

Structure–property behavior of poly(dimethylsiloxane) based segmented polyurea copolymers modified with poly(propylene oxide)

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Abstract

Poly(propylene oxide) (PPO) was incorporated in a controlled manner between poly(dimethylsiloxane) (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 microphase morphology as determined from dynamic mechanical analysis (DMA) and small angle X-ray scattering (SAXS). 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 the PPO-2000 and PDMS-7000 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 only PDMS as the soft segment component.

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1. Introduction

Polydimethylsiloxane's unique set of properties, such as an extremely low glass transition temperature (–123 to –130 °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 very weak intermolecular interactions, a relatively

high critical MW between entanglements of PDMS, ca. 24,500 g/mol [3], and the fact that at most application temperatures, generally around ambient, poly(dimethylsiloxane) chains are nearly 150 °C above their glass transition, modification of PDMS is often necessary to achieve usable mechanical properties. These modifications include addition of silica fillers or incorporation of covalent cross-links, via peroxides, for example [2]. Over the past two decades, considerable attention has been directed at exploiting the properties of PDMS by utilizing it as a soft segment component in segmented copolymers, mainly polyurethanes and polyurethaneureas [4–11]. We recently reported the structure–property behavior of high MW segmented polyurethanes and polyurea counterparts based on PDMS as the soft segment (SS) component [12]. We utilized the SS MW, the hard segment (HS) content, and the chain extender type as variables to compare these two different chemical

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types of copolymers. Within the HS content range that was utilized (16–50 wt%) the copolymers possessed a micro-phase separated morphology, the extent of which 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° (–55 to –145 °C) and 230° (–55 to –175 °C) wide. In spite of 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 poorer 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 the facilitation of the synthesis of PDMS based copolymers with high overall MW, and 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 pre-polymer method was mostly utilized. In the first step, PDMS and a selected *co*-SS were separately end-capped with a diisocyanate. Thereafter, in the second step, the two pre-polymers were mixed in selected proportions and then chain extended with a selected low MW diol (chain extender), such as 1,4-butanediol. 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 only PDMS as the SS component.

In this report, which is an extension of our earlier work [12], the structure–property behavior of PDMS based polyurea copolymers that contain a second soft segment component, namely poly(propylene oxide) (PPO) incorporated along the chain backbone in a very controlled manner is discussed. Specifically, the synthetic strategy adopted here enables the positioning of the PPO segments of selected

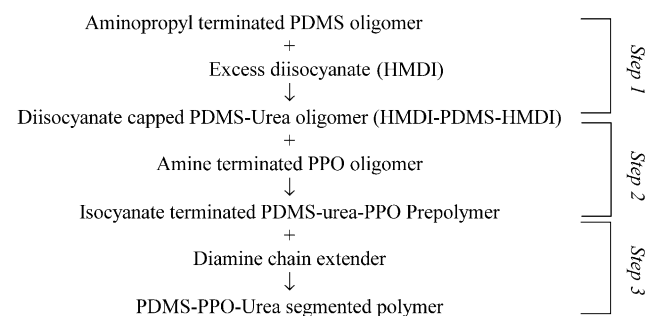
MW between the PDMS SS and the polyurea HS and this is the noteworthy feature of these copolymers. The solubility parameter of PPO (23.5 J^{1/2}/cm^{3/2}) is in between that of PDMS (15.6 J^{1/2}/cm^{3/2}) and urea (45.6 J^{1/2}/cm^{3/2}) [21]. In addition, and as noted above, PPO can undergo hydrogen bonding with the urea HS. Both of these factors 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 micro-phase 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.

2. Experimental

2.1. Materials and synthesis

α,ω -Aminopropyl terminated PDMS oligomers with $\langle M_n \rangle$ of 3200 g/mol and α,ω -*N*-methylaminopropyl terminated PDMS oligomers with $\langle M_n \rangle$ of 7000 g/mol were obtained from Wacker Chemie and Th. Goldschmidt AG, respectively. Amine terminated PPO oligomers with $\langle M_n \rangle$ of 450 and 2000 g/mol were obtained from Huntsman Chemical Corp. The $\langle M_n \rangle$ of amine-terminated oligomers were determined by titration of the end groups with standard hydrochloric acid. Bis(4-isocyanatocyclohexyl)methane (HMDI) of greater than 99.5% purity was supplied by Bayer AG. Du Pont provided 2-methyl-1,5-diaminopentane (Dytek A). Reagent grade isopropanol (IPA), purchased from Carlo Erba, was utilized as the reaction solvent without further purification.

All polymerizations were carried out in IPA at room temperature in a three-neck round bottom flask equipped with an overhead stirrer, nitrogen inlet, and an addition funnel. As shown in Scheme 1, polymers were prepared using a three-step procedure. A calculated amount of HMDI



Scheme 1.

was weighed into the reaction flask and dissolved in IPA. Calculated amounts of amine terminated PDMS and PPO oligomers were separately weighed into the Erlenmeyer flasks and dissolved in IPA. These solutions were sequentially introduced into the addition funnel and added drop-wise into the reactor containing the HMDI solution, under strong agitation, to prepare the prepolymer. Finally, a stoichiometric amount of diamine chain extender was dissolved in IPA and added drop-wise into the reactor, through the addition funnel. Progress and completion of the reactions was monitored by FTIR spectroscopy, following the disappearance of the strong isocyanate peak at 2270 cm^{-1} and formation of urea (N–H) and (C=O) carbonyl peaks around 3300 and 1700 cm^{-1} , respectively. Reaction mixtures were homogeneous and clear throughout; no precipitation was observed. The copolymer films (0.3–0.5 mm thick) utilized for analysis were cast from IPA solution into poly(tetrafluoroethylene) molds, dried at room temperature overnight and thereafter further dried at $65\text{ }^{\circ}\text{C}$ 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 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 450 g/mol and a HS content of 18 wt%. The six samples in Table 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. 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 1.

2.2. Characterization methods

A Seiko Instruments model DMS210 was used for dynamic mechanical analysis (DMA). Under a dry nitrogen atmosphere, the samples were quenched from room

temperature to $-150\text{ }^{\circ}\text{C}$ using liquid nitrogen and immediately thereafter subjected to a $2\text{ }^{\circ}\text{C}/\text{min}$ heating scan; $\tan\delta$ and storage modulus, E' , data were obtained at a frequency of 1 Hz.

A Phillips X-ray generator, model PW1729, operating at 40 kV and 20 mA and generating nickel filtered Cu K_{α} radiation with a wavelength of 1.542 \AA was used to record the small angle X-ray scattering (SAXS) profiles. The scattering patterns were collected by a Kratky camera with a $0.03 \times 5\text{ mm}^2$ slit collimation in conjunction with a Braun OED50 position-sensitive detector. The raw scattering data was corrected for parasitic scattering and normalized by sample thickness and exposure time. The intensity data was also normalized by using a Lupolen standard.

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.

3. Results and discussion

3.1. Dynamic mechanical analysis

The storage modulus, E' and $\tan\delta$ response of the three samples which are based on PDMS-3200 are presented in Fig. 1(a) and (b), respectively. These three specific samples contain only PDMS as the SS (P3.2-D0-36), 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

Table 1
Composition and average hard segment sequence MW of PDMS based segmented polyurea copolymers with or without PPO *co*-soft segments

Sample	Molar composition (PDMS/PPO/HMDI/Dytek)	PDMS (wt%)	PPO (wt%)	Average HS MW ^a (g/mol)	HS content ^a (wt%)
P3.2-D0-36	1/0/5/4	65.1	–	1780	35.7
P3.2-D0.4-18	1/2/5/2	57.3	16.1	1020	18.0
P3.2-D2.0-22	1/2/8/5	32.7	40.9	2150	21.8
P7.0-D0-20	1/0/5/4	80.3	–	1780	20.2
P7.0-D0.4-11	1/2/5/2	74.6	9.6	1020	10.8
P7.0-D2.0-16	1/2/8/5	51.5	29.5	2150	15.7

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

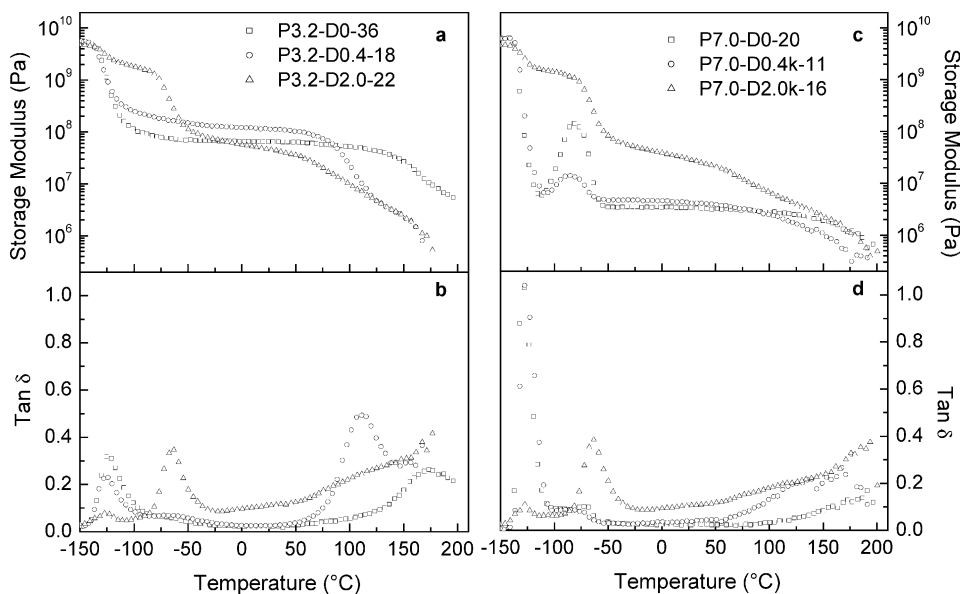


Fig. 1. Storage modulus and $\tan \delta$ responses of segmented polyurea copolymers based on PDMS-3200 (a) and (b), respectively, and PDMS-7000 (c) and (d), respectively, soft segments and containing PPO *co*-soft segments, where noted.

(P3.2-D2.0-22). It is important to note that due to the stoichiometry of the reaction mixtures and the differences in the oligomer MWs utilized during synthesis, the three samples in each set 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-D0-36 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°C , Ref. [22]) 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 region.

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 (Table 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 [14,23], 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-D0-36 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 an increase in its temperature sensitivity.

In contrast, in the E' response of P3.2-D2.0-22, a broader PDMS SS glass transition at ca. -125°C is noted after which follows a relatively narrow and temperature sensitive plateau that extends up to ca. -60°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°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°C , Ref. [24]). 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 [14] 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-D2.0-22.

The $\tan \delta$ response of the three copolymers, presented in Fig. 1(b) is slightly more informative than the corresponding E' response. The sample, P3.2-D0-36 displays a damping peak centered at ca. -125°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°C [22]. The melting of the PDMS segments in P3.2-D0-36 is also noted by the presence of a shoulder (between -75 and -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-D0-36. 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-D2.0-22 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-D2.0-22 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-D2.0-22 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 in our earlier study [12] 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-D2.0-22.

Turning attention to Fig. 1(c) 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 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. 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-D0.4-11 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-D2.0-16 displays a very similar E' response to P3.2-D2.0-22, 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°C , which is slightly lower than that in the former samples (at ca. -125°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-D0.4-11. In the sample, P7.0-D2.0-16, 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.

3.2. Small angle X-ray scattering

The ambient temperature normalized slit-smear SAXS intensity profiles of the six samples addressed in this report

are presented in Fig. 2 as a function of the scattering vector ' s ' ($=2 \sin(\theta/2)/\lambda$, where θ is the radial scattering angle and λ ($=1.542 \text{ \AA}$) the wavelength of incident radiation). All six samples listed in Table 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 DMA responses. The slit-smear'd ' 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. 2.

Within the PDMS-3200 as well as the 7000 based series shown in Fig. 2(a) 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. These results are consistent with our earlier study [12]. 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 the DMA data clearly indicated the presence of a PPO rich phase in P3.2-D2.0-22 and P7.0-D2.0-16. 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

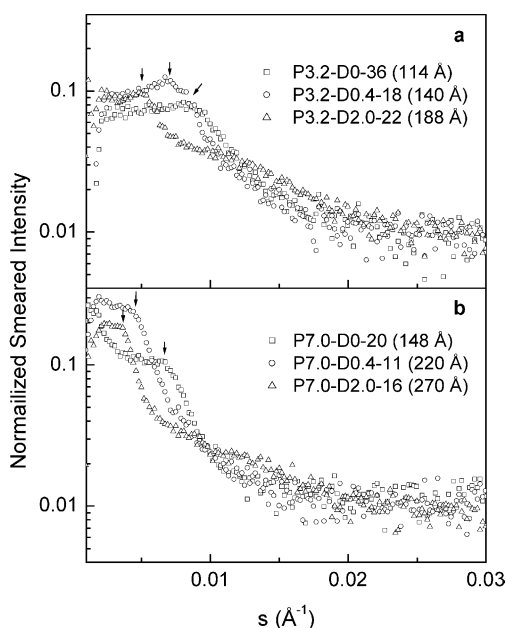


Fig. 2. Slit-smear'd small angle X-ray scattering profiles of segmented polyurea copolymers based on PDMS-3200 (a), and PDMS-7000 (b) soft segments and containing PPO *co*-soft segments, where noted. Arrows denote the approximate position of the first order interference shoulders in the respective sample. The slit-smear'd ' d ' spacing is indicated in parentheses.

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-D2.0-22 and P7.0-D2.0-16.

Based on the DMA and SAXS results, a simplified schematic illustration of the morphology in the segmented copolymers addressed in this study is presented in Fig. 3.

3.3. Stress–strain behavior

The ambient temperature stress–strain behavior of the polyurea copolymers is presented in Fig. 4. The respective Young's modulus values are listed in parentheses next to a sample's legend. From Fig. 4(a) it is observed that the sample containing only PDMS SS (P3.2-D0-36) 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 50% 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-D2.0-22 has

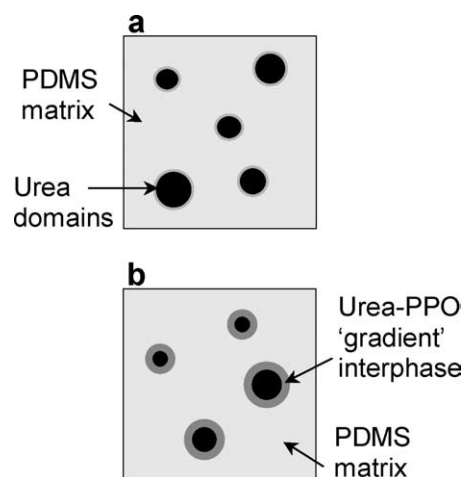


Fig. 3. Simplified schematic illustration of the microphase morphology of (a) PDMS–urea copolymers with a relatively sharp interphase between the PDMS matrix and the randomly dispersed urea hard domains; (b) the development of a urea-PPO 'gradient' interphase between the urea hard domains and the soft PDMS matrix upon incorporation of PPO. Note that isolated urea segments, which may be dissolved in the soft matrix, are not shown.

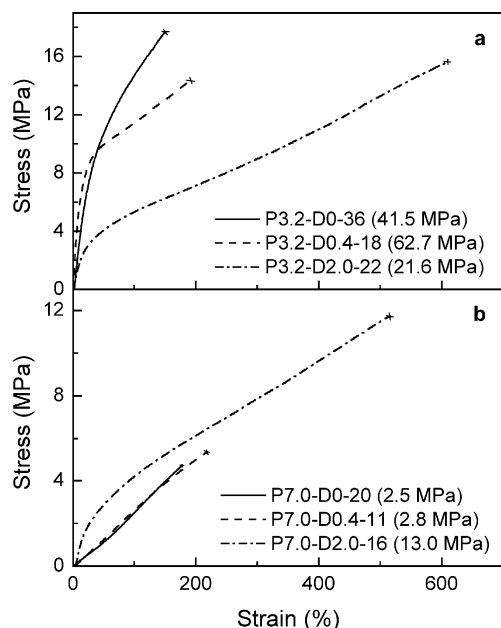


Fig. 4. Stress–strain response of segmented polyurea copolymers based on PDMS-3200 (a), and PDMS-7000 (b) soft segments and containing PPO *co*-SS segments, where noted. The Young's modulus of each sample is indicated in parentheses.

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-D2.0-22 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 these segmented copolymers.

Turning attention to Fig. 4(b), 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-D2.0-16 poses a greatly improved tensile behavior over the other two samples in the series.

3.4. 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 Fig. 5(a)–(d), respectively. The extent of the stress relaxation of a

sample was quantified as the ratio of the absolute decrease in the stress at $t = 10,000$ s (ca. 3 h) 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 s, respectively. The percent stress relaxation numbers are listed next to the respective sample legend in Fig. 5. From Fig. 5(a) 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.

Within both the 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 likely variation in 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 (Fig. 5(c) and (d)) also decreases nearly linearly with log (time), although there is a slight distinct curvature in some of the curves. 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.

3.5. Mechanical hysteresis

The mechanical hysteresis (MH) behavior, which is also of importance in structural applications, is presented in Fig. 6. Each copolymer listed in Table 1 was subjected to strain levels of 25% (Fig. 6(a)) and 100% (Fig. 6(b)) for two uniaxial deformation cycles each. From Fig. 6 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

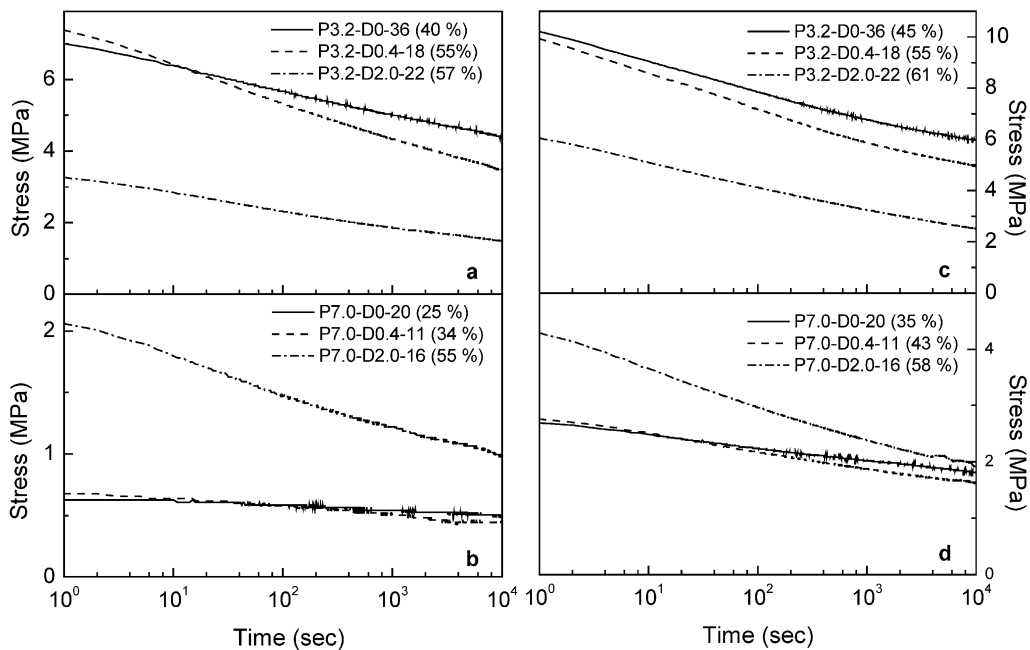


Fig. 5. Stress relaxation at 25% (a) and (b) or 125% (c) and (d) strain of segmented polyurea copolymers based on PDMS-3200 and PDMS-7000 soft segments and containing PPO *co*-soft segments, where noted. The extent of the stress relaxation of a sample, which is quantified as the ratio of the absolute decrease in the stress at $t=10,000$ s (ca. 3 h) to the stress immediately recorded after the sample was first stretched is indicated in parentheses.

copolymers. Within the PDMS-7000 series, at 25 and 100% 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.

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. 7. 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

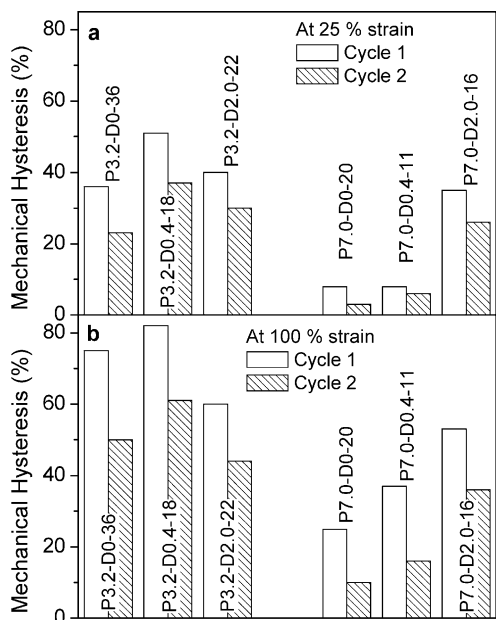


Fig. 6. Mechanical hysteresis exhibited by segmented polyurea copolymers based on PDMS-3200 and PDMS-7000 soft segments and containing PPO *co*-soft segments, where noted, at 25% strain (a), and 100% strain (b).

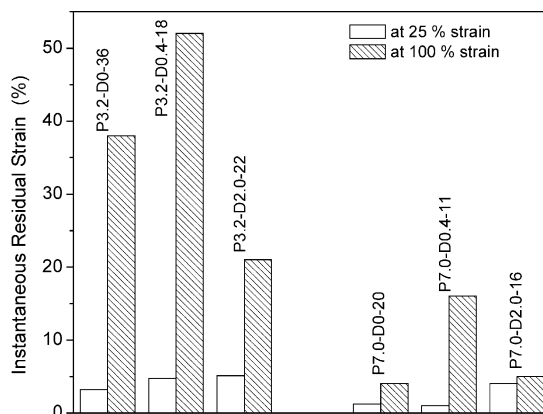


Fig. 7. Instantaneous residual strain at zero stress in segmented polyurea copolymers after the completion of the first hysteresis cycle.

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.

4. 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 7000 g/mol based counterpart due to the formation of a gradient interphase. The samples, P3.2-D2.0-22 and P7.0-D2.0-16 exhibited an elongation at break in excess of 500% and tensile strength of ca. 16 and 12 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.

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