# Preparation and Properties of Segmented Thermoplastic Polyurethane Elastomers with Two Different Soft Segments

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ABSTRACT: Thermoplastic polyurethane elastomers were prepared from 4,4-diphenylmethane diisocyanate (MDI)/1,4-butanediol (BD)/poly(propylene glycol) (PPG) and MDI/BD/poly(oxytetramethylene glycol) (PTMG). The MDI/BD-based hard-segment content of polyurethane prepared in this study was of 39-65 wt %. These polyurethane elastomers had a constant soft-segment molecular weight ( $\overline{M_n}$ , 2000), but a variable hard-segment block length (n, 3.0-10.1;  $\overline{M_n}$ , 1020-3434). The effects of the hardsegment content on the thermal properties and elastic behavior were investigated. These properties of the PPG-based MPP samples and the PTMG-based MPT samples were compared. The polyurethane prepared in this study had a hard-segment crystalline melting temperature in the range of 185.5-236.5°C. With increasing hard-segment content, the dynamic storage modulus and glass transition temperature increased in both the MPP and MPT samples. The permanent set (%) increased with increasing hard-segment content and successive maximum elongation. The permanent set (%) of the MPP samples was higher than that of MPT samples at the same hard-segment content. The value of K (area of the hydrogen-bonded carbonyl group/area of the free carbonyl group) increased with increasing hard-segment content in both the MPP and MPT samples, and the K value of the MPT samples was higher than that of the MPP samples at the same hard-segment content. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 345-352, 1999

**Key words:** thermoplastic polyurethane elastomer; hard segment; thermal properties; elastic behavior

## **INTRODUCTION**

Segmented thermoplastic polyurethane elastomers (STPUEs) are an important class of polymeric materials consisting of thermodynamically incompatible hard and soft segments.<sup>1</sup> The soft segments are usually high molecular weight (600-4000) polyether or polyester macroglycols of high flexibility at room temperature, which largely control the low-temperature properties, solvent resistance, and weather-resistant properties of thermoplastic polyurethane elastomers. The hard segments consist of a diisocyanate and a low molecular weight (60-400) diol (chain extender). In the solid state, unique elastomeric properties are observed due to microdomain formation.<sup>2-4</sup> The so-called hard domains provide both physical crosslink sites and fillerlike reinforcement to the soft-segment matrix. At higher temperatures, the polymer forms a homogeneous viscous melt that can be processed by thermoplastic techniques such as injection molding, extrusion, and blow molding. Subsequent cooling again leads to segregation of hard and soft segments.

The segmented structure of the polyurethane elastomer is characterized mainly by hydrogen

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| Designation<br>MPP<br>Samples | Composition<br>(mol %)<br>MDI/PPG/<br>BD   | Hard-Segment<br>Content<br>(wt %) | Soft-Segment<br>Molecular<br>Weight<br>(g/mol) | Hard-Segment<br>Molecular<br>Weight<br>(g/mol) | Average<br>Block Length of<br>Hard Segment<br>(n) | Inherent<br>Viscosity <sup>a</sup><br>(dL/g) |
|-------------------------------|--|-----------------------------------|--|--|---|--|
| MPP1<br>MPP2<br>MPP3          | 50/12.5/37.5<br>50/9.0/41.0<br>50/4.5/45.5 | 39<br>47<br>65                    | 2000<br>2000<br>2000                           | $1020 \\ 1564 \\ 3434$                         | $3.0 \\ 4.6 \\ 10.1$                              | $0.73 \\ 0.82 \\ 1.12$                       |
| MPT<br>Samples                | MDI/PTMG/<br>BD                            |                                   |  |  |   |  |
| MPT1<br>MPT2<br>MPT3          | 50/12.5/37.5<br>50/9.0/41.0<br>50/4.5/45.5 | 39<br>47<br>65                    | 2000<br>2000<br>2000                           | $1020 \\ 1564 \\ 3434$                         | 3.0<br>4.6<br>10.1                                | $1.88 \\ 1.92 \\ 2.10$                       |

 Table I
 Description of Thermoplastic Polyurethane Elastomers

<sup>a</sup> Measured at 25°C using THF as solvent.

bonding between adjacent urethane groups, which causes relatively strong interactions. The polar nature of the hard urethane segments causes a strong reciprocal attraction, leading to domain formation. The existence of hard domains through hydrogen bonding, namely, physical crosslinking, are responsible for the elastic behavior of the polyurethane elastomer. STPUEs are now widely used due to their unique properties of combining high tensile strength and high modulus with high elongation at break. Their unique combination of properties are now replacing plastics and conventional rubbers. The morphology and physical properties of segmented polyurethane elastomers have been studied extensively5-7 and have been found to depend on several factors such as the composition ratio of urethane and polyether or polyester segments, the molecular weight of the individual segments, and segmental compatibility.

In this study, the dynamic mechanical thermal properties and the elastomeric behavior of thermoplastic polyurethane elastomers based on 4,4'-diphenylmethane diisocyanate (MDI)/1,4-butan-diol (BD)/poly(propylene glycol) (PPG;  $\overline{M_n}$ , 2000) and MDI/BD/poly(oxytetramethylene glycol) (PTMG;

 $M_n$ , 2000) were examined. The MDI/BD-based hard-segment content was 39–65 wt %. The effects of the hard-segment content or the block length on the properties of these materials were also investigated.

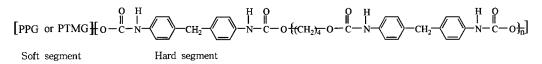
## **EXPERIMENTAL**

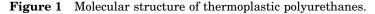
#### Materials

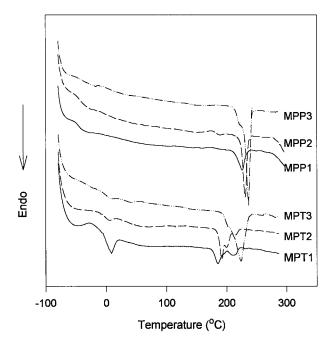
MDI (Aldrich, USA) and BD (Aldrich) were used as received. PPG (Aldrich,  $\overline{M_n}$ , 2000) and (PTMG BASF, Germany,  $\overline{M_n}$ , 2000) were used after vacuum drying.

#### Synthesis of Polymers

Stoichiometric amounts of the dry macroglycol (PPG or PTMG) and MDI was charged into a separable flask and stirred for 1 h at 70°C, and then the reaction temperature was increased to 90°C. To this mixture, an equivalent amount of the chain extender (BD) was added in one portion to the stirred mixture. This mixture was stirred for 5 min, then poured into a kneader and reacted





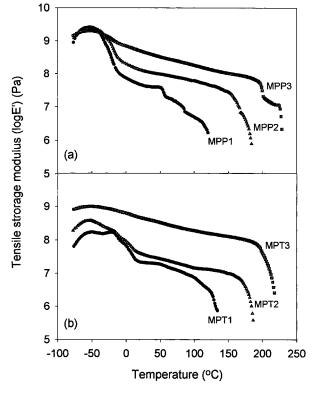


**Figure 2** DSC thermograms for the MPP and MPT samples.

for 5 min at  $80^{\circ}$ C while kneading. The product was compression-molded into 0.45-mm-thick plaques at  $180-210^{\circ}$ C for 30 min using a press.

## Infrared Spectroscopy

To examine the degree of hydrogen bonding between the hard segments, infrared spectroscopy was performed using an FTIR spectrometer (Impact 400D, Nicolet). For each sample, 32 scans at  $2 \text{ cm}^{-1}$  resolution were collected in the absorption mode. The spectra were then analyzed, employing a curve-resolving technique based on a linear least-squares analysis to fit a combination of the Lorentzian and Gaussian curve shapes.



**Figure 3** Dynamic storage modulus for (a) MPP and (b) MPT samples.

## **Differential Scanning Calorimetry**

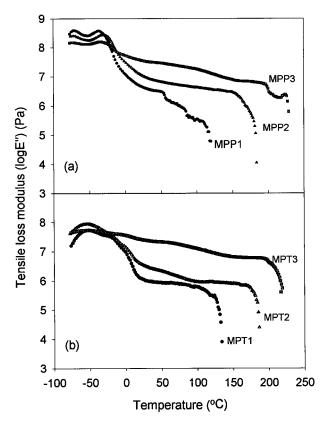
The thermal behavior of the samples was examined using a DSC 220C (Seiko) at a heating rate of 20°C/min under a nitrogen atmosphere.

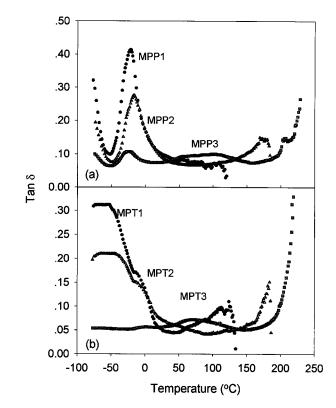
### **Dynamic Mechanical Measurement**

The dynamic mechanical thermal behaviors were obtained by DMTA measurement using a DMTA MkIII (Rheometric Scientific). The DMTA was operated from -80 to  $250^{\circ}$ C at a heating rate of

|         | Soft-  | Н        |          |          |                    |
|---------|--|----------|----------|----------|--------------------|
| Samples | $\begin{array}{c} \text{Segment} \\ T_m \ (^\circ \text{C}) \end{array}$ | $T_{m1}$ | $T_{m2}$ | $T_{m3}$ | $\Delta H$ (mJ/mg) |
| MPP1    | _  | 225.8    | _        | _        | 8.8                |
| MPP2    |  | 231.2    | _        | _        | 18.0               |
| MPP3    | —  | 236.5    |          | —        | 36.0               |
| MPT1    | 6.0  | 185.5    | 211.5    | _        | 11.3               |
| MPT2    | 5.1  | 191.8    | 199.9    | 215.1    | 18.5               |
| MPT3    | 6.3  | 224.0    | —        | _        | 36.0               |

Table II Thermal Properties of MPP and MPT Samples





**Figure 5** Tan  $\delta$  for (a) MPP and (b) MPT samples.

 $\label{eq:Figure 4} \begin{array}{ll} \mbox{ Dynamic loss modulus for (a) MPP and (b)} \\ \mbox{ MPT samples.} \end{array}$ 

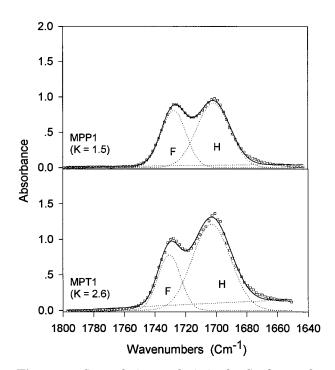
3°C/min in a double-clamp tensile mode. The sample size was  $8 \times 0.45 \times 2 \text{ mm}^3$  and the analysis frequency was 2 Hz.

#### **Tensile Retraction Test**

Tensile retraction tests were carried out with a Tinius Olsen 1000 on dumbbell specimens of a cross-sectional area of  $2 \times 0.45 \text{ mm}^2$  at room temperature. The compression-molded sheet sample was clamped to the tester and subjected to successive maximum elongations of 50, 100, 150, 200, and 300%. The crosshead speed was 20 mm/min, while the chart drive speed was 50 mm/min. The permanent set (percentage set) was taken as the percentage of elongation at which the retraction curve returns to zero stress.

# **RESULTS AND DISCUSSION**

The compositions of the polyurethane elastomers synthesized in this study are given in Table I. As can be seen, all the samples have a constant soft-



**Figure 6** Curve-fitting analysis in the C==O stretching region of two representative samples for MPP1 and MPT1 (*K*: area of hydrogen-bonded C==O/area of free C==O).

| Samples              | Area of<br>H-Bonded<br>C==O | Area of<br>Free C=O | $K \ (H/F)$         | Samples              | Area of<br>H-Bonded<br>C==O | Area of<br>Free C=O | <i>K</i><br>( <i>H</i> / <i>F</i> ) |
|----------------------|-----------------------------|---------------------|---------------------|----------------------|-----------------------------|---------------------|-------------------------------------|
| MPP1<br>MPP2<br>MPP3 | $16.7 \\ 17.6 \\ 22.6$      | 11.1 $8.7$ $4.1$    | $1.5 \\ 2.2 \\ 5.5$ | MPT1<br>MPT2<br>MPT3 | 25.1<br>26.4<br>22.7        | 9.6<br>8.8<br>2.9   | 2.6<br>3.0<br>7.8                   |

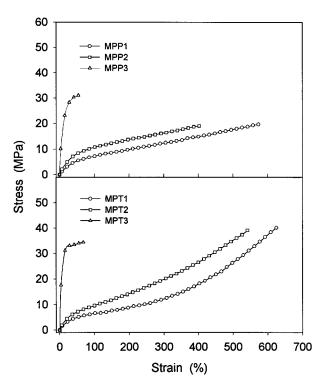
Table III Curve-Fitting Analysis Results of the C=O Stretching Region for MPP and MPT Samples

segment molecular weight of 2000 g/mol, with a variable hard-segment content and average hardsegment block length. The molecular structure of the thermoplastic polyurethane prepared here is shown in Figure 1. The inherent viscosities of the MPP and MPT samples were in the ranges of 0.73–1.12 and 1.88–2.10 dL/g, respectively. The inherent viscosities increased with increasing hard-segment content in both the MPP and MPT samples (see Table I).

The DSC thermograms of the MPP and MPT samples are shown in Figure 2. The melting temperatures of the crystalline hard segment of the MPP and MPT samples were in the ranges of 225.8–236.5°C and 185.5–224°C, respectively. A sharp endotherm peak at the melting transition of the hard segment was observed in the MPP samples, while two or three endotherm peaks were detected in the MPT samples. The heat of fusion  $(\Delta H_m)$  of the hard segment for the MPP and MPT samples increased with the hard-segment content, increasing from 8.8 to 36 J/g and from 11.3 to 36 J/g, respectively (see Table II). In the case of the MPT samples, the melting transition temperature of the soft segments was detected near 6°C. The heat of fusion  $(\Delta H_m)$  of the soft segment decreased as the hard-segment content increased. However, soft-segment transitions of the MPP samples were not detected.

Figure 3 illustrates a comparison of the dynamic storage modulus for the MPP and MPT samples. Generally, the hard-segment content significantly affects the physical properties such as the hardness, Young's modulus, and tear strength. Also, the performance of polyurethane elastomers at elevated temperature is very dependent upon the structure of the rigid segments and their ability to remain coherent at a higher temperature. As expected, the storage moduli of the MPP and MPT samples increased with increasing hard-segment content. At the same hard-segment content, the storage modulus of the MPP sample was higher than that of the MPT sample for most regions of temperature. Figures 4 and 5 show the dynamic loss modulus and tan  $\delta$ , respectively. As the hard-segment content increased, the glass transition temperatures  $(T_g)$  of the soft segment increased for the MPP and MPT samples, which was due to the decrease of the phase separation with increasing hard-segment content. The dynamic storage modulus and the  $T_g$  of the MPP samples were higher than those of the MPT samples at the same hard-segment content. This may be due to the side methyl group of PPG that could entangle the molecular chains and prevent molecular rotation in the amorphous regions

The existence of hard domains through hydrogen bonding, namely, the physical crosslinking, are responsible for the elastic behavior of polyure-



**Figure 7** Tensile properties of MPP and MPT samples.

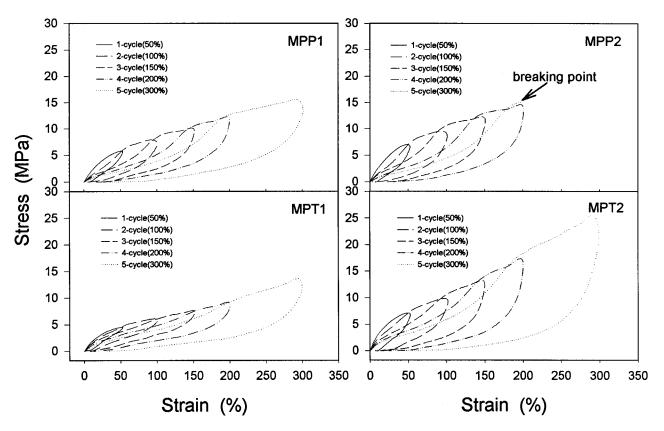


Figure 8 Stress-strain hysteresis curve for samples MPP1, MPT1, MPP2, and MPT2.

thane. Generally, hydrogen bonding is investigated by FTIR in the C=O and N-H regions. There is some absorption of the carbonyl bands of urethane groups as reported by Zharkov and co-

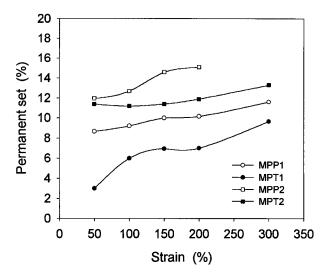
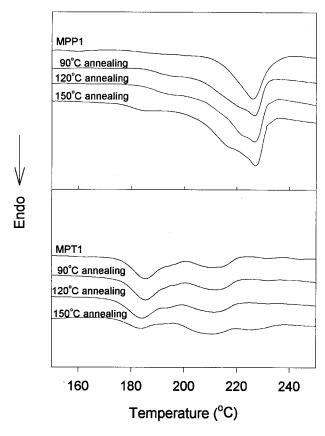


Figure 9 Permanent set (%) for samples MPP1, MPT1, MPP2, and MPT2.

workers.<sup>8</sup> The band of 1730 cm<sup>-1</sup> is characteristic of the free carbonyl group. The peak at  $1702 \text{ cm}^{-1}$ is assigned to the absorption of urethane groups involved in ordered hydrogen bonds, and the peak at  $1713 \text{ cm}^{-1}$  is assigned to weaker interactions and less ordered structures. These peaks were analyzed using Fourier analysis and the obtained curves are shown in Figure 6. The values of K(area of hydrogen-bonded C=O/area of free C=O) were calculated and are given in Table III. With increasing hard-segment content, the value of Kincreased. The K value of the MPT samples was higher than that of the MPP samples, which may be attributed to easier phase separation and movement of the PTMG segments compared to the PPG segments.

Figure 7 shows a stress-strain curve for the (a) MPP and (b) MPT samples, respectively. With increase of the hard-segment content, the tensile modulus and tensile strength increased in the MPP samples. In the MPT samples, however, the tensile strength decreased with increasing hard-segment content, due to the strength orientation of the soft segment during the extension process.<sup>9</sup> Figure 8



**Figure 10** DSC thermograms of annealed MPP1 and MPT1 samples.

represents the stress-strain hysteresis curves of the compression-molded sheet samples of MPP1, MPT1 and MPP2, MPT2 for various maximum elongations (%). The permanent set (%) of these samples with various maximum elongations are shown in Figure 9. In general, the segmented thermoplastic elastomers require a greater stress to produce a given elongation in the first extension than during subsequent extensions.<sup>10</sup> Bonart<sup>11–13</sup> proposed that the lamellalike hard-segment domains orient at low elongations with their long axis toward the stress direction due to local torques acting through the force strands of the soft segments. Further stretching causes the hard segments to slip past one another, breaking up the original structure. As the elongation continues, the hard segments become progressively oriented in the stretch direction. The deformation and restructuring of the hard segments during elongation are related to stress softening and hysteresis phenomena, which are characteristics of these polymers. The permanent set (%), of course, results from the wide distribution of relaxation times exhibited by the viscoelastic response of the macromolecules and the domain texture, some of which occur during the deformation and therefore promote irrecoverable flow.

As shown in Figure 8, the thermoplastic polyurethane elastomers prepared in this study also required greater stress to produce a given elongation in the first extension than during subsequent extensions. The MPT sample required a higher stress to produce a given elongation compared to the MPP sample. Figure 9 shows that the permanent set (%) of the MPP and MPT samples increased with increasing hard-segment content from 39 to 58 wt % and with successive maximum elongation from 50 to 300%. The permanent set (%) of the MPT samples MPT1 and MPT2 were lower than those of MPP samples MPP1 and MPP2 at the same hard-segment content. From this result, it is concluded that the MPT sample has better elastomeric behavior than that of the MPP sample. The samples MPP1 and MPT1 were too soft to use as elastomeric materials, and samples MPP2 and MPT2 containing 47% hard-segment content were the best elastic materials among the polyurethanes prepared in this study. The samples (MPP3 and MPT3) having a hardsegment content of 65 wt % had hard elastoplastic behavior rather than rubberlike elasticity. Therefore, it was not possible to use those samples to do retraction tests.

Figure 10 and Table IV show the influence of the annealing temperature on the melting tran-

| Table IV | <b>Thermal Properties of Annealed MPP</b> |
|----------|---|
| and MPT  | Samples                                   |

|                        | -Segment<br>(°C) | $T_m$    |          |                    |
|------------------------|------------------|----------|----------|--------------------|
| Samples                | $T_{m1}$         | $T_{m2}$ | $T_{m3}$ | $\Delta H$ (mJ/mg) |
| MPP1                   | 225.8            | _        | _        | 8.8                |
| 90°C annealed<br>MPP1  | 226.0            | —        | —        | 13.7               |
| 120°C annealed<br>MPP1 | 226.3            | —        | —        | 16.2               |
| 150°C annealed<br>MPP1 | 226.5            | —        | _        | 16.5               |
| MPT1                   | 185.5            | 211.5    | _        | 11.3               |
| 90°C annealed<br>MPT1  | 185.0            | 211.8    | —        | 18.5               |
| 120°C annealed<br>MPT1 | 184.3            | 210.5    | —        | 36.0               |
| 150°C annealed<br>MPT1 | 183.4            | 210.1    | _        | 36.0               |

sition of the hard segment for the MPP1 and MPT1 samples. All samples were annealed at 90, 120, and 150°C for 12 h. In comparison with the original sample, as the annealing temperature increased, the heat of fusion  $(\Delta H_m)$  of the hard segment for MPP1 increased but there was little change of the melting temperature. In the case of MPT1, the  $\Delta H_m$  of the hard segment increased little by little and the melting temperatures decreased slightly with the annealing temperature (Table IV).

## **CONCLUSIONS**

The dynamic mechanical and thermal properties and the elastic behavior of thermoplastic polyurethane elastomers based on MDI/BD/PPG and MDI/BD/PTMG were compared. The effect of the hard-segment content on the properties was also investigated. MPP samples based on PPG and MPT samples based on PTMG had a constant soft-segment molecular weight  $(\overline{M_n}, 2000)$ , but a variable hard-segment block length (n: 3-10.1)and content (39-65 wt %). The glass transition temperature  $(T_g)$  of both the MPP and MPT samples increased with increasing hard-segment content. The  $T_g$  and storage modulus of the MPP samples were higher than those of the MPT samples at the same hard-segment content. Different transition behavior was observed, indicating the different microscopic structures as shown by the thermal properties. However, they showed no distinct morphological difference and more detailed investigation might be necessary to elucidate such behavior in the thermoplastic polyurethane elastomers. The permanent set (%), taken as the percentage of elongation at which the retraction curve returns to zero stress for both the MPP and MPT samples, increased with increasing hardsegment content and maximum elongation. When

the hard-segment content and the maximum elongation were the same, the permanent set (%) of the MPT samples was lower than that of the MPP samples. From the comparison of the tensile retraction behavior for the MPP based on the PPG samples and the MPT based on the PTMG samples, it was found that the MPT samples had a higher elastomeric behavior than that of the MPP samples at the same hard-segment content. With increasing hard-segment content, the value of K(area of the hydrogen-bonded carbonyl group/area of the free carbonyl group) increased, and the value of the MPT samples was higher than that of the MPP samples.

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