

# Comparison of Properties of Thermoplastic Polyurethane Elastomers with Two Different Soft Segments

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Received 15 September 1997; accepted 6 December 1997

**ABSTRACT:** Two series of thermoplastic polyurethane elastomers [poly(propylene glycol) (PPG) based PP samples and poly(oxytetramethylene)glycol (PTMG) based PT samples] were synthesized from isophorone diisocyanate (IPDI)/1,4-butanediol (BD)/PPG and IPDI/BD/PTMG. The IPDI/BD based hard segments contents of polyurethane prepared in this study were 40–73 wt %. These polyurethane elastomers had a constant soft segment molecular weight (average  $M_n$ , 2000) but a variable hard segment block length ( $n$ , 3.5–17.5; average  $M_n$ , 1318–5544). Studies were made on the effects of the hard segment content on the dynamic mechanical thermal properties and elastic behaviors of polyurethane elastomers. These properties of PPG based PP and PTMG based PT samples were compared. As the hard segment contents of PP and PT samples increased, dynamic tensile modulus and  $\alpha$ -type glass transition temperature ( $T_g$ ) increased; however, the  $\beta$ -type  $T_g$  decreased. The permanent set (%) increased with increasing hard segment content and successive maximum elongation. The permanent set of the PT sample was lower than that of the PP sample at the same hard segment content. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1349–1355, 1998

**Key words:** thermoplastic polyurethane elastomers; soft segments; dynamic mechanical thermal properties; elastic behaviors

## INTRODUCTION

Thermoplastic polyurethane elastomers<sup>1</sup> are linear segmented copolymers with a (S—H)<sub>n</sub> type structure, where the soft segment (S) is usually formed from polyester or polyether macroglycol and the hard segment (H) is formed by extending a diisocyanate with a low molecular weight diol such as 1,4-butanediol (BD). At room temperature, the soft segments are incompatible with the polar hard segments, which leads to a microphase separation. Upon heating above the glass transition temperature ( $T_g$ ) of the hard segments, 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.

When the diisocyanate segment is equal to the stoichiometric one, the number of chemical crosslinks is almost negligible and the rubbery behavior is entirely due to the physical crosslinks. Generally, the hard segment content is a key parameter to control the properties such as rubbery plateau modulus, solvent resistance, melting point, hardness, and tensile strength. The long flexible soft segment largely controls the low temperature properties, solvent resistance, and weather resistant properties of thermoplastic polyurethane elastomers. Due to the polar nature

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*Journal of Applied Polymer Science*, Vol. 69, 1349–1355 (1998)  
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of the urethane groups in the hard segments and their ability to form hydrogen bonds, these hard segments are capable of intermolecular associations and possible microdomain segregation.<sup>2–4</sup> The so-called hard domains provide both physical crosslink sites and fillerlike reinforcement to the soft segment matrix. The thermally reversible network structure of thermoplastic polyurethane copolymers provides for the elastomeric or apparent crosslinked nature of these polymers.

When the diisocyanate content is in excess, chemical crosslinking through allophanate is also introduced in the polymer.<sup>5</sup> The existence of hard domains through hydrogen bonding (physical crosslinking and chemical crosslinking) are responsible for the elastomeric behavior of polyurethanes. The effects of physical and chemical crosslinkings on the properties such as swelling and elastic behavior of polyurethane elastomers with NCO/OH ratio of 0.9–1.22 were studied.<sup>6</sup>

Several studies<sup>7–15</sup> dealt with the various relationships of structure and properties for thermoplastic polyurethane elastomers. The morphology and properties of thermoplastic polyurethane elastomers are greatly influenced by the ratio of hard and soft block components and the average block lengths. The effects of the polymerization method (one- or two-stage) on the morphology and properties of segmented polyurethanes were studied.<sup>16</sup> Ng et al.<sup>12</sup> employed the dynamic mechanical thermal analysis method to characterize several linear segmented polyurethanes.

In this study, the dynamic mechanical thermal properties and elastomeric behaviors of thermoplastic polyurethane elastomers based on isophorone diisocyanate (IPDI)/BD/poly(propylene glycol) (PPG; average  $M_n$ , 2000) and IPDI/BD/poly(oxytetramethylene) glycol (PTMG; average  $M_n$ , 2000) were compared. The IPDI/BD based hard segments content was 40–73 wt %. The effects of hard segment content or block length on the properties of these materials were also investigated.

## EXPERIMENTAL

### Materials

IPDI (Aldrich reagent grade), BD (Aldrich reagent grade), and dibutyltin dilaurate (Aldrich reagent grade) were used as received. PPG (Aldrich; average  $M_n$ , ca. 2000), and PTMG (average

$M_n$ , ca. 2000) were dehydrated at 80°C under a vacuum (1–2 mmHg) until no bubbling was observed.

### Synthesis of Polymers

The dry macroglycol was heated to 90°C with mechanical stirring in a separable flask; then IPDI/dibutyltin dilaurate (catalysis, 0.01 wt %) was added in one portion, and the reaction between macroglycol and IPDI was continued at 90°C for 2 h while stirring. The temperature of the reaction mixture was then raised to 140°C, and an equivalent amount of dry chain extender (glycol BD) was added in one portion to the stirred mixture. The reaction mixture became thick as soon as the chain extender was added. This hot thickening mixture was stirred for 5 min, poured into a kneader, and reacted for 5 min at 140°C while kneading. The product was compression molded into sheets.

### Identification of Reaction

For the purpose of identifying the remained NCO groups in the reaction mixture, an FTIR spectrometer (Impact 400D, Nicolet) was used. For each sample, 32 scans at 2 cm<sup>-1</sup> resolution were collected in the absorption mode.

### Tensile Retraction Test

This test was carried out with a Tinius Oslen 1000 on dumbbell specimens of 2 × 0.45 mm<sup>2</sup> cross-sectional area at room temperature. The compression molded sheet sample was clamped in the tester and subjected to successive maximum elongations of 50, 100, 150, 200, and 300%. The cross-head speed was 20 mm/min, and 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 polyurethane elastomers synthesized in this study had constant soft segment molecular weights of 2000 g/mol, variable hard segment contents with 40–73 wt %, and average hard segment block length with 3.5–17.5 or average  $M_n$  of 1318–

**Table I** Description of Thermoplastic Polyurethane Elastomers

Sample Designation	Composition (Molar Ratio) IPDI/BD/PPG	Hard Segment Content (wt %)	Molecular Weight (g/mol)		Average Block Length of Hard Segment ( <i>n</i> )	Ambient Temp. Dynamic Tensile Modulus (Pa)	Inherent Viscosity (100 mL/g)	$\alpha$ -Transition Temp. (°C)	$\beta$ -Transition Temp. (°C)
			Soft Segment	Hard Segment					
PP1	1/0.78/0.22	40	2000	1318	3.5	6.5	0.73	40	-24
PP2	1/0.83/0.17	47	2000	1788	5.0	7.6	0.81	42	-25
PP3	1/0.89/0.11	58	2000	2727	8.0	8.4	0.97	73	-33
PP4	1/0.92/0.08	65	2000	3666	11.0	8.5	1.11	94	-39
PP5	1/0.93/0.07	70	2000	4605	14.0	8.9	1.13	96	-39
PP6	1/0.94/0.06	73	2000	5544	17.0	9.1	1.57	102	-40
IPDI/BD/PTMG									
PT1	1/0.78/0.22	40	2000	1318	3.5	6.4	1.88	39	-57
PT2	1/0.83/0.17	47	2000	1788	5.0	7.2	1.92	40	-54
PT3	1/0.89/0.11	58	2000	2727	8.0	8.1	2.00	74	-61
PT4	1/0.92/0.08	65	2000	3666	11.0	8.7	2.13	85	-70
PT5	1/0.93/0.07	70	2000	4605	14.0	8.8	2.40	90	-71
PT6	1/0.94/0.06	73	2000	5544	17.0	9.0	2.64	95	-61

5544. (see Table I). Figure 1 shows the molecular structure of the thermoplastic polyurethane prepared in this study. The composition, mechanical, and elastomeric properties of the thermoplastic polyurethane elastomers synthesized in this study are shown in Table I.

The reaction between diol and diisocyanate was determined by FTIR spectroscopy. The characteristic peak of the N=C=O group around 2270  $\text{cm}^{-1}$  was used to determine the extent of the unreacted diisocyanate group. Figure 2 shows the IR spectra of before and after reaction (5 min) in the kneading process at 140°C for PT1 and PP1. The peak completely disappeared after 5 min, indicating the completion of the reaction.

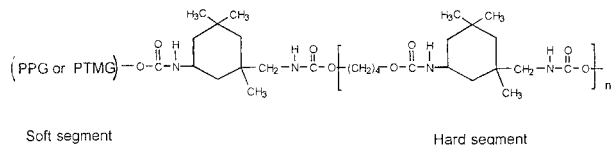
The inherent viscosities of PP and PT samples were in the ranges of 0.73–1.57 and 1.88–2.64 (100 mL/g), respectively. The inherent viscosities increased with increasing hard segment content for both PP and PT samples (see Table I). The thermoplastic polyurethanes (PP and PT sam-

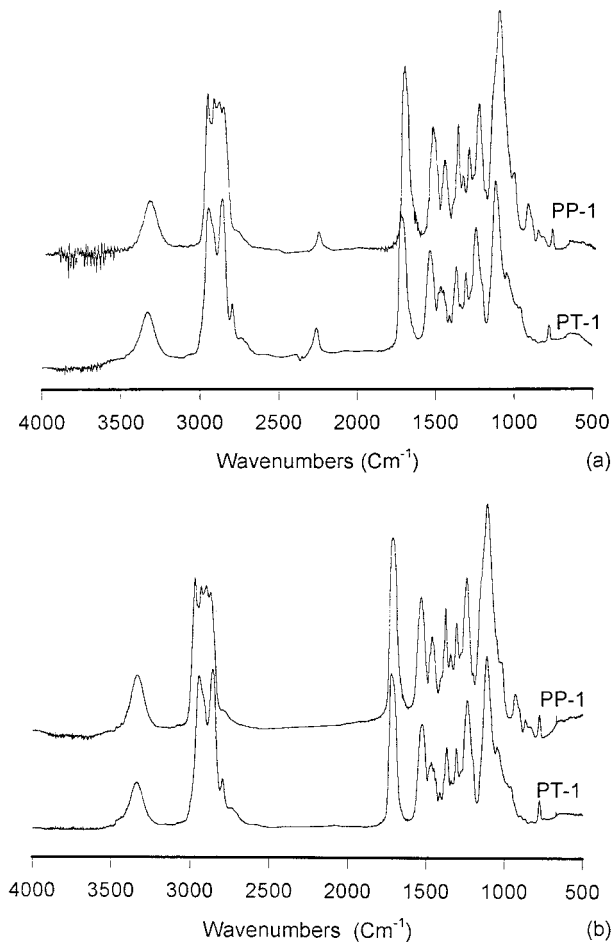
ples) prepared in this study are noncrystalline polymers.

Figure 3 illustrates the comparison of dynamic storage modulus for PP and PT samples. Generally, hard segment content significantly affects physical properties such as hardness, the 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 PP and PT samples increased with increasing hard segment content. At the same hard segment content, the storage modulus of the PP sample was higher than that of the PT 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  $\alpha$ -type  $T_g$  increased; however, the  $\beta$ -types  $T_g$  decreased for PP and PT samples (see Table I). This was due to the increase of phase separation with increasing hard segment content. The dynamic storage modulus and  $T_g$  of PP samples were higher than those of PT samples at the same hard segment content. This may be due to the side methyl group of PPG that could entangle molecular chains and prevent molecular rotation in the amorphous regions.

Figure 6 represents the stress–strain hysteresis curves of compression molded sheet samples

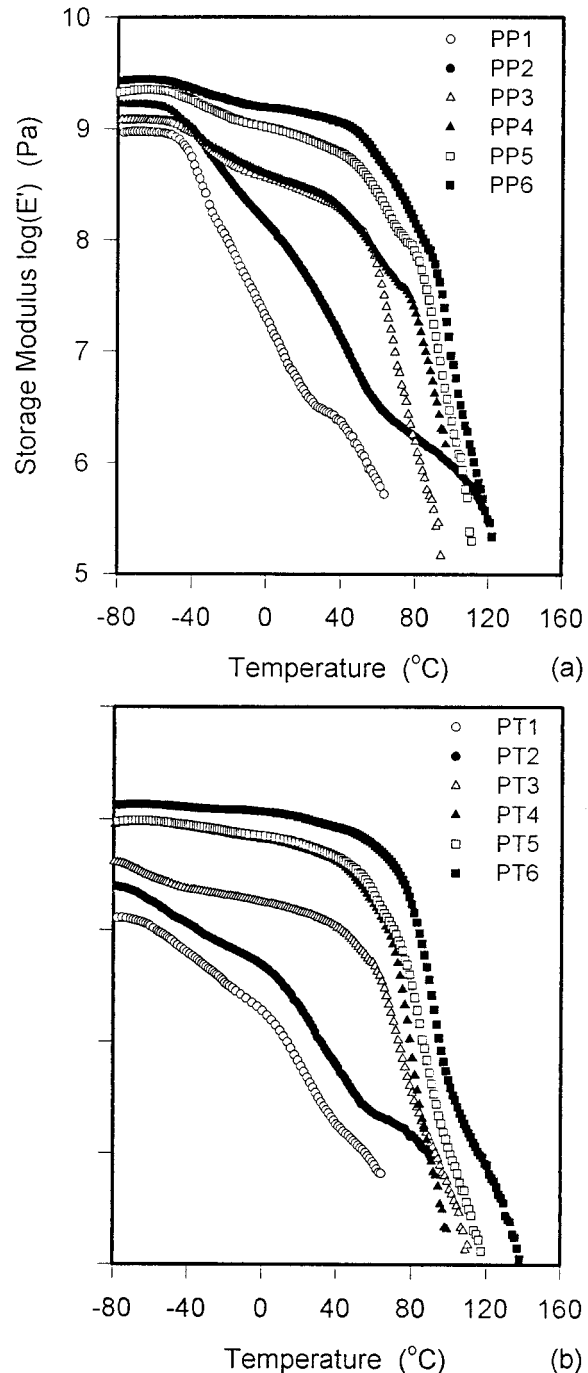
**Figure 1** Molecular structure of thermoplastic polyurethane elastomers prepared in this study.



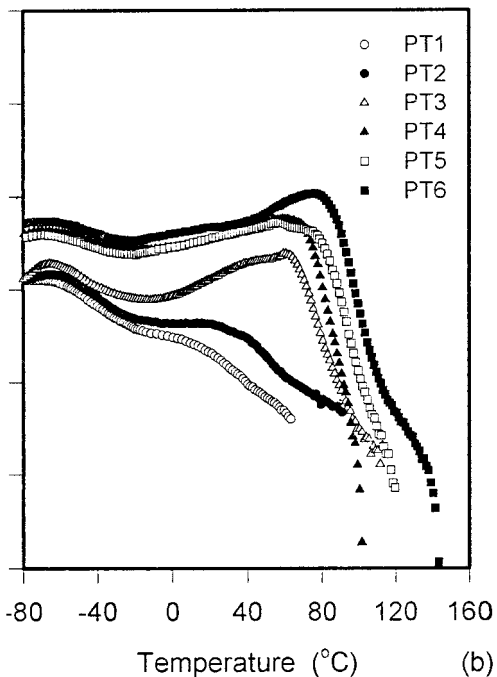
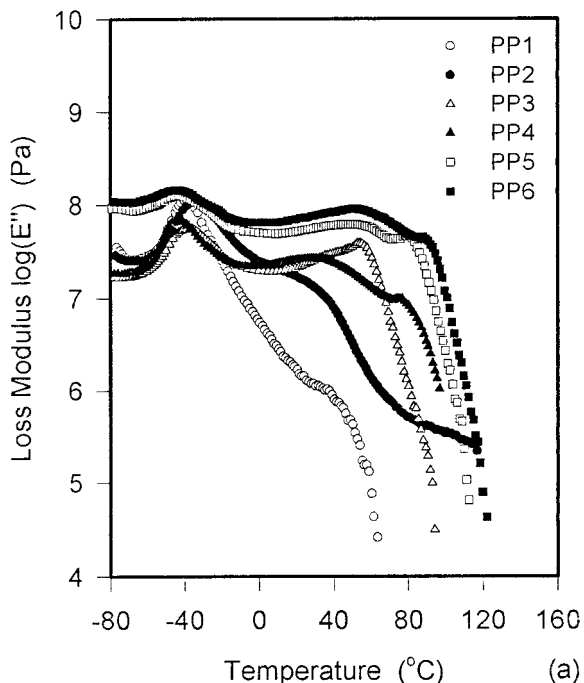
**Figure 2** FTIR spectra of (a) before and (b) after reaction (5 min) in the kneading process for PP1 and PT1.

PP1, PT1, PP2, PT2, PP3, and PT3 for various maximum elongations (%). The permanent sets of these samples with various maximum elongations are shown in Figure 7. In general, the segmented thermoplastic elastomers require a greater stress to produce a given elongation in the first extension than during subsequent extensions.<sup>18</sup> Bonart<sup>19–21</sup> proposed that the lamellarlike 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 hard segments during elongation are related to stress softening and hysteresis phenomena, which are characteristics of these poly-

mers. The permanent set, of course, results from the wide distribution of relaxation times exhibited by the viscoelastic response of the macromolecules and domain texture, some of which occur during the deformation and therefore promote irrecoverable flow. As shown in Figure 6, the thermoplastic



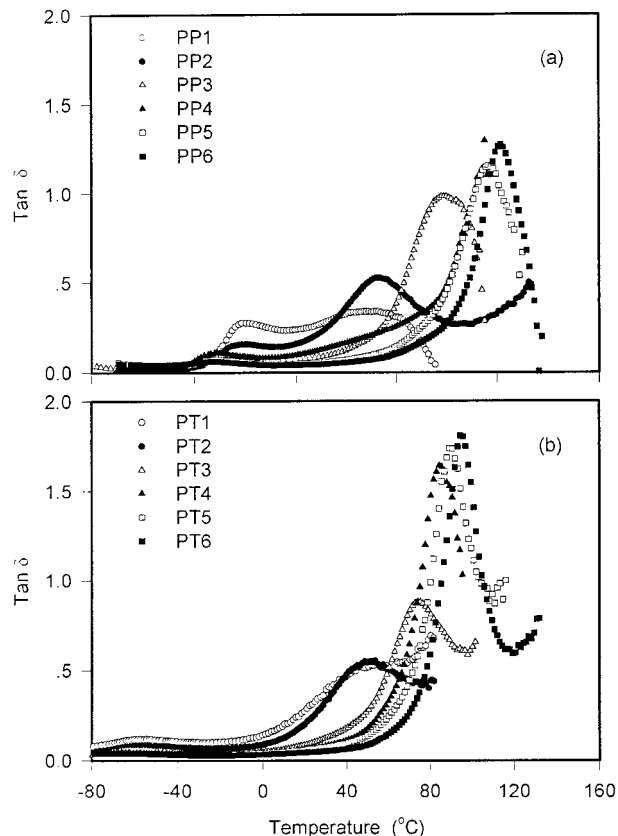
**Figure 3** Dynamic storage modulus for (a) PP samples and (b) PT samples.



**Figure 4** Dynamic loss modulus for (a) PP samples and (b) PT samples.

polyurethane elastomers prepared in this study also required greater stress to produce a given elongation in the first extension than during subsequent extensions. The PT sample required a higher stress to produce a given elongation com-

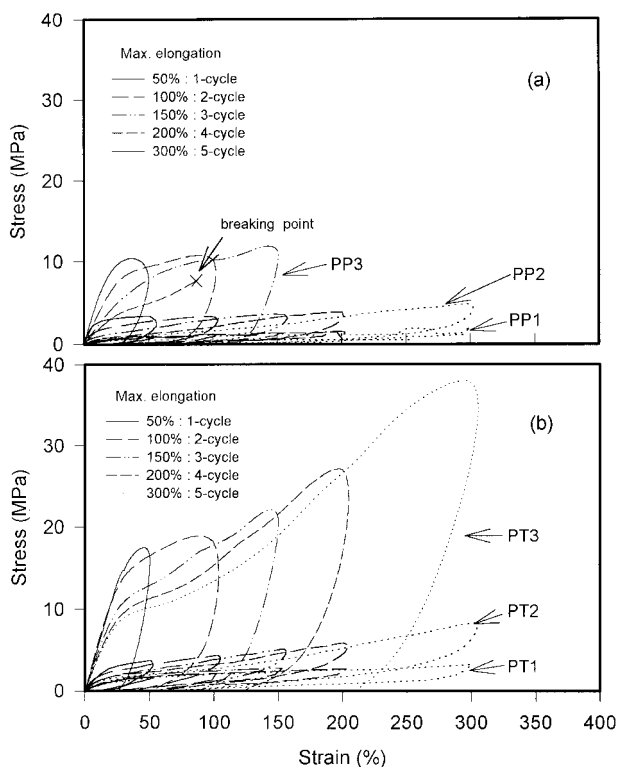
pared to the PP sample. Figure 7 shows that the permanent set of the PP and PT samples increased with increasing hard segment content from 40 to 58 wt % and with successive maximum elongation from 50 to 300%. The permanent set of PT samples (PT1–PT3) were lower than those of PP samples (PP1–PP3) at the same hard segment content. From this result it is concluded that the PT sample has better elastomeric behavior than that of the PP sample. This may be attributed to easier phase separation and movement of PTMG segments compared to PPG segments. Samples PP1 and PT1 were too soft to use as a elastomeric materials, and samples PP2 and PT2 were the best elastic materials among the polyurethanes prepared in this study. Samples PP4–PP6 and PT4–PT6 had hard segment content in the range of 65–73 wt % and had hard elastoplastic behavior rather than rubberlike elastic. Therefore, it was not possible to use those samples for the retraction test.



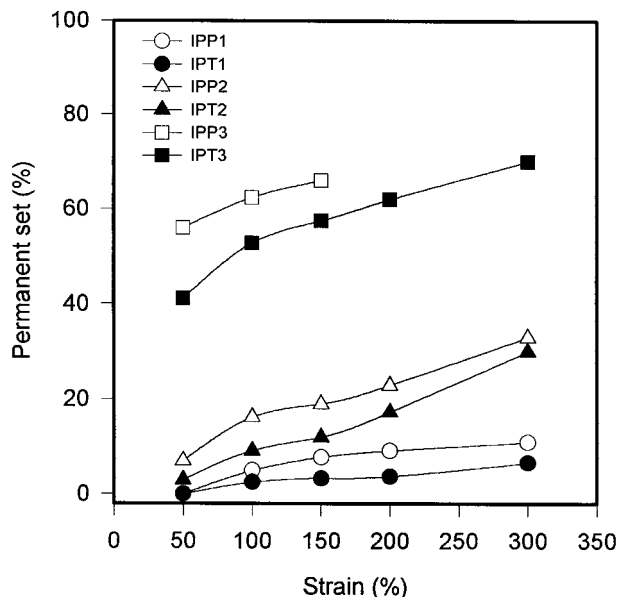
**Figure 5** Tan  $\delta$  for (a) PP samples and (b) PT samples.

## CONCLUSIONS

The dynamic mechanical thermal properties and elastic behavior of thermoplastic polyurethane elastomers based on IPDI/BD/PPG and IPDI/BD/PTMG were compared. The effect of hard segment content on the properties was also investigated. The PPG based PP sample and the PTMG based PT sample had constant soft segment molecular weight (average  $M_n$ , 2000) but variable hard segment block length and content (40–73 wt %). The  $\alpha$ -type  $T_g$  of the PP and PT samples increased with increasing hard segment content; however,  $\beta$ -type  $T_g$  decreased. The  $T_g$  and storage modulus of PP samples were higher than those of PT samples at the same hard segment content. The permanent set (the percentage of elongation at which the retraction curve returns to zero stress) for PP and PT samples increased with increasing hard segment content and maximum elongation. When the hard segment content and the maximum elongation were the same, the permanent set of PT samples was lower than that of PP samples. Samples PP4–PP6 and PT4–PT6 con-



**Figure 6** Stress–strain hysteresis curves for samples (a) PP1, PP2, and PP3 and (b) PT1, PT2, and PT3.



**Figure 7** Permanent set (%) versus strain for PP1, PP2, PP3, PT1, PT2, and PT3.

taining 65–73 wt % of hard segments had hard elastoplastic behavior rather than rubberlike elastic. From the comparison of the tensile retraction behaviors for PPG based PP and PTMG based PT samples, it was found that PTMG based PT samples had higher elastomeric behavior than PPG based PP samples at the same hard segment content.

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