

## **5. INVESTIGATING THE STRUCTURE-PROPERTY BEHAVIOR OF POLYDIMETHYLSILOXANE BASED SEGMENTED POLYUREA COPOLYMERS WITH A SECOND POLYPROPYLENE OXIDE SOFT SEGMENT COMPONENT**

### **5.1 CHAPTER SUMMARY**

Polypropylene oxide (PPO) was incorporated in a controlled manner between polydimethylsiloxane (PDMS) and urea segments in segmented polyurea copolymers and their solid state structure-property behavior was investigated. The copolymers contained PDMS segments of MW 3200 or 7000 g/mol and an overall hard segment content of 10-35 wt %. PPO segments of MW 450 or 2000 g/mol were utilized. Equivalent polyurea copolymers based on only PDMS as the soft segment (SS) component were used as controls. The materials (with or without PPO) utilized in this study were able to develop a microphase morphology as determined from dynamic mechanical analysis and small angle X-ray scattering. DMA and SAXS results suggested that the ability of the PPO segments to hydrogen bond with the urea segments results in a limited inter-segmental mixing which leads to the formation of a gradient interphase, especially in the PPO-2000 co-SS containing copolymers. DMA also demonstrated that the polyureas based on only PDMS as the SS possessed remarkably broad and nearly temperature insensitive rubbery plateaus that extended up to *ca.* 175°C, the upper temperature limit depending upon the PDMS MW. However, the incorporation of PPO resulted in more temperature sensitive rubbery plateaus. A distinct improvement in the Young's modulus, tensile strength, and elongation at break in PPO-2000 containing copolymers was observed due to inter-segmental hydrogen bonding and the formation of a gradient interphase. However, when PPO was incorporated as the co-SS, the extent of stress relaxation and mechanical hysteresis of the copolymers increased relative to the segmented polyureas based on the utilization of the PDMS soft segment component.

## 5.2 INTRODUCTION

Polydimethylsiloxane's unique set of properties, such as an extremely low glass transition temperature (*ca.*  $-123^{\circ}\text{C}$ ), good thermal, oxidative, hydrolytic, and UV stability, low surface energy, high permeability to many gases, good biocompatibility, *etc.* have prompted many investigations in its usage for commercial applications [1,2]. Due to the relatively high critical MW between entanglements of PDMS, *ca.* 24,500 g/mol [3], very weak intermolecular interactions, and the fact that at most application temperatures, generally around ambient, PDMS chains are nearly  $150^{\circ}\text{C}$  above their glass transition, modification of polydimethylsiloxane (PDMS) is often necessary to achieve usable mechanical properties. As noted earlier, these modifications include addition of silica fillers or incorporation of covalent cross-links, via peroxides [2]. More recently, considerable attention is being directed at exploiting the properties of PDMS by utilizing it as a soft segment component in segmented copolymers, mainly polyurethanes and polyurethaneureas [4-11]. The extremely non-polar nature of PDMS requires that the solubility parameter of the reaction medium be carefully controlled to match the gradually changing solubility parameter of the copolymer being synthesized and thus prevent precipitation. In the above studies, dimethylacetamide, dimethyl formamide, or tetrahydrofuran was utilized as a reaction medium to synthesize PDMS based polyurethanes and polyurethaneureas. The structure-property behavior of high MW segmented polyurethanes and polyurea counterparts based on PDMS as the soft segment (SS) component was discussed in Chapter 4. As noted earlier, this study has been published in a peer-reviewed journal [12]. The SS MW, the hard segment (HS) content, and the chain extender type were utilized as variables to compare these two different chemical types of copolymers. Within the HS content range that was utilized (16-50 wt %) the copolymers possessed a microphase separated morphology, whose extent was predominantly governed by the SS MW. In addition, the polyurethane and polyurea copolymers based on PDMS of MW 7000 g/mol and containing *ca.* 25 wt % HS content displayed broad, nearly temperature insensitive rubber plateaus (above the SS glass transition) that were respectively *ca.*  $200^{\circ}$  ( $-55$  to  $145^{\circ}\text{C}$ ) and  $230^{\circ}$  ( $-55$  to  $175^{\circ}\text{C}$ ) wide. Aside from such remarkably high temperature stability, the use of these copolymers in most structural applications is expected to be somewhat limited for high deformation structural applications due to their inferior ultimate properties, such as tensile strength and elongation at break, as compared to those based on

polyether or polyester SS. Other laboratories have also reported similar comparatively inferior mechanical properties of PDMS based polyurethanes [5,7,10,11]. Li *et al.* [13] attributed such behavior to the extremely high incompatibility between the urethane (or urea) and the PDMS segments, which they postulated, could lead to poor “interfacial adhesion” between the soft and the hard phases. Yilgor *et al.* [14] have noted that the urea-siloxane interaction energy is 7.5 kJ/mol. Such low interaction energy, as compared to the 19.2 kJ/mol hydrogen bond energy of urea-ether, suggests that the urea-siloxane interaction is of a dipole-dipole type. Thus, a lack of inter-segmental hydrogen bonding in PDMS based polyurethane copolymers is another important reason for their poor ultimate tensile properties. Various laboratories have utilized a co-SS, such as poly(tetramethylene oxide), poly(propylene oxide), or poly(ethylene glycol)adipate, in varying proportions with PDMS during the synthesis of polyurethanes [7, 15-20]. Generally in these studies, (1) the facilitation of the synthesis of PDMS based copolymers with high overall MW, and (2) the improvement of their ultimate tensile properties, as compared to those of pure PDMS based polyurethanes were the twin aims driving the use of a co-SS. The two-step prepolymer method has also been mostly utilized. In the first step, PDMS and a selected co-SS are separately end-capped with a diisocyanate. Thereafter, in the second step, the two prepolymers are *mixed* in selected proportions and then chain extended with a selected low MW diol (chain extender), such as 1,4-butane diol. In general and as expected, the structure, the MW, and the relative content of the co-SS greatly influenced the extent of the observed modification of the copolymers’ morphology and tensile properties as compared to those based on pure PDMS as the SS component.

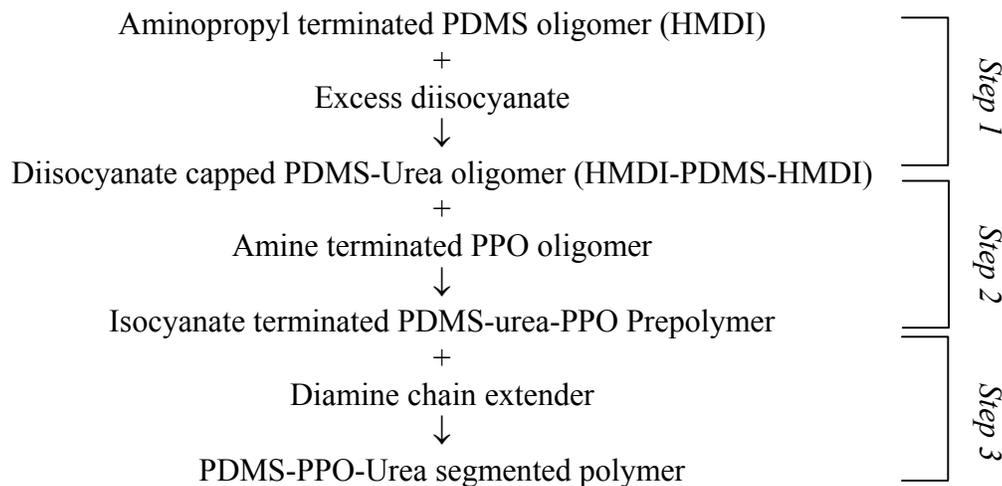
In this chapter, the earlier work presented in Chapter 4 is extended; the structure-property behavior of PDMS based polyurea copolymers that contain a second soft segment component, namely poly(propylene oxide) (PPO) *placed along the chain backbone in a very controlled manner* is discussed. Specifically, the synthetic strategy adopted in this chapter enables the positioning of the PPO segments of selected MW between the PDMS SS and the polyurea HS and *this is the noteworthy feature of these copolymers*. As noted above, PPO can undergo hydrogen bonding with the urea HS. Such inter-segmental hydrogen bonded network can potentially lead to inter-segmental mixing (between PPO and urea segments), which would then modify the nature of the interphase between the soft matrix and the hard

urea microdomains (provided the material develops a microphase morphology) Such behavior would preferably lead to the formation of a *gradient* interphase instead of a sharp interface, which is expected in polyureas based on pure PDMS as the SS. Under an applied load, a gradient interphase can aid in transferring the stresses from the soft matrix to the hard domains more effectively, thereby potentially improving the tensile properties of the silicone-urea copolymers.

### 5.3 EXPERIMENTAL

#### 5.3.1 Materials

All the copolymers addressed in this chapter were synthesized by the research group of Dr. I. Yilgor at Koc University in Turkey according to the modified prepolymer method, which is described in Scheme 5.1. For the reader's interest the synthesis procedure is presented in Appendix C.



**Scheme 5.1**

The copolymers films (0.3-0.5 mm thick) utilized for analysis were cast from isopropanol solution into Teflon molds, dried at room temperature overnight, thereafter they were further dried at 65°C until a constant weight was reached. The copolymers were stored at ambient temperature under vacuum until they were analyzed. The samples utilized in this report are listed in Table 5.1 and identified by the nomenclature:

PDMS MW-PPO MW-HS content (wt %)

Thus, P3.2-D0.4-18 for example refers to a segmented polyurea based on PDMS of MW 3200 g/mol, PPO of MW 400 and a HS content of 18 wt %. The six samples in Table 5.1 are divided into two sets. One set of three samples is based on PDMS of MW 3200 g/mol and the other on PDMS of MW 7000 g/mol. In addition to the PDMS, PPO, and HS content, the *average* overall MW of the HS of the samples is also tabulated. The reader may note that in the present report, *the single HMDI molecules that connect the PDMS segments to the PPO segments are not considered to be part of the HS sequence*. The overall HS content is thus calculated on this basis. If, on the other hand, one were to consider these HMDI molecules to be part of the HS then the HS content of the copolymers with PPO co-SS would be higher by 5-9 wt % than stated in Table 5.1.

**Table 5.1** Composition of PDMS based segmented polyurea copolymers with or without PPO co-SS.

Sample	Molar Composition (PDMS/PPO/HMDI/Dytek)	PDMS (wt %)	PPO (wt %)	Average HS MW* (g/mol)	HS Content* (wt %)
P3.2-D0-35	1 / 0 / 5 / 4	65.1	-	1780	34.9
P3.2-D0.4-18	1 / 2 / 5 / 2	57.3	16.1	1020	17.6
P3.2-D2.0-21	1 / 2 / 8 / 5	32.7	40.9	2150	21.3
P7.0-D0-20	1 / 0 / 5 / 4	80.3	-	1780	19.7
P7.0-D0.4-10	1 / 2 / 5 / 2	74.6	9.6	1020	10.2
P7.0-D2.0-15	1 / 2 / 8 / 5	51.5	29.5	2150	15.3

\*The HMDI molecules in the SS sequence are not considered to be part of the HS.

### 5.3.2 Methods

A Seiko Instruments model DMS210 was used for the dynamic mechanical analysis (DMA) measurements. The experimental details are identical to those given in Section 3.3.2.

An assembly consisting of a Phillips X-ray generator, model PW1729, coupled with a Kratky camera and a position sensitive detector operating was utilized to record slit-smear

small angle X-ray scattering (SAXS) profiles at ambient temperature. The instrumentation details can be found in Section 3.3.2.

Ambient temperature tensile testing was conducted by utilizing an Instron model 4400R equipped with a 1-kN tension load cell and calibrated with a 2 kg standard (19.61 N). “Dog-bone” shaped film specimens, 2.9 mm wide and having a grip separation distance of 10 mm were used to generate the stress-strain curves at a crosshead speed of 25 mm/min. Three samples were tested for each copolymer and the average Young’s modulus of these three runs is reported. Only representative stress-strain responses are presented in the appropriate figure. Stress relaxation studies were also performed on similar dog-bone shaped specimens. Strain levels of 25 % or 125 % were utilized. Mechanical hysteresis experiments were conducted by utilizing strain levels of 25 % or 100% for two uniaxial deformation cycles each and at a crosshead speed of 25 mm/min. A given deformation cycle was started immediately after the completion of the previous one.

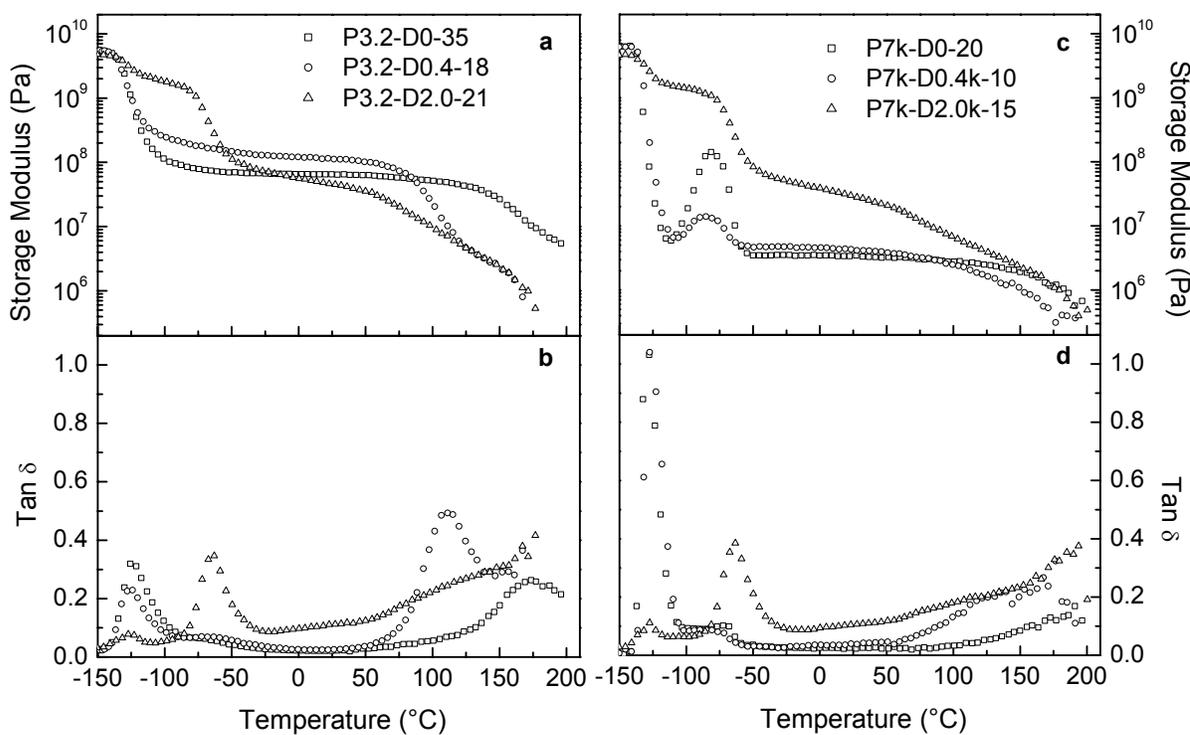
## 5.4 RESULTS AND DISCUSSION

### 5.4.1 *Dynamic Mechanical Analysis*

The storage modulus,  $E'$  and  $Tan \delta$  response of the three samples which are based on PDMS-3200 are presented in Figs. 5.1a and b respectively. These three specific samples contain only PDMS as the SS (P3.2-D0-35), PDMS plus PPO co-SS of MW 450 g/mol as the SS (P3.2-D0.4-18), or PDMS plus PPO co-SS of MW 2000 g/mol as the SS (P3.2-D2.0-21). The reader’s attention is also directed to the fact that due to the molar compositions of the precursors and the oligomer MWs utilized during synthesis, the three samples not only have different HS content (hence, average HS length) but their overall SS MW is also different. These facts have important ramifications on the copolymers’ DMA response, which is discussed below.

Focusing on the  $E'$  response of P3.2-D0-35 having only PDMS as the SS component, note that below the relatively sharp PDMS SS glass transition (at *ca.* -125°C from  $Tan \delta$  peak), as expected, the sample behaves as a rigid solid. A broad and nearly temperature insensitive rubbery plateau follows thereafter, which extends from -100 to 140°C. The low

SS  $T_g$ , which is only slightly higher than that of pure PDMS (*ca.*  $-130^\circ\text{C}$ , Ref. 21) coupled with the remarkably broad rubbery plateau or ‘service window’ indicates that this sample has a well microphase separated morphology. The increase in the PDMS SS  $T_g$  as compared to that of the neat PDMS no doubt arises due to the restrictions imposed on the PDMS segment ends by the covalently linked HS. Thus, the factors that facilitate the observed rubbery plateau breadth and the average plateau modulus are (1) the HS content and the extent of HS connectivity of the sample, (2) the bidentate hydrogen bonding mediated cohesiveness of the urea HS, (3) the sample’s relatively high extent of microphase separation, (4) low  $T_g$  of its SS phase, and (5) the high thermal stability of PDMS. As expected, the softening of the HS



phase results in a decline in  $E'$  after the rubbery plateau region.

**Figure 5.1** Storage modulus and  $Tan \delta$  responses of segmented polyurea copolymers based on PDMS-3200 (a and b respectively) and PDMS-7000 (a and b respectively) soft segments and containing PPO co-soft segments, where noted.

The  $E'$  behavior of the sample, P3.2-D0.4-18 having PPO-450 as co-SS is in general similar to the pure PDMS based copolymer but with a few distinct differences. The former sample displays a higher average plateau modulus than the latter despite having a longer SS and only about half the HS content as the latter (see Table 5.1). Such behavior is believed to

arise due to (1) the ability of the PPO SS to establish a hydrogen bond network with the urea HS, which results in a more effective stress transfer from the PDMS dominated soft matrix to the hard urea domains, and (2) increased restrictions imposed by the urea segments that may be mixed with the PPO segments. The narrower rubbery plateau in P3.2-D0.4-18 as compared to that in P3.2-D0-35 is, no doubt also due to the lower HS content (hence, shorter HS's) of the sample. In addition, the formation of the above noted inter-segmental hydrogen bond network, shorter HS, and greater segmental mixing (between PPO and urea segments) may also lower the temperature range over which the HS soften, thereby resulting in a reduction in the breadth of the rubbery plateau and also its temperature sensitivity.

In contrast, in the  $E'$  response of P3.2-D2.0-21, a broader PDMS SS glass transition at *ca.*  $-125^{\circ}\text{C}$  is noted after which follows a relatively narrow and temperature sensitive plateau which extends up to *ca.*  $-60^{\circ}\text{C}$ . The average modulus of the plateau in this temperature range is on the order of  $10^9$  Pa. Such behavior indicates that above the PDMS  $T_g$  but below the  $T_g$  of PPO, the soft PDMS phase is reinforced not only by the urea hard domains but also experiences restriction to its movement from the glassy PPO phase. Thereafter, interestingly, a distinct decrease in  $E'$  is noted, which is due to the PPO SS glass transition ( $T_g$  at *ca.*  $-65^{\circ}\text{C}$ , from  $Tan \delta$  peak). The PPO SS  $T_g$  is also slightly higher than that of the uncoupled pure PPO-2000 oligomeric (*ca.*  $-73^{\circ}\text{C}$ , Ref. 22). A temperature sensitive rubbery plateau follows this transition after which one observes a decline in  $E'$  that starts at a significantly lower temperature than in the other two PDMS-3200 based samples. From this DMA data, the extent of the PPO-2000 and PDMS-3200 inter-segmental mixing above the PPO  $T_g$  cannot be easily discerned. However, the possible inter-segmental hydrogen bonding between the PPO and urea segments is expected to enrich the interphase around the urea domains by the PPO segments. A limited PPO and urea inter-segmental mixing is therefore inevitable, which may well be the underlying reason for the temperature sensitive and narrower rubbery plateau of P3.2-D2.0-21.

The  $Tan \delta$  response of the three copolymers, presented in Fig. 5.1b is slightly more informative than the corresponding  $E'$  response. The sample, P3.2-D0-35 displays a damping peak centered at *ca.*  $-125^{\circ}\text{C}$ , which is the PDMS glass transition. Pure PDMS oligomers of  $\langle M_n \rangle$  greater than 2200 g/mol have been shown to crystallize; they melt at *ca.*  $-55^{\circ}\text{C}$  [21]. The melting of the PDMS segments in P3.2-D0-35 is also noted by the presence of a

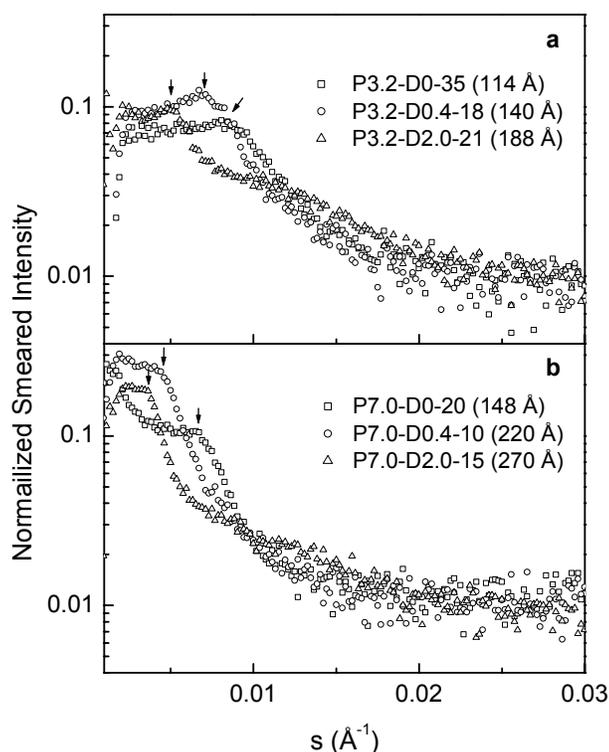
shoulder (between -75 to -50°C), which is convoluted with the higher temperature region of the PDMS glass transition peak. The PDMS melting transition cannot be clearly noted in this sample's  $E'$  response. An increase in the  $Tan \delta$  response above 130°C due to the softening of the hard domains is again observed, which corresponds to the decrease in  $E'$  as discussed earlier. In the sample, P3.2-D0.4-18 the intensity of the PDMS glass transition is slightly lower due to the lower PDMS content of this sample as compared to that in P3.2-D0-35. However, the transition maximum in the former sample still occurs at *ca.* -125°C. In light of the higher PDMS content in this sample (57 wt %) as compared to its PPO content (16 wt %) and the low MW of the PPO segments (450 g/mol), the convoluted shoulder in the  $Tan \delta$  response of P3.2-D0.4-18 in the upper temperature limit of the PDMS glass transition peak is conjectured to arise due to the melting of that fraction of the PDMS segments that crystallized, as was discussed earlier. However, the PDMS melting transition is not clearly evident in the  $E'$  response of P3.2-D0.4-18. In contrast, the PDMS glass transition peak in the final sample P3.2-D2.0-27 is greatly suppressed. Thus, *within the series of the three PDMS-3200 based samples*, it is noted that the decrease in the PDMS glass transition peak intensity is consistent with the overall decrease in the PDMS content of the samples. However, the peak intensity in P3.2-D2.0-21 is much lower than that of the PPO glass transition peak in this sample despite the PPO content of the sample (41 wt %) being only slightly higher than its PDMS content (33 wt %). Such behavior is observed because while the PDMS segments are undergoing a glass transition, they experience restrictions to their movement not only by the urea HS but also by the glassy PPO segments. As discussed earlier, the high average plateau value between *ca.* -125 and -60°C in sample P3.2-D2.0-21 also occurs due to similar reasons. Furthermore, in this sample a distinct PPO glass transition peak centered at -65°C can be seen. Thus, it is interesting to observe that the PPO-2000 segments are long enough to segregate and form a PPO rich phase. The dependence of the extent of microphase separation in segmented polyurethanes on the SS MW is well known and such behavior was also demonstrated earlier in Chapter 4 in both segmented polyurethanes as well as polyureas based on PDMS as the SS. Due to the similar temperature range over which PDMS melting and PPO glass transition occur, no distinct sign of a PDMS melting transition, if any, is evident in sample P3.2-D2.0-21.

Turning attention to Fig. 5.1c and d in which the DMA response of the three samples based on PDMS-7000 are presented, it can be observed that, in general, their  $E'$  response is similar to the PDMS-3200 counterparts but with some noteworthy differences. Despite the lower HS content of the PDMS-7000 samples (recall Table 5.1) they display rubbery plateaus that remain temperature insensitive up to higher temperatures as might be expected due to an improved extent of microphase separation in these comparatively high PDMS MW (7000 g/mol) based copolymers. Note from Table 5.1 that the average HS length of the PDMS-7000 based samples is identical to their corresponding PDMS-based counterparts. In addition, a peak in the  $E'$  response of P7.0-D0-20 can be observed following the PDMS glass transition, which occurs due to some further distinct crystallization and melting of the PDMS-7000 segments. This transition in P7.0-D0.4-17 is greatly suppressed despite only a slightly lower PDMS content as compared to that in P7.0-D0-20. Such behavior clearly indicates that the PPO co-SS greatly suppresses any further crystallization of the PDMS phase during the heating cycle. As expected, the average rubbery plateau moduli of these two samples are lower than the corresponding PDMS-3200 based counterparts due to the lower HS contents of the former coupled with the fewer restrictions experienced by the longer length of the PDMS-7000 segments. Despite the obvious structural differences, P7.0-D2.0-20 displays a very similar  $E'$  response to P3.2-D2.0-27, which suggests the presence of limited PPO and urea inter-segmental mixing in both samples, which potentially results in the formation of a gradient interphase between the hard urea microdomains and the soft matrix.

The  $Tan \delta$  response of the PDMS-7000 based samples is also very similar to the PDMS-3200 counterparts other than the nearly PPO MW independent  $T_g$  of the PDMS-7000 phase occurs at *ca.*  $-129^\circ\text{C}$ , which is slightly lower than that in the former samples (at *ca.*  $-125^\circ\text{C}$ ). Moreover, the PDMS melting transition is more clearly separated from the PDMS glass transition peak in P7.0-D0-20 and also P7.0-D0.4-17. In the sample, P7.0-D2.0-20, the PPO-2000 segments suppress the low temperature PDMS crystallinity to such an extent that its presence cannot be clearly discerned in the  $Tan \delta$  response and as noted above, the large PPO glass transition peak in the temperature range where PDMS melting generally occurs further complicates deconvolution of these two transitions.

#### 5.4.2 Small Angle X-ray Scattering

The ambient temperature normalized slit-smear SAXS intensity profiles of the six samples addressed in this chapter are presented in Fig. 5.2 as a function of the scattering vector 's' ( $= 2\sin(\theta/2)/\lambda$ , where  $\theta$  is the radial scattering angle and  $\lambda$  ( $= 1.542 \text{ \AA}$ ) the wavelength of incident radiation). All six samples listed in Table 5.1 exhibit a broad shoulder in their respective scattering profiles. The clear message from the SAXS data is that all six samples distinctly possess some level of a microphase separated morphology and therefore it is consistent with the respective ambient temperature DMA responses. The slit-smear 'd' spacing of a given sample, which is approximated by  $1/s_{\text{max}}$  according to Bragg's law, is noted in brackets next to the respective legend in Fig. 5.2.



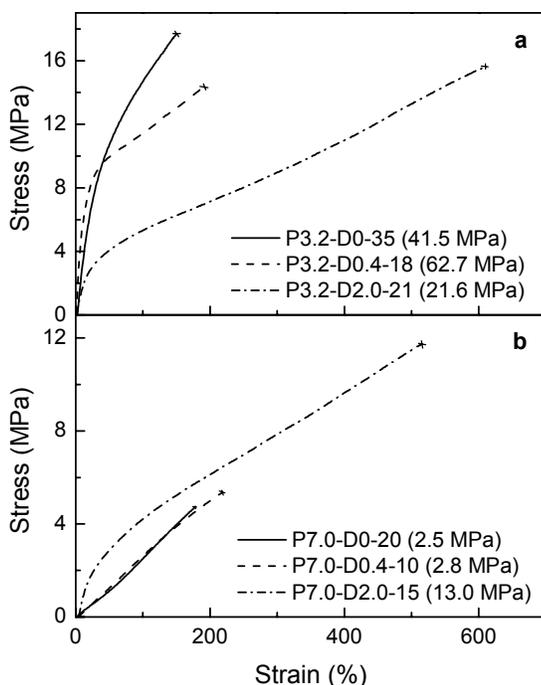
**Figure 5.2** Slit-smear small angle X-ray scattering profiles of segmented polyurea copolymers based on PDMS-3200 (a), and PDMS-7000 (b) soft segments and containing PPO co-soft segments, where noted. Arrows denote the approximate position of the first order interference shoulders in the respective given samples.

Within the PDMS-3200 as well as the 7000 based series shown in Figs. 5.2a and b respectively, as expected, the 'd' spacing increases with increasing PPO MW. In the two pure PDMS based samples it is clear from the DMA and SAXS data that the morphology should

consist of urea hard domains dispersed in a matrix dominated by the PDMS segments but which must also contain limited dissolved HS. In the samples with a co-SS also, the preceding results distinctly indicate the presence of hard domains dispersed in the soft matrix. However, it is difficult to determine the extent of the PPO-PDMS and PPO-urea inter-segmental mixing, especially in the PPO-450 based samples. In addition, the reader may recall that DMA data clearly indicated the presence of a PPO rich phase in P3.2-D2.0-21 and P7.0-D2.0-15. For reasons discussed earlier, the interfacial region between the hard domains and the soft matrix, however, is certainly expected to be richer in PPO as compared to PDMS segments. In fact, based on the DMA and SAXS results, it is reasonable to expect a gradient interphase (consisting of mixed PPO and urea segments) between the hard urea microdomains and the soft matrix in P3.2-D2.0-21 and P7.0-D2.0-15.

#### 5.4.3 Stress-strain Behavior

The ambient temperature stress-strain behavior of the polyurea copolymers is presented in Fig. 5.3.



**Figure 5.3** Stress-strain response of segmented polyurea copolymers based on PDMS-3200 (a), and PDMS-7000 (b) soft segments and containing PPO co-soft segments, where noted.

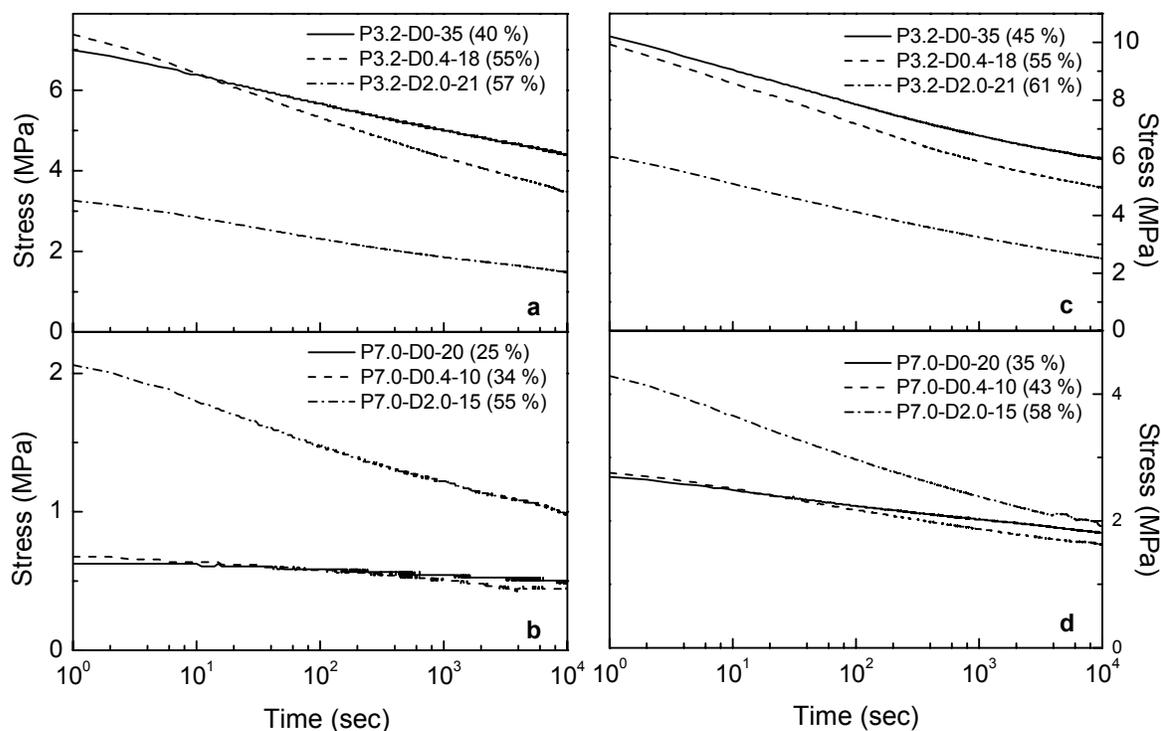
The respective Young's modulus values are listed in brackets next to a sample's legend. From Fig. 5.3a it is observed that the sample containing only PDMS SS (P3.2-D0-35) displays a Young's modulus and tensile strength of 41.5 and *ca.* 18 MPa respectively and a strain at break, which is only slightly higher than 100 %. The lack of a yield point suggests that there is insufficient percolation of the hard phase through the soft matrix despite its relatively high HS content. The Young's modulus of P3.2-D0.4-18 is nearly fifty percent higher despite the lower HS content of the sample (18 versus 35 wt %). However, the incorporation of PPO segments along the chain backbone and its lower HS content lead to a distinctly lower tensile strength. The strain at break exhibited by the sample with PPO-450 co-SS is similar to the pure PDMS based copolymer. The sample, P3.2-D2.0-18 displays the lowest Young's modulus amongst the three PDMS-3200 based copolymers. A distinct improvement in the strain at break without any considerable loss in tensile strength can also be observed in this sample. It must be noted that P3.2-D2.0-21 has comparable HS content as P3.2-D0.4-18 but the average MW of the HS in the former is greater than the other two samples in the PDMS-3200 based copolymers due to the incorporation of PPO co-SS of MW 2000 g/mol. Therefore, the considerably improved elongation at break exhibited by P3.2-D2.0-21 underscores *the importance of the length of the HS and inter-segmental hydrogen bond network (which generates a more diffuse or gradient interphase between the hard domains and the soft matrix), apart from the overall HS content, in governing the stress-strain response of segmented copolymers.*

Turning attention to Fig. 5.3b, in the PDMS-7000 based samples note that P7.0-DO-20 displays the lowest Young's modulus, tensile strength, and strain at break. The PDMS copolymer with PPO-450 co-SS displays similar behavior as the pure PDMS-7000 sample. On the other hand, for reasons noted above, P7.0-D2.0-20 possesses a greatly improved tensile behavior over the other two samples in the series.

#### 5.4.4 Stress relaxation

In addition to the stress-strain response it is also of practical interest to investigate the effect of PPO co-SS on these segmented polyurea copolymers' stress relaxation behavior. In light of the inter-segmental mixing promoted by the PPO co-SS, the extent of stress relaxation in the samples containing PPO is expected to be greater than in those copolymers containing only

PDMS as the SS component. For all six copolymers, the stress relaxation results at strains of 25 % and 125 % are presented in Figs. 5.4a-d respectively. The extent of the stress relaxation of a sample was quantified as the ratio of the absolute decrease in the stress at  $t = 10,000$  seconds (*ca.* 3 hours) to the stress immediately recorded after the sample was first stretched. The samples were stretched to a fixed strain of 25 % or 125 % in 1 and 5 seconds respectively. The percent stress relaxation numbers are listed next to the respective sample legend in Fig. 5.4. From Figs. 5.4a and b, it can be noted that at 25 % strain, both the PDMS-3200 and 7000 based copolymers (no PPO) display a nearly linear stress relaxation with log (time). These results indicate that the copolymer chains in these samples have a single relaxation time, or at least a narrow distribution, under these experimental conditions. Furthermore, the relaxation is mainly expected to occur in the soft matrix due to its higher degree of mobility at ambient temperature.



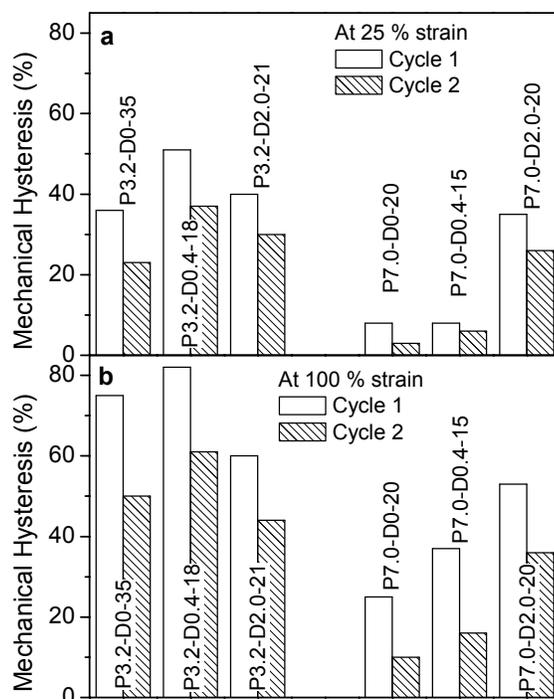
**Figure 5.4** Stress relaxation at 25 % (a and b) or 125 % (c and d) strain of segmented polyurea copolymers based on PDMS-3200 and PDMS-7000 soft segments and containing PPO co-soft segments, where noted.

Within both sub-series, the extent of stress relaxation increases with increasing PPO MW (hence, content). As noted earlier, the PPO-2000 co-SS containing samples are expected to have a distinct gradient interphase between the urea hard domains and the soft matrix, which may be responsible for the increased extent of stress relaxation in these copolymers. The increased stress relaxation may well be disadvantageous in certain structural applications of these copolymers where the material is expected to resist a constant strain. However, it must be pointed out that due to the very different compositions of the soft matrix in the copolymers within a given sub-series and the thickness of the interphase between the soft matrix and the dispersed urea domains, the constant applied strain is expected to generate very different levels of stress, which in turn will result in differing extents of activation of the soft matrix.

At 125 % strain, the stress relaxation for the six copolymers (Figs. 5.4c and d) also decreases linearly with log (time). The trend of increasing stress relaxation with PPO incorporation is also evident at 125 % strain. Interestingly, in the two pure PDMS based samples the stress relaxation is distinctly higher at 125 % strain than at 25 %. However, in the remaining samples it is comparable at both the strain levels.

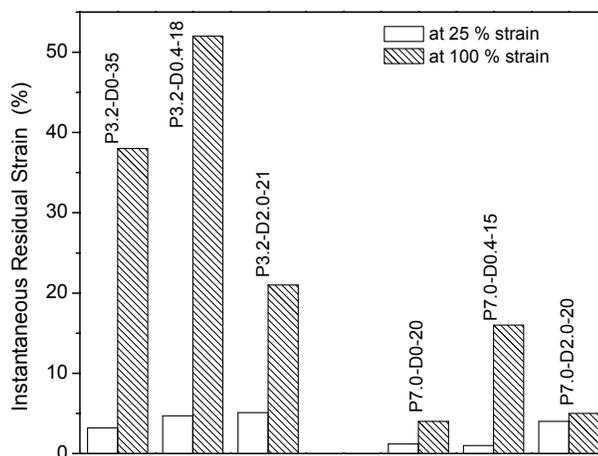
#### 5.4.5 *Mechanical hysteresis*

The mechanical hysteresis (MH) behavior, which is also of importance in structural applications, is presented in Fig. 5.5. Each copolymer listed in Table 5.1 was subjected to strain levels of 25 % (Fig. 5.5a) and 100 % (Fig. 5.5b) for two uniaxial deformation cycles each. From Fig. 5.5 it can be noted that under the test conditions employed, for a given copolymer the extent of MH, not surprisingly, is higher during the first cycle than the second. Such behavior arises due to the fact that once the original microstructure becomes disrupted during the first cycle it does not have enough time to completely ‘heal’ before the next cycle is initiated. In addition, the MH during the two cycles of any PDMS-3200 based sample is higher than the corresponding PDMS-7000 copolymers. Within the PDMS-7000 series, at 25 % and 125 % strain, the extent of MH during both cycles increases with increasing PPO MW (or content) believed due to the inter-segmental mixing promoted by the PPO co-SS. On the other hand, in the PDMS-3200 series, it is the highest in the PPO-450 containing samples.



**Figure 5.5** Mechanical hysteresis exhibited by segmented polyurea copolymers based on PDMS-3200 and PDMS-7000 soft segments and containing PPO co-soft segments, where noted, at 25 % strain (a), and 100 % strain (b).

Another parameter that can be measured during hysteresis experiments is the residual strain at zero stress that is exhibited by the sample immediately after the completion of one full cycle. Such an ‘instantaneous set’ should not be confused with the more commonly utilized quantity, permanent set, which, as the term suggests, is the residual strain at a given temperature after a fixed time interval. The instantaneous set exhibited by the six copolymers immediately after the completion of the first cycle is presented in Fig. 5.6. Interestingly, all six samples display very comparable instantaneous set when the samples are elongated to 25 % strain. However, at 100 % strain, the PDMS-7000 based copolymers return closer to their initial dimensions than the PDMS-3200 counterparts which is believed due to the comparatively lower levels of stresses experienced by the matrix of the PDMS-7000 samples. In addition, the two PPO-450 containing samples display a higher relative instantaneous set than the other two samples in their respective series due to potential greater amount of inter-segmental mixing of the shorter PPO segments and the shorter urea hard segments.



**Figure 5.6** Instantaneous residual strain at zero stress in segmented polyurea copolymers after the completion of the first hysteresis cycle.

## 5.5 CONCLUSIONS

In conclusion, PPO co-SS were incorporated in PDMS based segmented polyurea copolymers in order to improve the ultimate tensile properties of polyureas copolymers that utilize only PDMS as the SS component. The PPO co-SS of MW 450 or 2000 g/mol were incorporated in a controlled manner between the PDMS and the urea segments. PPO was selected as the co-SS due to its ability to undergo inter-segmental hydrogen bonding with the urea segments and such a network was expected to generate a diffuse or gradient interphase between the hard domains and the soft matrix. In turn, such a gradient interphase, instead of a sharp one, was expected to improve the effectiveness with which the stresses are transferred from the soft matrix to hard domains. PDMS of MW 3200 or 7000 g/mol were utilized and the HS content of the copolymers ranged between 10 and 35 wt %. DMA demonstrated that copolymers with only PDMS as the SS component possessed a remarkably broad and nearly temperature insensitive rubbery plateau; it extended from -100 to 140°C in PDMS-3200 based polyurea whereas in PDMS-7000 based polyurea it originated from -55°C and extended up to 175°C. The incorporation of PPO segments resulted in narrower and more temperature sensitive rubbery plateaus. DMA also indicated that the PPO co-SS containing copolymers utilized in this study also possessed a microphase morphology. DMA and SAXS results suggested that a limited inter-segmental mixing between the PPO and the urea

segments leads to the formation of a gradient interphase, especially in the PPO-2000 co-SS containing copolymers. Interestingly, the PPO segments of MW 2000 were also able to segregate from the PDMS segments (MW 3200 or 7000) thereby leading to a complex multiphase morphology. Microphase separation in the copolymers utilized in this study was also confirmed with ambient temperature SAXS measurements and which, as expected, also demonstrated that the inter-domain spacing in the copolymers increased systematically with increasing overall SS MW.

Distinct improvements in tensile strength and elongation at break were achieved by PPO 2000 g/mol co-SS containing polyureas as compared to only PDMS based counterparts due to the formation of a gradient interphase. The samples, P3.2-D2.0-21 and P7.0-D2.0-15 exhibited an elongation at break in excess of 500 % and tensile strength of *ca.* 12 and 16 MPa respectively. However, the extent of stress relaxation and mechanical hysteresis of the PPO c-SS containing copolymers increased as compared to only PDMS based segmented polyureas.

The results of this study clearly demonstrate the importance of inter-segmental hydrogen bonding between the co-SS and the HS and the resulting gradient interphase in addition to other factors such as the extent of microphase separation, the copolymer's HS content, the MW of PDMS, and the MW of the co-SS in improving the ultimate tensile properties of PDMS based polyurea copolymers. Thus, the approach adopted in this study provides new direction in incorporating co-SS in segmented PDMS based polyureas to modify their properties for specific applications.