethanes

The three series of polyurethanes investigated in this study were prepared by a one-step bulk poly-

Table I   Formulation Details and Molecular Weights of Polyurethanes

Polyurethane[a]	Wt % PDMS in PDMS–PHMO Mixture (%)	Film Clarity[b]	M_n	M_w/M_n
PU1-13	80	17	62460	1.88
PU1-35	80	57	—[c]	
PU1-85	80	90	—[c]	
PU2-13	20	86	53655	2.4
PU2-35	20	70	—[c]	
PU2-85	20	95	—[c]	
PU3–PDMS-13	100	14	75300	1.5
PU3–PDMS-95	100	99	—[c]	
PU3–PHMO-13	0	16	69000	1.6
PU3–PHMO-95	0	29	—[c]	

[a] All polyurethanes contained 42 wt % of hard segment based on H_{12}MDI and BDO with an isocyanate index of 1.00.
[b] % Absorption of visible light, as measured by a Gardener Haze meter.
[c] Insoluble in DMF for GPC analysis.

merization procedure. Synthesis of the polyurethanes with the commercial diisocyanate (13% trans,trans was relatively easy, having longer reaction gel times (>3 min); and all ingredients mixed well very early in the reaction, resulting in a clear and homogeneous solution. Accordingly, the polyurethanes prepared were clear, transparent, and rubbery. However, in comparison the formulations with higher trans,trans content showed relatively poor compatibility of the reagents early during synthesis. The mixture stayed slightly cloudy to very opaque for compositions with 95% trans,trans-H_{12}MDI during the synthesis, although there were no signs of producing compositionally heterogeneous materials as evidenced by the absence of any precipitation. The resulting polyurethanes varied from slightly opaque for compositions with 35% trans,trans-H_{12}MDI to very opaque for those with 95% trans, trans. Further, the materials based on H_{12}MDI with 35% trans,trans or higher were insoluble in solvents such as DMF, making it difficult to characterize these materials for their molecular weights.

As seen in Table I, only the polyurethanes based on commercial H_{12}MDI were soluble in DMF for molecular weight determination. For the soluble materials, the number-average molecular weights ranged between 54,000 and 75,300, while the polydispersity ranged from 2.4 to 1.5. All polyurethanes were easily thermally processable at temperatures in the 190–250°C range. Materials based on commercial diisocyanate compression-molded easily to produce clear, rubbery, and transparent films, with the exception of PU2-13,

which processed easily, but the film was slightly opaque. The other materials, which processed easily to form films, had poor clarity which decreased with increasing trans,trans content of the diisocyanate. Generally, the PDMS-rich PU1 series was clearer than the PHMO-rich PU2 series. The clarity of the thermally processed films as measured by a Gardiner Haze meter are summarized in Table I.

Table II summarizes the mechanical properties of the three series of polyurethanes. Polyurethanes based on commercial H_{12}MDI produced softer and more flexible polyurethanes than those produced from the higher trans,trans-content diisocyanates. The Shore A hardness of the soft materials varied between 68 A and 86 A with PHMO-based material, with PU3–PHMO-13, being the softest. In the PU1 series, the fail stress decreased as the trans,trans content of the diisocyanate increased from 13% for the commercial diisocyanate to that containing 95% trans,trans. There was a significant difference between PU1-13 and PU1-85. The elongation at break also followed a similar trend, with PU1-13 being the most elastomeric, and PU1-85 being the most rigid. This was also reflected in the Young's modulus, Shore hardness, and stress at 100% elongation results.

Likewise, the PU2 series followed a very similar trend to that of PU1 series. PU2-13, which was based on commercial H_{12}MDI, showed the highest tensile strength and elongation at break. With increasing trans,trans content of the diisocyanate, the materials became less elastomeric, as indicated by low elongation at break, high

Table II   Mechanical Properties of Polyurethane Elastomers

Polyurethane	Fail Stress (MPa)	Elongation at Break (%)	Young's Modulus (MPa)	Stress at 100% Elongation (MPa)	Shore Hardness
PU1-13	24.4 ± 0.9	385 ± 15	33.0 ± 3.0	10.1 ± 0.1	82A
PU1-35	10.9 ± 1.0	310 ± 52	47.6 ± 4.7	9.8 ± 0.3	85A
PU1-85	12.8 ± 0.2	140 ± 33	99.3 ± 15	12.7 ± 0.0	48D
PU2-13	22.3 ± 0.6	390 ± 22	8.8 ± 0.2	7.2 ± 0.1	71A
PU2-35	13.0 ± 0.6	380 ± 26	20.5 ± 2.5	8.1 ± 0.1	77A
PU2-85	11.7 ± 0.1	185 ± 36	80.6 ± 7	11.3 ± 0.1	38D
PU3–PDMS-13	16.1 ± 0.6	400 ± 21	71.5 ± 5.6	9.9 ± 0.0	86A
PU3–PDMS-95	13.8 ± 0.3	55 ± 29	93.2 ± 24	—	43D
PU3–PHMO-13	16.8 ± 0.4	401 ± 34	6.3 ± 0.7	5.2 ± 0.1	68A
PU3–PHMO-95	13.8 ± 0.2	160 ± 70	105 ± 12	12.9 ± 0.0	45D

Young's modulus, and stress at 100% elongation results.

The properties of the PU3 series of materials also followed the same trend observed for the other two series. Since PU3 materials contained a single macrodiol-based soft segment, it was worthwhile comparing their properties with those based on mixed macrodiols. As illustrated in Figure 1, it was interesting to note that the polyurethane (PU1-13) based on a 80/20 mixture of PDMS and PHMO polyols showed a much higher fail stress compared to that of either PU3–PDMS-13 or PU3–PHMO-13. The improvement in fail stress was approximately 50%. Also, the materials showed good elastomeric properties. The properties, such as Young's modulus and Shore hardness, were intermediate to those of the two control materials. Overall, PU1-13 had the best combination of properties.

In contrast, such improvements in properties were not observed for materials based on H_{12}MDI with 95% trans,trans, resulting from the use of a mixed macrodiol. There was no significant change in UTS, Young's modulus, Shore hardness, or the elongation at break. All three materials (PU1-85, PU3–PDMS-95, and PU3–PHMO-95) generally had very poor elastomeric properties.

Likewise, the polyurethane PU2-13, based on PDMS–PHMO 20/80, showed higher tensile strength than the two control materials based on single polyols (PU3–PDMS-13 and PU3–PHMO-13), and comparable elongation at break (see Fig. 1 and Table II). The other properties were intermediate to those of the two materials based on single macrodiols. As demonstrated with the PU1 series, a similar effect was seen with increasing the trans,trans content in the diisocyanate.

The results in our study contrast the general findings on the effect of trans,trans isomer con-

tent in H_{12}MDI on properties of polyurethanes based on poly(tetramethylene oxide) (PTMO) and BDO. Results reported by Seneker et al.[14] showed that in this system, the ultimate tensile strength, elongation at break, and tear strength all increased with the increase of trans,trans isomer content of the diisocyanate. For example, a poly-

Figure 1   The effect of macrodiol composition on fail stress and Young's modulus of polyurethanes based on commercial H_{12}MDI containing 13% trans,trans isomer.

urethane based on 100% trans,trans isomer of H_{12}MDI, PTMO (MW 2000), and BDO showed an ultimate tensile strength of 36.5 MPa and 645% elongation at break, compared to 26.2 MPa and 360% for the materials based on a 20% trans, trans isomer. The opposite behavior observed in our study is attributed to the use of significantly less polar macrodiols. Both PDMS and PHMO are less polar than PTMO, and this may promote phase separation to an extreme extent, where there is very poor interfacial adhesion. Therefore, it appears that one needs to have a reasonable balance in phase separation and interfacial adhesion in order to achieve good mechanical properties in polyurethanes.

In summary, our results clearly demonstrated that the increasing trans,trans content of the diisocyanate was the dominating factor that influenced the tensile properties of the polyurethanes in this study. The observed trend of decreased tensile properties, opposite to the general findings with polyols such as PTMO, is attributed to the use of relatively nonpolar polyols in our study. However, it is noteworthy that polyurethanes containing high levels of PDMS with good tensile strength and elasticity could be successfully prepared with commercial H_{12}MDI, particularly using a mixture of PDMS and PHMO macrodiols as the soft segment.

Thermal Analysis of Polyurethanes

Differential scanning calorimetry (DSC) analysis provided information about the different morphologies resulting from variation of the trans,trans isomer content of H_{12}MDI, as well as the change in soft segment composition. This analysis was carried out to understand and correlate polyurethane morphology and mechanical properties in the three series of materials. All polyurethanes were subjected to identical thermal treatments prior to recording DSC thermograms so that the thermal history of all materials was identical. Figures 1 to 3 show the DSC thermograms of materials investigated in this study. Among the three materials in the PU1 series (Fig. 2), polyurethane PU1-85 showed the most phase-separated morphology (poorest mechanical properties in the series), as clearly evidenced by the presence of a very sharp hard segment melting endotherm at 254°C. As seen from the results in Table III, the heat of fusion for this transition was the second highest of all materials investigated. However, it was interesting to note that the T_g of the soft segment (predominantly PDMS) had shifted

Figure 2   DSC thermogram of PU1 series of polyurethanes based on mixed macrodiols PDMS–PHMO (80/20).

to higher temperatures than those of the other two materials in the series. These two materials showed very little order in the hard segment, as evidenced by the presence of only very weak melting endotherms in the 100 to 250°C temperature range. The melting endotherms at 69.6 and 82.1°C, respectively, for PU1-13 and PU1-35 could result from some order associated with hard segments derived from relatively high level of cis,cis and cis,trans isomers present in these materials. It was also noted that PU1-85 exhibited a very weak endotherm at 78.7°C, consistent with the presence of only 15% of the other isomers in this material. The observed shift (about 16°C higher than that of pure PDMS T_g) in soft segment T_g of PU1-85 may be explained by considering the role of the 20% PHMO present in this series of materials. In PU1-13 and PU1-35, the PHMO present in the soft segment may be more associated with the less ordered hard segment, while the PDMS-based soft segment remaining largely unassociated with either PHMO or the hard segments due to its generally nonpolar nature. Accordingly, the soft segment T_g remains close to that of the pure PDMS (120°C). In PU1-85, because of the highly crystalline order of the hard segment, PHMO may be somewhat more associated with PDMS shifting the T_g to higher temperatures.

Figure 3 DSC thermogram of PU2 series of polyurethanes based on mixed macrodiols PDMS–PHMO (20/80).

The recent study reported by Steinlein et al.[18] on isomerically pure urethane model compounds of trans,trans-H_{12}MDI was useful in the assignment

of various hard segment melting endotherms observed in our study. Their results showed that dimethoxybutyl urethanes of trans,trans-H_{12}MDI containing one H_{12}MDI, and two and three H_{12}MDI units linked by BDO, to have sharp DSC endothermic peaks at 142, 216, and 246°C, respectively. Accordingly, the melting endotherm for PU1-85 observed at 254°C could be assigned to melting of crystalline regions formed by (trans,trans-H_{12}MDI–BDO)$_3$ units. On the other hand, the polyurethane with only 35% trans,trans isomer showed only very weak and broad endotherms at 254.4 and 193.9°C, assigned respectively to melting of crystalline domains due to three- and two-unit structures. The melting endotherms at 82 and 129.7°C could be attributed to some weak order resulting from other two less-symmetrical isomers of H_{12}MDI. All transitions in PU1-35 were generally very broad due to the presence of significantly high levels of the two less-symmetrical isomers. Likewise, PU1-13 showed a broad endotherm at 69.6°C as the major peak, assigned to melting of urethane structures formed from these isomers. The materials also showed a broad but very weak absorption at 205.3°C due to trans,trans isomer based hard segment.

In the PU2 series, where the soft segment is richer in the relatively more polar PHMO, a similar trend followed, and PU2-85 appeared to be the most phase-separated of the three. However, as seen from the DSC thermograms in Figure 3,

Table III   Thermal Transitions Melting Endotherm Heat of Fusion for Polyurethanes

Polyurethane	Soft Segment T_g (Onset, Midpoint, and End Point) (°C)	Soft Segment Heat of Fusion (J/g)	Hard Segment Melting Peaks, Peak Temperature (°C) (Heat of Fusion, J/g)
PU1-13	−117.5, −102.5, −86.0	0.09	69.6 (7.0), 205.3 (1.4)
PU1-35	−111.4, −103.2, −95.0,	0.03	82.1 (1.8), 129.7 (3.5), 193.9 (1.9) and 254.4 (2.3)
PU1-85	−104.2, −88.2, −72.2	0.10	78.7 (0.8), 173.9 (0.9), 254 (16.2)
PU2-13	−71.6, −38.1, −4.5	0.53	73.2 and 109.9 (13.6), 197.9 (0.5)
PU2-35	−68.8, −38.3, −7.8	0.40	84.0 (2.4), 126.1 (3.1)
PU2-85	−68.4, −53.2, −38.0	0.16	76.9 (1.6), 115.4 (0.3), 194.1 and 221.8 (14.9)
PU3–PDMS-13	−111.1, −90.9, −70.6	0.17	56.6 (5.6), 109.8 (1.6), 212.5 (2.7)
PU3–PDMS-95	−113.3, −99.1, −78.5	0.19	49.3 (2.3) and 255.7 (23.3)
PU3–PHMO-13	−48.1, −26.9, −5.8	0.44	62.1 and 106.1 (8.6), 208.8 (2.2)
PU3–PHMO-95	−60.7, −42.1, −23.5	0.30	73.3 (2.2), 194.2 (10.9), 216.3 (0.6), 240.1 (0.8)

Figure 4 DSC thermogram of PU3 series of polyurethanes based on individual macrodiols PDMS and PHMO.

the morphology in this series appears to be more phase-mixed than the PU1 series, which is consistent with the presence of more polar PHMO-rich soft segment. As expected, PU2-85 exhibited the highest hard segment order in this series, evidenced by the melting endotherm at 194.1°C, with a heat of fusion of 14.9 J/g. All three polyurethanes showed a pair of endotherms in the 60 to 140°C temperature range with increasing intensity as trans,trans isomer content was decreased. These endotherms are again attributable to the low hard segment order, resulting from less-symmetrical cis,trans and cis,cis isomers. The T_g of the PHMO-rich soft segment appeared very broad, covering 67°C between the onset and end point for PU2-13 and PU2-35, indicating phase-mixed morphology, while that of the more phase-separated PU2-85 was narrower, covering about 30°C. The most phase-separated material also had the poorest mechanical properties similar to the PU1 series.

DSC thermograms of the polyurethanes in the PU3 series are shown in Figure 4. Of the four materials, PU3-PDMS-95 exhibited the most highly phase-separated morphology with a highly

ordered hard segment, as expected. The presence of nearly all trans,trans isomer in the diisocyanate, as well as the nonpolar PDMS soft segment, one would expect the polyurethane to exhibit such a highly phase-separated morphology. The hard segment melting endotherm observed at 255.7°C for this polymer also had the highest heat of fusion of all the materials studied. As discussed before, this peak could be assigned to melting of the crystalline domains based on predominantly $(trans,trans\text{-}H_{12}MDI\text{--}BDO)_3$ segments. It was interesting to note that the polyurethane (PU3–PHMO-95) based on the more polar PHMO showed only a very weak endotherm at 240.1°C (0.8 J/g), and a broad, but strong (10.9 J/g) endotherm at 194.2°C, due to melting of possibly the $(trans,trans\text{-}H_{12}MDI\text{--}BDO)_2$ units. As expected, materials based on $H_{12}MDI$ with 13% trans,trans isomer showed only very weak endotherms at temperatures above 200°C. The endotherms observed at 62.1 and 106.1°C could be assigned to melting of some ordered domains associated with urethane groups resulting from the other two isomers. The soft segment glass transition temperatures of both PDMS-based materials were similar, indicating that the PDMS phase was not affected by the isomer composition and remained largely phase-separated. However, in the two PHMO-based materials, the soft segment was more phase mixed in the commercial $H_{12}MDI$-based material than in the other. These differences can be attributed to the relative differences in polarity of the two macrodiols.

Infrared Spectroscopy

FTIR spectroscopy of PU1 series materials was carried out to obtain further supportive evidence on the different phase separation behaviour of the three materials in this series. Figure 4 shows the transmission infrared (IR) spectra recorded from 2.5-μm-thick films sectioned from compression-molded samples subjected to similar thermal treatments as the samples for DSC. As clearly seen from Figure 5, the most notable spectral changes were associated with carbonyl region absorptions and the urethane NH absorption. The carbonyl absorption of PU1-13 was broad with bands due to nonhydrogen-bonded carbonyl (1720 cm^{-1}) and hydrogen-bonded carbonyl (1700 to 1680 cm^{-1}) resolved very poorly. As the trans, trans isomer content was increased, the absorption due to hydrogen-bonded carbonyl (1687 cm^{-1}) became the more prominent peak[40]; and in PU1-85, the nonhydrogen-bonded carbonyl peak

Figure 5 FTIR spectra of PU1 series of polyurethanes.

was very low in intensity. The NH absorption centered at 3350 cm^{-1} also became sharper as the trans,trans content of the material was increased. These results, the DSC results corroborated well in confirming that in polyurethanes based on H$_{12}$MDI, increasing trans,trans isomer content leads to increased hard segment crystallinity and phase separation.

The morphological information obtained from DSC and IR analyses was useful in understanding the observed differences in mechanical properties of the materials in the three series (see Table II). Although the materials based on high trans,trans-H$_{12}$MDI exhibited a well-phase-separated and highly ordered hard segment, their mechanical properties were generally poor. These results, therefore, further confirm that some level of interfacial mixing is critical to obtain a good balance of mechanical properties. In materials that exhibited good mechanical properties (high tensile strength and elongation at break), PHMO appeared to have played a significant role in achieving such interfacial mixing with the hard segment.

CONCLUSION

Three series of polyurethane elastomers were synthesized having hard segments based on hydrogenated MDI with trans,trans isomer levels in the 13 to 95 mol % range and 1,4-butanediol. The soft segments were based on PDMS and PHMO, and two mixed macrodiol compositions with 80 and 20% PDMS. Irrespective of the soft segment type, polyurethanes based on H$_{12}$MDI with a high trans, trans isomer level yielded opaque and insoluble polyurethanes, and only polyurethanes based on commercial H$_{12}$MDI (only 13% trans,trans yielded transparent materials soluble in DMF, and their number-average molecular weights ranged between 53,655 and 75,300.

The mechanical properties of the polyurethanes showed a strong dependency on the level of trans,trans isomer content in the diisocyanate. The fail stress and elongation at break decreased with increasing trans,trans isomer content, while Young's modulus and Shore hardness increased. The polyurethanes based on commercial H$_{12}$MDI exhibited good overall tensile properties. The fail stress of the mixed macrodiol PDMS- and PHMO-

based polyurethanes was significantly higher than that of the polyurethanes based on individual macrodiols. This improvement in mechanical properties is attributed to the presence of PHMO, which helps to enhance a controlled level of phase mixing resulting in improved interfacial adhesion.

DSC and FTIR results confirmed that the polyurethanes containing high level of trans,trans isomer were associated with higher melting hard domain structures and were generally well-phase-separated. The consequent lack of interfacial adhesion assumed to be primarily responsible for their poor mechanical properties. However, it is noteworthy that polyurethanes containing high level of PDMS with good tensile strength and elasticity could be successfully prepared with commercial $H_{12}MDI$, particularly using a mixture of PDMS and PHMO macrodiols as the soft segment.

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