

# Properties of Segmented Polyurethanes Derived from Different Diisocyanates

DA-KONG LEE, HONG-BING TSAI

Department of Chemical Engineering, National I-Lan Institute of Technology, I-Lan 26015, Taiwan, Republic of China

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**ABSTRACT:** Various segmented polyurethane materials with a polyurethane hard segment (HS) content of 40 wt % were prepared by bulk polymerization of a poly(tetramethylene ether) glycol with  $M_n$  of 2000, 1,4-butanediol, and various diisocyanates. The diisocyanates used were pure 4,4'-diphenylmethane diisocyanate (MDI), 2,4-toluene diisocyanate (T100), toluene diisocyanate containing 80% 2,4-isomer and 20% 2,6-isomer (T80), isophorone diisocyanate (IPDI), hydrogenated 4,4'-diphenylmethane diisocyanate (HMDI), and 1,6-hexane diisocyanate (HDI). The segmented polyurethane materials were characterized by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), tensile properties, tear strength, and Shore A hardness. The DSC and DMA data show that the thermal transitions are influenced significantly by the diisocyanate structure. In the segmented polyurethane materials with aliphatic HS, the polyether soft segment (SS) is immiscible with the HS. However, in the segmented polyurethane materials with aromatic HS, the SS is partially miscible with the HS. The diisocyanate structure also influences the mechanical properties significantly and is described as the effect of symmetry and chemical structure of the HS. Various solution polymerized polyurethane resins with solid content of 30 wt % were also prepared and their thickness retention, water resistance, and yellowing resistance were determined for the evaluation of their usage as wet process polyurethane leather. The polyurethane resin with aliphatic HS show poorer thickness retention but better yellowing resistance. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 167–174, 2000

**Key words:** segmented polyurethane; aliphatic diisocyanate; aromatic diisocyanate; chemical structure

## INTRODUCTION

Polyurethane materials have been widely used in many products due to the diversity of the properties and processing technologies.<sup>1,2</sup> Synthetic leather is one of the most important applications of polyurethanes in Taiwan.<sup>3</sup> Most synthetic leathers use 4,4'-diphenylmethane diisocyanate

(MDI) and toluene diisocyanate containing 80% 2,4-isomer and 20% 2,6-isomer (T80) as the major raw materials due to their low cost. The yellowing problems of the products derived from MDI and T80 limits their applications for outdoors usages and high-quality products. Therefore, the utilization of various diisocyanates in producing synthetic polyurethane leather will be an interesting topic. It is necessary to be familiar with the effect of the diisocyanate chemical structure and the structure–property relationships for the new product design.

In this article, various segmented polyurethane materials with polyurethane hard segment

Correspondence to: D.-K. Lee.

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(HS) content of 40 wt % were prepared from a poly(tetramethylene ether) glycol with  $M_n$  of 2000, 1,4-butanediol, and various diisocyanates, including pure MDI, 2,4-toluene diisocyanate (T100), T80, isophorone diisocyanate (IPDI), hydrogenated 4,4'-diphenylmethane diisocyanate (HMDI), and 1,6-hexane diisocyanate (HDI). The properties of segmented polyurethane materials were investigated. Similar polyurethane resins with a solid content of 30 wt % were also prepared and their thickness retention, water resistance, and yellowing resistance were investigated for the evaluation of their use as wet process polyurethane leather.

## EXPERIMENTAL

### Materials

Pure 4,4'-diphenylmethane diisocyanate (MDI) was Merck reagent grade. MDI has a tendency to dimerize at room temperature, and hot-sintering is required to eliminate any MDI dimer or other impurities insoluble in molten MDI.<sup>4</sup> After hot-sintering and filtering, MDI was cooled rapidly and placed in a sealed bottle and stored in a refrigerator at  $-30^\circ\text{C}$ . The equivalent weight of the purified MDI was determined by a di-*n*-butylamine back titration method<sup>5</sup> to be 125.4 g/mol. 2,4-Toluene diisocyanate (T100) and toluene diisocyanate containing 80% 2,4-isomer and 20% 2,6-isomer (T80) were supplied by Merck, and their equivalent weights determined were 88.7 and 89.0 g/mol, respectively. Isophorone diisocyanate (IPDI); Desmodur<sup>®</sup> I; hydrogenated 4,4'-diphenylmethane diisocyanate (HMDI); Desmodur<sup>®</sup> W, which contains 20% *t,t*-HMDI,<sup>6</sup> and 1,6-hexane diisocyanate (HDI), Desmodur<sup>®</sup> H, were obtained from Bayer; and the measured equivalent weights were 113.5, 133.2, and 85.6 g/mol, respectively. All the diisocyanates except MDI were used as received. A poly(tetramethylene ether) glycol with  $M_n$  of 2000 was supplied by Du Pont. 1,4-Butanediol was Merck reagent grade and vacuum-distilled at 5 mm Hg/ $80^\circ\text{C}$  before use. Dibutyltin dilaurate was also Merck reagent grade and used as received.

### Preparation

Polyurethane materials were prepared by a one-shot, hand-cast bulk polymerization process. A typical example is as follows: 68.0 g (0.542 equiv-

alent) of MDI, 19.9 g (0.442 equivalent) of 1,4-butanediol, 100 g (0.10 equivalent) of PTMEG, and 0.1 g ( $1.6 \times 10^{-4}$  mol) of dibutyltin dilaurate were thoroughly mixed and reacted at  $50^\circ\text{C}$  for 10 min. The reaction mixtures were molded and then heated at  $100^\circ\text{C}$  for 1 h. After demolding, the samples were heated at  $100^\circ\text{C}$  for 3.5 h and then at  $150^\circ\text{C}$  for an additional 1.5 h to ensure a thorough reaction. This polyurethane is denoted as MDI-40, in which the first part indicates the diisocyanate used is MDI and the second number indicates the HS content is 40 wt %.

The polyurethane resins with 30 wt % solid content were prepared by a prepolymer polymerized route. For MDI-40 resin, 100 g (0.1 equivalent) of PTMEG, 64.6 g (0.517 equivalent, 95% total weight) of MDI, and 0.1 g DBTDL were reacted in 175 g of DMF (dimethyl formamide, as the solvent) at  $70^\circ\text{C}$  in a four-necked flask for 1 hour. Then, 19.9 g (0.442 equivalent) of 1,4-butanediol and 131.5 g of DMF were added, and the reaction proceeded at  $70^\circ\text{C}$  for 30 min. Afterwards, a viscosity adjustment procedure was carried out. The rest 5% of MDI (3.4 g, 0.027 equivalent) was added drop by drop and 131.5 g of DMF were added slowly to regulate the viscosity through a torque meter. After all, DMF was added, and the torque meter value maintained at 4 kg cm, the viscosity adjustment procedure was completed, and 1 g of methanol were added to stop the polymerization. The reaction solution was stirred for another 30 min, and the resin was discharged into a flask for testing.

### Measurements

The DSC heating curves from  $-100$  to  $250^\circ\text{C}$  were determined by a Du Pont DSC 910 at a heating rate of  $20^\circ\text{C}/\text{min}$  under nitrogen. The dynamic properties of beam specimens ( $40 \times 10 \times 3$  mm) were measured by a Perkin-Elmer Dynamic Mechanical Analysis, DMA7, in the dual cantilever mode at a forced vibration frequency of 1 Hz at a heating rate of  $5^\circ\text{C}/\text{min}$ . The tensile stress-strain data of dumbbell specimens were determined by a Testometric Micro 350 testing machine at an extension rate of 100 mm/min. The tear strength was determined by a Testometric Micro 350 testing machine according to ASTM D-624. The Shore A hardness was measured according to ASTM D-2240. The polyurethane resins were casted into coating films, then immersed in 16% DMF aqueous solution at room temperature for 2.5 min for interchange of DMF followed by the same proce-

ture to interchange DMF in hot water of 60°C for 2.5 min, and the thickness was measured. The interchanged polyurethane film was dried at 120°C for 2.5 min, and the thickness was measured. The ratio of thickness after and before drying is defined as the thickness retention. The casted polyurethane films were immersed in 5% NaOH aqueous solution at 80°C for 5 h, then the tensile strength of the films were measured, and the ratio of the tensile strength after and before immersion is defined as the water resistance according to ASTM D-543. The yellowing tests were carried out according to ASTM D-4329. In the test, the polyurethane films were placed in an oven equipped with a UV lamp, after irradiation of UV light at 40°C for 72 h, the yellowing phenomenon on the surface was investigated. The color of the specimens was characterised by a Gardener color comparator (Dr Lange Micro Color II).

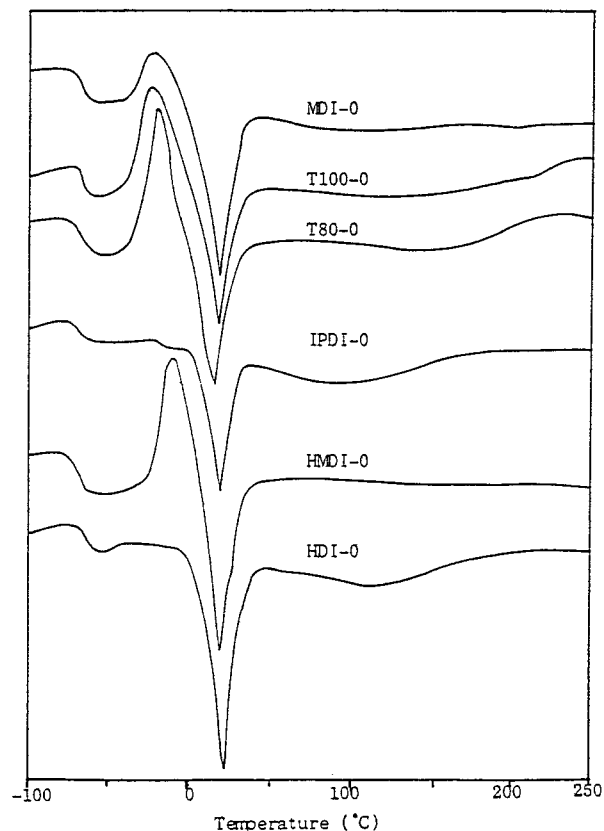
## RESULTS AND DISCUSSION

### DSC

Six polyurethanes without any chain extender were prepared and their DSC heating curves were determined for comparison. Their DSC heating curves are shown in Figure 1. The DSC heating curves exhibit a step inflection corresponding to the glass transition temperature at about  $-70^{\circ}\text{C}$  and a large endothermic peak at a peak temperature of about  $20^{\circ}\text{C}$ , corresponding to the melting transition.

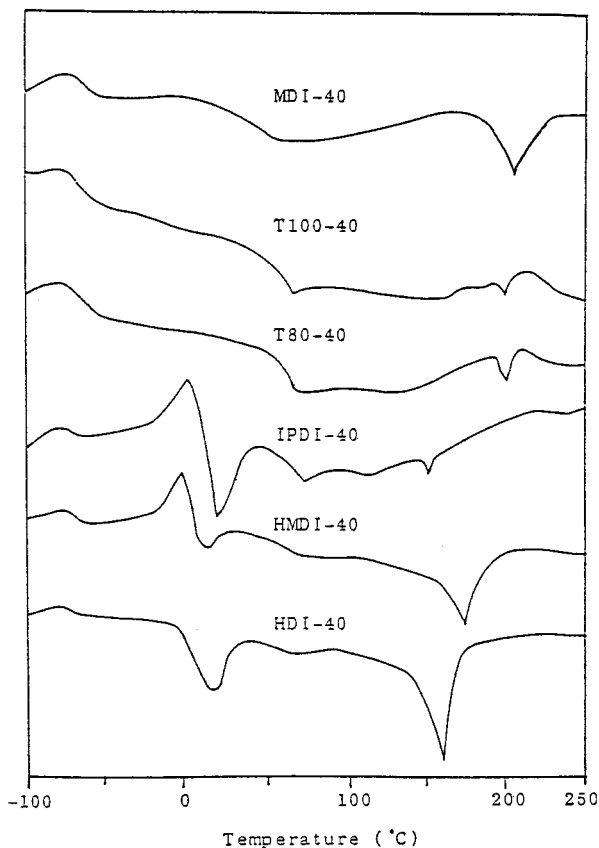
Six segmented polyurethane materials with HS content of 40 wt % have been prepared. The samples are denoted as MDI-40, T100-40, T80-40, IPDI-40, HMDI-40, and HDI-40.

The DSC heating curves of these segmented polyurethane materials are shown in Figure 2. It can be seen that the diisocyanate structure has significant influence on the thermal properties of the polyurethane materials. In the temperature range from  $-100$  to  $50^{\circ}\text{C}$ , the DSC heating curves of MDI-40, T100-40, and T80-40 exhibit a step inflection, and those of IPDI-40, HMDI-40, and HDI-40 exhibit a step inflection and an endothermic peak. It can be seen the thermal transitions within these temperature are attributed to the polyether soft segments (SS) in comparison with the DSC heating curves of the polyurethanes without chain extender. The midpoint of the step inflection is taken as the glass transition temper-



**Figure 1** The DSC heating curves of polyurethanes without chain extender.

ature of SS,  $T_g(\text{S})$ , and the peak temperature of the endotherm is taken as the melting point of SS,  $T_m(\text{S})$ . The results are listed in Table I. It can be seen from Figures 1 and 2 and Table I that the presence of HS affects the crystallizability of the SS significantly, depending on the structure of the diisocyanate. The presence of aromatic HS renders the SS of the segmented polyurethane materials uneasy to crystallize after cooling; thus, no  $T_m(\text{S})$  has been observed for MDI-40, T100-40, and T80-40. The presence of aliphatic HS also hinders the SS of the segmented polyurethane materials to crystallize after cooling ( $\Delta H_m(\text{S})$  values are significantly lower than those of the corresponding polyurethanes without HS), but to a lesser extent. A possible reason is due to the different miscibilities between the SS and HS. The segmented polyurethane materials with aliphatic HS, IPDI-40, HMDI-40, and HDI-40 exhibit a  $T_g(\text{S})$  of about  $-69^{\circ}\text{C}$ , which is close to that of the corresponding polyurethanes without HS. Thus, the SS would be immiscible with the HS in these segmented polyurethane materials with aliphatic



**Figure 2** DSC heating curves of segmented polyurethane materials: (1) MDI-40, (2) T100-40, (3) T80-40, (4) IPDI-40, (5) HMDI-40, and (6) HDI-40.

HS.<sup>7</sup> However, the  $T_g(S)$  of the segmented polyurethane materials with aromatic HS is higher than that of the corresponding polyurethanes without HS, indicating that their SS may par-

tially miscible with the HS.<sup>8</sup> The trend of  $T_g(S)$  is similar to that of the results studied by Garey.<sup>9</sup> This can be seen more clearly by DMA data and will be discussed later.

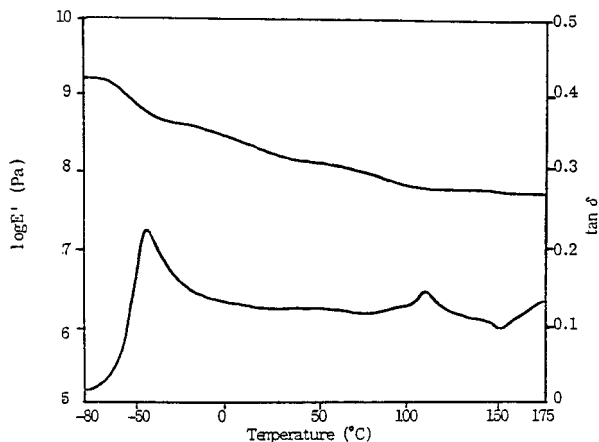
In the temperature range of 50–250°C, the DSC heating curves of the segmented polyurethane materials exhibit an endotherm corresponding to the melting transition of the HS. The  $T_m(H)$  and  $\Delta H_m(H)$  values are listed in Table I. The segmented polyurethane materials with aromatic HS exhibit a higher  $T_m(H)$  than those with aliphatic HS.<sup>10</sup> More interesting, the segmented polyurethane materials with symmetrical HS, MDI-40, HMDI-40, and HDI-40, exhibit a considerably higher  $\Delta H_m(H)$ , thus higher crystallinity, than the segmented polyurethane materials with asymmetrical HS, T100-40, T80-40, and IPDI-40, as expected.<sup>7,10</sup> It was described that the HS of HMDI-based polyurethanes were more amorphous in nature.<sup>6</sup> However, our HMDI-40 exhibits a rather high value of  $\Delta H_m(H)$ , it is probable due to the high-temperature annealing procedure (100°C for 3 h and 150°C for 1.5 h)<sup>11–13</sup> and relative low reactivity of HMDI at the same catalyst amount used,<sup>14–16</sup> which might cause increasing hard segment crystallinity, as well as phase separation in HMDI-40 specimen.<sup>11,13</sup>

## DMA

Figure 3 shows typical dynamic mechanical property curves of the segmented polyurethane materials. The  $\tan \delta$  versus temperature curves of the segmented polyurethane materials exhibit two damping peaks, the lower temperature one corresponds to  $T_g(S)$  and the higher temperature one

**Table I** Thermal Transitions of the Polyurethane Materials Determined by DSC

Sample	$T_g(S)$ (°C)	$T_m(S)$ (°C)	$\Delta H_m(S)$ (J/g)	$T_m(H)$ (°C)	$\Delta H_m(H)$ (J/g)
MDI-0	-69	18	38.2	—	—
T100-0	-70	18	36.1	—	—
T80-0	-70	16	35.4	—	—
IPDI-0	-72	19	33.4	—	—
HMDI-0	-72	21	28.4	—	—
HDI-0	-72	22	45.7	—	—
MDI-40	-63	—	—	208	19.9
T100-40	-64	—	—	200	1.5
T80-40	-65	—	—	203	4.4
IPDI-40	-70	22	11.5	150	1.2
HMDI-40	-69	15	3.5	174	20.2
HDI-40	-69	17	19.6	168	44.5



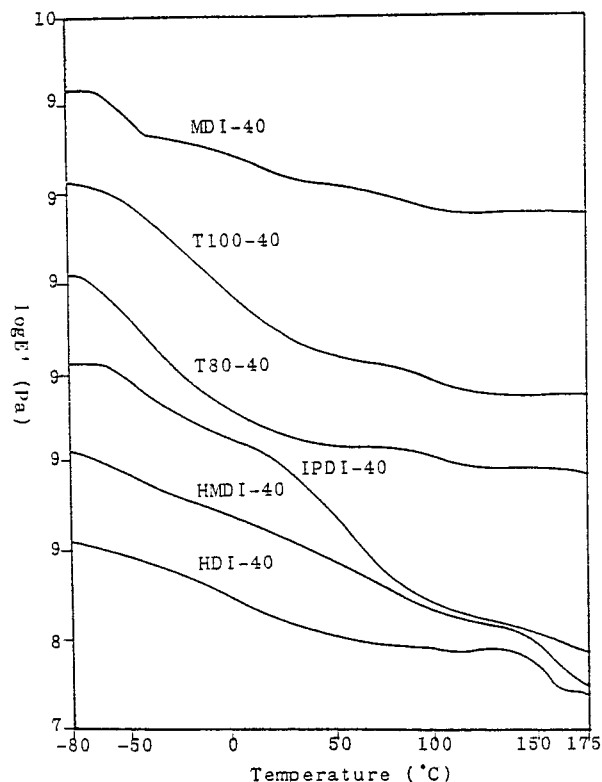
**Figure 3** Typical DMA curves of segmented polyurethane materials: MDI-40.

corresponds to  $T_g(H)$ . The results are listed in Table II. The  $T_g(S)$  values of the segmented polyurethane materials with aliphatic HS determined by DMA is about  $-65^\circ\text{C}$ , which are lower than those of the polyurethane materials with aromatic HS. Thus, the SS would be immiscible with the HS in these segmented polyurethane materials with aliphatic HS. However, the  $T_g(S)$  of the segmented polyurethane materials with aromatic HS is about  $-42^\circ\text{C}$  and significantly higher than that of the corresponding polyurethanes without HS. The significant shift in  $T_g(S)$  indicates that SS is partially miscible with the HS in these segmented polyurethane materials with aromatic HS.<sup>17</sup>

The  $\log E'$  versus temperature curves of the segmented polyurethane materials are shown in Figures 3 and 4. It can be seen that the diisocyanate structure has significant influence on the dynamic moduli of the segmented polyurethane materials. At a temperature of about  $-80^\circ\text{C}$ ,  $E'$  is slightly greater than  $10^9$  Pa and is almost inde-

**Table II** Thermal Transitions of the Polyurethane Materials Determined by DMA

Sample	$T_g(S)$ ( $^\circ\text{C}$ )	$T_g(H)$ ( $^\circ\text{C}$ )
MDI-40	-44	110
T100-40	-42	102
T80-40	-41	101
IPDI-40	-65	48
HMDI-40	-63	96
HDI-40	-63	85

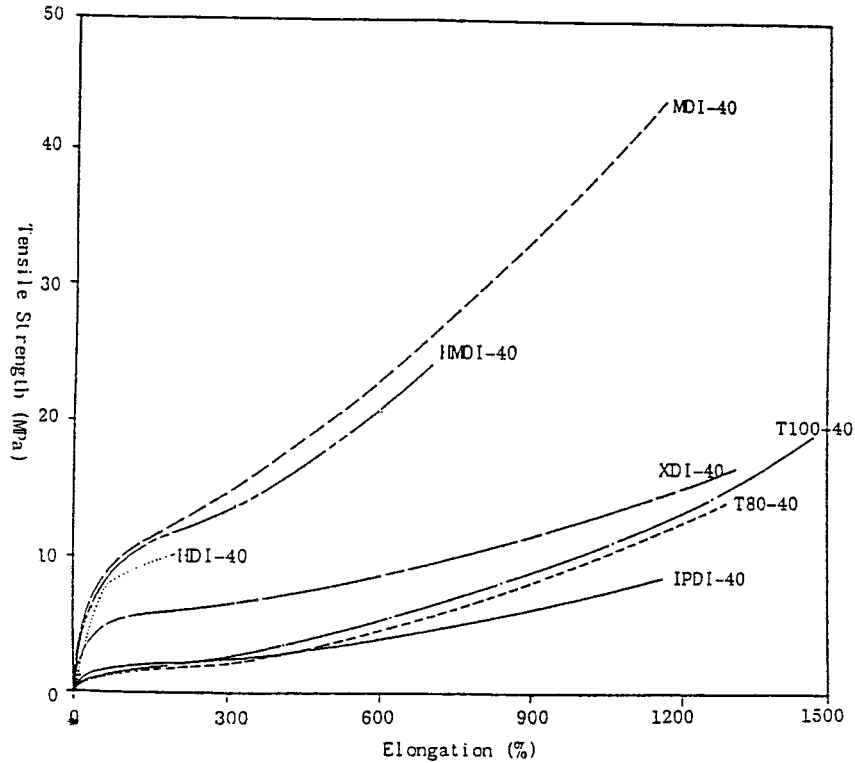


**Figure 4**  $\log E'$  versus temperature curves of (1) MDI-40, (2) T100-40, (3) T80-40, (4) IPDI-40, (5) HMDI-40, and (6) HDI-40.

pendent of the diisocyanate structure. The steeper decreases in  $\log E'$  as the temperature increases can be related to the various transitions such as  $T_g(S)$ ,  $T_m(S)$ , and  $T_g(H)$ . For example, the steeper decrease in  $\log E'$  in the range of  $-60$  to  $-35^\circ\text{C}$  is attributed to  $T_g(S)$ , and a second steeper decrease in  $\log E'$  in the range of  $10$  to  $60^\circ\text{C}$  is attributed to  $T_m(S)$  and  $T_g(H)$  for IPDI-40. And as the temperature increases, T80-40 exhibits a steeper decrease in  $\log E'$  in the range of  $-50$  to  $0^\circ\text{C}$  attributed to  $T_g(S)$ , then a plateau, and a steeper but smaller decrease in  $\log E'$  around  $100^\circ\text{C}$  attributed to  $T_g(H)$ .

### Mechanical Properties

Figure 5 shows the tensile stress versus strain curves of the segmented polyurethane materials. The Young's modulus, tensile strength, elongation at break, tear strength, and Shore A hardness are tabulated in Table III. All segmented polyurethane materials except HDI-40 exhibit high elongation ( $>700\%$ ) and show ductile behavior. HDI-40 shows brittle and exhibits poorer



**Figure 5** Tensile stress versus strain curves of (1) MDI-40, (2) T100-40, (3) T80-40, (4) IPDI-40, (5) HMDI-40, and (6) HDI-40.

tensile strength than expected maybe due to its very high crystallinity of HS (see Table I). MDI-40 shows the best tensile strength and tear strength, and IPDI-40 shows the poorest tensile strength and tear strength in these segmented polyurethane materials. The segmented polyurethane materials with symmetrical HS, MDI-40, HMDI-40, and HDI-40 exhibit higher crystallinity of HS and thus, show higher Young's modulus and hardness, as expected. This trend is consistent with dynamic modulus data. Overall, the diiso-

cyanate structure affects the mechanical properties significantly.

#### Evaluation of the Polyurethane Resins

Six polyurethane resins with compositions the same as the segmented polyurethane materials in DMF with solid content of 30 wt % were prepared. The thickness retention of the polyurethane resins, the water resistance and the yellowing resistance of the casted films were determined. The

**Table III** Tensile Properties, Hardness, and Tear Strength of the Polyurethane Materials

Sample	Young's Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Shore A Hardness	Tear Strength (kN/m)
MDI-40	49.3	42.9	1160	96	139
T100-40	18.7	16.8	1480	80	64
T80-40	17.5	14.0	1290	77	61
IPDI-40	17.8	9.5	1280	75	55
HMDI-40	43.6	24.3	710	94	110
HDI-40	40.5	10.4	200	94	76

**Table IV** Thickness Retention, Water Resistance, and Yellowing Test of the Polyurethane Resins

Resin	Thickness Retention (%)	Water Resistance (%)	Yellowing Test	
			Color Value	Evaluation
MDI-40	94.2	94	1.5	<sup>a</sup> F <sup>a</sup>
T100-40	92.1	93	1.3	F
T80-40	91.0	93	1.5	F
IPDI-40	65.8	92	1.1	F
HMDI-40	84.3	97	0.7	P
HDI-40	75.5	94	0.7	P

<sup>a</sup> F stands for "fail"; P, for "pass".

results are summarized in Table IV. In the thickness retention test, the obtained wet process polyurethane leather were dried at 120°C for 2.5 min after the resin had been interchanged with 16% DMF aqueous solution and hot water (60°C). Thus, the thickness retention is directly related to the heat resistance at 120°C. The polyurethane resins with aromatic HS show better thickness retention. HMDI-40 shows fair thickness retention. However, IPDI-40 shows the poorest thickness retention. The trend is consistent with the dynamic modulus data (Figs. 3 and 4). All the casted polyurethane films exhibit good water resistance, as expected, since the polyol used is polyether diol.<sup>18</sup> The polyurethanes derived from polyether diols display better hydrolysis resistance than those derived from polyester diols.<sup>18</sup> HMDI-40 shows the best hydrolysis resistance similar to the trend studied by Seneker and coworkers.<sup>6</sup> The casted polyurethane films derived from aromatic diisocyanate show poor yellowing resistance due to the quinonization in the presence of ultraviolet (UV) light.<sup>19</sup> HMDI-40 and HDI-40 show good yellowing resistance, as expected, since the quinonization reaction is avoided. The yellowing phenomenon of IPDI-40 is not due to the quinonization. It is probably due to the thermal degradation. The heat resistance of IPDI-40 is poor. When exposed to the UV light at 40°C for a long time, the heat accumulated to a significant extent that caused IPDI-40 to be degraded, and yellowing phenomenon was observed. In fact, when the test was carried out at room temperature, no yellowing phenomenon was observed. Thus, IPDI-40 can also be considered as a nonyellowing resin.

## CONCLUSION

The DSC and DMA data show that the thermal transitions of the segmented polyurethane materials are influenced significantly by the diisocyanate structure. The segmented polyurethane materials with aliphatic HS exhibit a  $T_m(S)$ , indicating that their SS can crystallize after cooling. The segmented polyurethane materials derived from symmetrical diisocyanate exhibit significantly higher  $\Delta H_m(H)$  and, thus, higher crystallinity of the HS. In the segmented polyurethane materials with aliphatic HS, the  $T_g(S)$  is close to the polyurethanes without chain extender, indicating that the SS is immiscible with the HS. However, significant shift in  $T_g(S)$  has been observed in the segmented polyurethane materials with aromatic HS, indicating that the SS is partially miscible with the HS. The diisocyanate structure also influences the mechanical properties significantly and is described as the effect of the chemical structure, symmetry, and crystallinity of the HS. The polyurethane resins with solid content of 30 wt % were characterized by thickness retention, water resistance, and yellowing resistance for the evaluation of their use as wet process polyurethane leather. The polyurethane resin with aliphatic HS show poorer thickness retention but better yellowing resistance.

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