Exploring the contributions of variable network structure on rubber elasticity using model silicone elastomers

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Abstract:

Poly dimethyl siloxane (PDMS) is a highly flexible inorganic polymer currently widely used in soft lithography and microfluidics applications due to its optical transparency, biocompatibility, and gas permeability in addition to the simplicity in fabrication process and ease of controlling the mechanical properties. Recent work has explored phenomenological and structure based entanglement models for a better understanding of entropic mechanisms in elastomers and to address limitations in classical rubber elasticity theory vis-à-vis the topological interaction arising due to chain crossing and their finite extensibility. To quantify the individual effects of physical entanglements and chemical crosslinking on the network structure-property relationships, we prepared two differently crosslinked PDMS elastomers and used swelling of the polymer in xylene to obtain variable microstructures. Highly crosslinked PDMS networks show isotropic swelling in xylene and high values of storage modulus as compared to PDMS obtained using low amounts of crosslinker. Uniaxial tension and biaxial experiments show that an increase in crosslinker leads to a higher modulus of the elastomers. Biaxial mechanical experiments show that the slip link model best fits our experimental data obtained using equibiaxial and nonequibiaxial tests that add constraints to the chain deformations. Dynamic mechanical analysis (DMA) studies show the dynamic variations in the chemical crosslinks and physical entanglements on the properties of the elastomer networks. Such studies relate structure-property relationships in PDMS networks that may be useful in microfluidics, mechanobiology studies to assess effects of substrate stiffness on cellular responses and biosensor applications.

Keywords Polydimethysiloxane, Swelling, Entanglement, Crosslinking

1. Introduction

Poly (dimethylsiloxane) (PDMS) is one of the most flexible known inorganic polymers and is a widely used as adhesives, dampers, and in microelectronics and biomedical devices [1]. PDMS is obtained through differential crosslinking of a base polymer to form tailored networks that can be used to produce dramatic changes the material properties of the crosslinked elastomer. Network properties are dependent on the amount of chemical crosslinking coupled with a high number of physical entanglements produced while keeping all other processing variables constant. Classical rubber elasticity models, obtained using the Gaussian description of the networks, show that the molecular weight of crosslinked polymer networks is directly proportional to the measured shear modulus. Recent investigations have focused on the individual contributions of the chemical crosslinks and physical entanglements to the mechanical properties of elastomers using phenomenological and microstructure based models for the total strain energy [2, 3]. Of these, the Edward-Vilgis tube model, also referred to as the slip link model [4], and the Arruda-Boyce model [5] are promising models to describe mechanics of crosslinked networks.

Recent investigations in our lab show that the SL model describes the network properties of PDMS networks, crosslinked using differential amounts, to produce PDMS networks with varying network topography of individual chains. The goals of this study are to investigate the effects of varying physical entanglements on the mechanical properties of the PDMS elastomers that are hypothesized to produce a measurable difference in the material properties of the networks. We prepare PDMS elastomers by varying the crosslinking compound to produce two different network compositions and use swelling of the elastomers in xylene to alter the physical entanglements in the structure. Because swelling in solvents may cause removal of the uncrosslinked sol fraction of the polymers comprised of unreacted PDMS and star molecules [6], we use dynamic mechanical analysis (DMA) methods to distinguish between the properties of the prepared elastomers using a linear viscoelasticity framework. Further, to clearly distinguish between the entanglements and crosslinks, we use methods to swell the elastomers and assess changes in network microstructures using DMA measurements. The dynamics of the elastically active networks can be individually tested to quantify the elastic and viscous contributions to the mechanical properties of PDMS and investigate the effects of stoichiometric imbalance caused by differential chemical crosslinking and physical entanglements on the network properties.

2.Materials and Methods

Poly (dimethylsiloxane) was prepared by mixing base silicone elastomer with crosslinker (PDMS, Sylgard®184, Dow Corning) in weight ratios of 10:1 and 40: 1, represented as P10 and P40, in this study. The mixture was degassed to remove air bubbles and cured at 40 ^{0}C for 8 hours to obtain the silicone specimens for the mechanical experiments.

2.1 Swelling behavior

PDMS elastomers were completely immersed in xylene at room temperature for 24 hours and the swollen sample dimensions in the three directions were recorded using a digital camera (n=3). The images were processed to quantify three dimensional changes following swelling. Further, sample weights were obtained to characterize the swelling ratios at various time intervals. Swelling of elastomers in organic solvents is designed to produce alterations to the network conformations whose effects must be quantified using mechanical experiments. Finally, swollen specimens were air dried for 24 hours and tested to delineate differences in chemical crosslinks and physical entanglements on the measured mechanical properties.

2.2 Mechanical characterization

To characterize mechanical properties of PDMS elastomers prepared using differing crosslinking ratios, monotonic compression and tension experiments were used. Because uniaxial experiments are insufficient to quantify the constitutive properties of elastomers, we also use planar biaxial experiments using variable stretches in two orthogonal directions to produce a wide range of deformations in parameter space. Such data, although scarce in literature, are necessary to quantify the differences in material behaviors and obtain a suitable strain energy function to describe the material. Finally, we use dynamic mechanical analysis (DMA) experiments to quantify changes in specimen microstructure caused due to swelling in xylene.

Uniaxial and biaxial tensile mechanical tests were performed using a custom planar biaxial instrument (Bangalore Integrated System Solutions (P) Ltd, India) details of which are published elsewhere [7]. Dumbbell (ASTM D412–06) shaped samples of P10 and P40 were cut from prepared PDMS sheets using a punching machine with die for uniaxial mechanical experiments. Specimens were clamped between two stretcher arms, preloaded to 20 gram force, and stretched uniaxially under force control (5 gm/sec). Marker points, placed 14 mm apart in the gauge region, were imaged using a video extensometry system, their displacements measured using centroid tracking with a custom MATLAB (v7.8.0.347 (R2009a)) programs which were finally used to quantify strains in the sample. Stretch (λ) at any point of elongation was calculated using a direct method obtained as a ratio of change in length during deformation to the original length. Loads in the specimen during deformation were continuously recorded and converted to engineering stresses using the cross sectional dimensions following prior to the experiment. Young's modulus was calculated using the linear portion of the stress-strain plot which corresponded to about 10% stretch. Biaxial and nonequibiaxial experiments were performed on flat P10 and P40 sample of dimensions 40 mm x 40 mm with thickness ranging from 1-1.6 mm. In this protocol, the elastomer sample was preloaded to 20 grams and stretched in the two orthogonal directions in various load ratios of 4.3:1.7, 3.3:5, 1:2, 2.3:3.3 and 1:1 at a rate of 2 gram/sec.

Monotonic compression test was done using Zwick/RoellZ005 Universal Testing Machine, GmbH Germany. Cylindrical samples (n=3) of PDMS of length 13 mm and diameter 30 mm were prepared and the specimens were compressed at a rate of 0.5 mm/sec, following a preload of 20 gm.

DMA experiments were carried out using P10 and P40 PDMS samples (n=3) of dimensions 40 mm length, 10 mm width and 4-5 mm thickness prepared using the two crosslinking ratios as described earlier. A Bose Electroforce® 3200 instrument (Bose Corp. USA) was used to preload PDMS samples to 0.1 N load followed by sinusoidal cyclic displacement of amplitude 1.5mm over a frequency range from 0.5 to 80 Hz. Discrete Fourier transforms of the analog force and displacement traces were calculated using custom MATLAB programs and the phase difference between these traces, δ, were used to compute the storage (E'), loss moduli (E'') and loss tangent ($\tan\delta$) defined as

$$E' = \mathrm{E}\cos\delta,\ E'' = \mathrm{E}\sin\delta,\ \tan\delta = \frac{E'}{E''} \tag{1}$$

where E is Youngs modulus.

3. Results and discussion

3.1. Effects of swelling on PDMS samples

Weight ratio of swollen PDMS samples, calculated as

$$\%\,Swelling\ Ratio = \frac{W_s - W_u}{W_u} * 100 \tag{2}$$

W_u and W_s in equation (2) are the weights of unswollen and swollen sample respectively. Swelling ratio for P40 and P10 are plotted for various time intervals (Figure 1). These results clearly show that swelling ratio for P40 specimens is significantly higher than that for P10 group at each time interval. Further, specimens from both groups reach equilibrium swelling by 24 hours. Specimens swollen in xylene for 4 and 24 hours were air dried for one day to remove residual xylene and obtain an altered polymer microstructure produced by changes to the physical entanglements in the polymer networks.

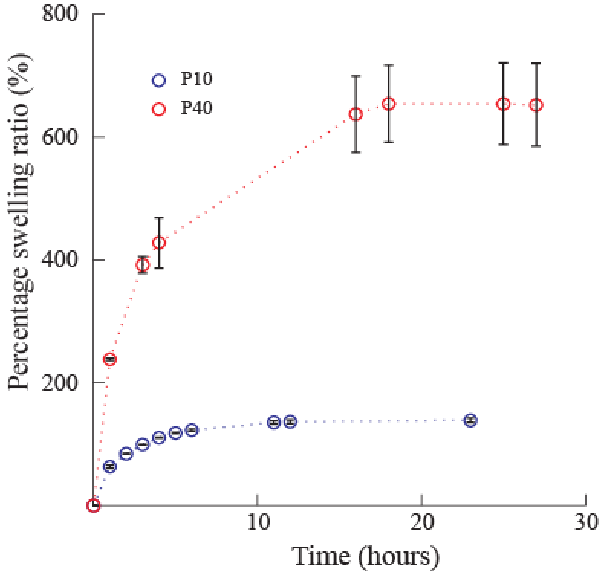

Figure 1. Variations in swelling ratio of P10 and P40 specimens swollen in xylene over a 28 hour period. At each time interval, P40 samples have a higher swelling ratio as compared to P10 specimens.

Table 2 shows corresponding changes in specimen length, width, and thickness following swelling in xylene for 4 hours calculated based on initial sample dimensions before swelling.

	Length (%)	Width (%)	Thickness (%)	
			Before drying	After 24 drying
P10	34.27± 6.02	33.70± 8.88	49.56±12.74	-0.84±0.85
P40	71.62±3.36	63.55±8.61	75.71±2.81	-10.82±3.93

Differences in the swollen weights of P10 and P40 samples correlate with changes in the sample dimensions. All samples swell isotropically in the three dimensions albeit the changes in P40 specimens were significantly higher than P10 samples respectively. We dried the samples in air for 24 hours to investigate possible changes in weight and thickness. Our results show that dried P40 samples have significantly lower weight (-17.03±9.73 %) as compared to control unswollen samples. However, there were no differences in the corresponding dry weights for the P10 specimens (-3.80±0.07%). These differences in specimen weights correlated with a decreased thickness of P40 samples by about -10.82±3.93%. that suggest removal of uncrosslinked PDMS polymer, commonly referred to as sol, from the network structure due to swelling in xylene [5, 8]. Spectroscopic methods, among others, may be useful to investigate such effects and will be used in the future to quantify the effects of xylene treatment on PDMS elastomers. These results are similar to those seen by others to investigate the effects of swelling of different solvents, including xylene, on solubility of PDMS [9].

3.2. Mechanical Characterization

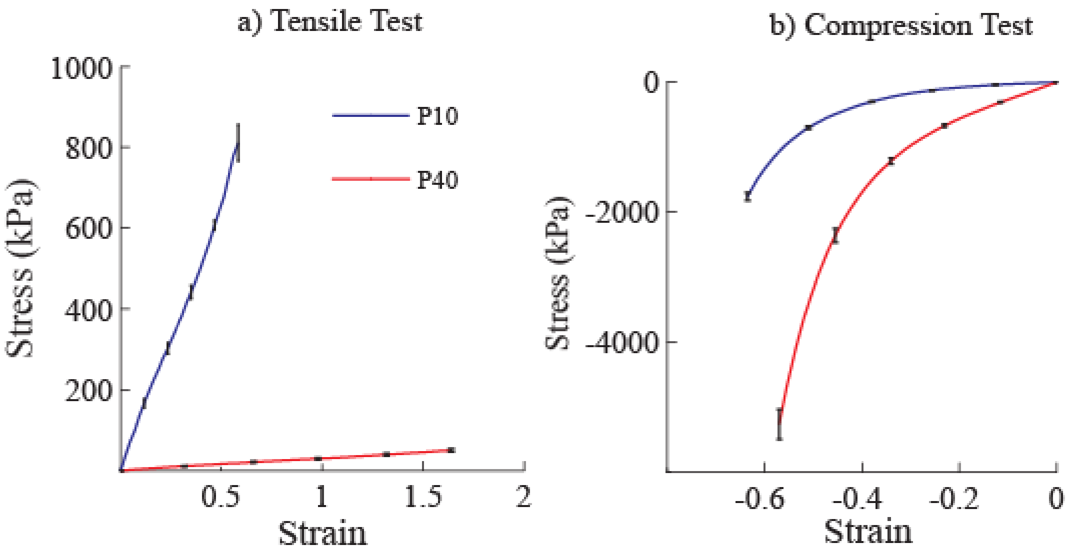

Figure 2. Uniaxial tension (a) and compression (b) results for P10 and P40 samples.

Uniaxial tensile tests in compression and tension were performed on the P10 and P40 specimens (n=2) and the average values of the stress corresponding to each strain value are represented in Figure 2a,b. Tensile moduli were obtained using the slope of stress-strain curves corresponding to strains of about 10%. Results show that P10 samples have a significantly higher modulus ($p<0.05$) of 1400.02±15.84 kPa as compared to P40 specimens (39.46±4.34 kPa). Hence, a decrease in chemical crosslinking amounts causes dramatic differences in the mechanical properties of PDMS. We note a corresponding trend in results from compression experiments with a modulus of 2687±75.65 kPa and 300.48±9.15 kPa for P10 and P40 respectively.

Although uniaxial tests are useful to provide comparisons between the stiffness between groups, they are insufficient to be used to obtain a strain energy function to describe the microstructural properties of elastomers. We must instead rely on comprehensive biaxial tests performed using constraints in two orthogonal directions to obtain a parameter space of deformations. We performed nonequibiaxial and equibiaxial experiments on P10 and P40 samples to explore the contributions caused by strain induced topological adaptations in network structure due to loading in the two orthogonal directions (Figure 3). Equibiaxial experiments confirm that P10 sample has stiffer response as compared to the P40 specimen.

We use results from biaxial experiments to evaluate phenomenological and microstructural based strain energy models to describe the PDMS networks. These investigations show that the slip link model [10], which considers individual contributions of physical entanglements and chemical crosslinks on microstructural mechanics of elastomer networks, fit the biaxial and uniaxial experimental results better (r^2 =0.958) than Mooney Rivlin model, Arruda-Boyce, and the neo-Hookean models. However comparisons between the model fits to the P40 and P10 samples shows that in highly crosslinked P10 stress-strain behavior have contributions from physical entanglements.

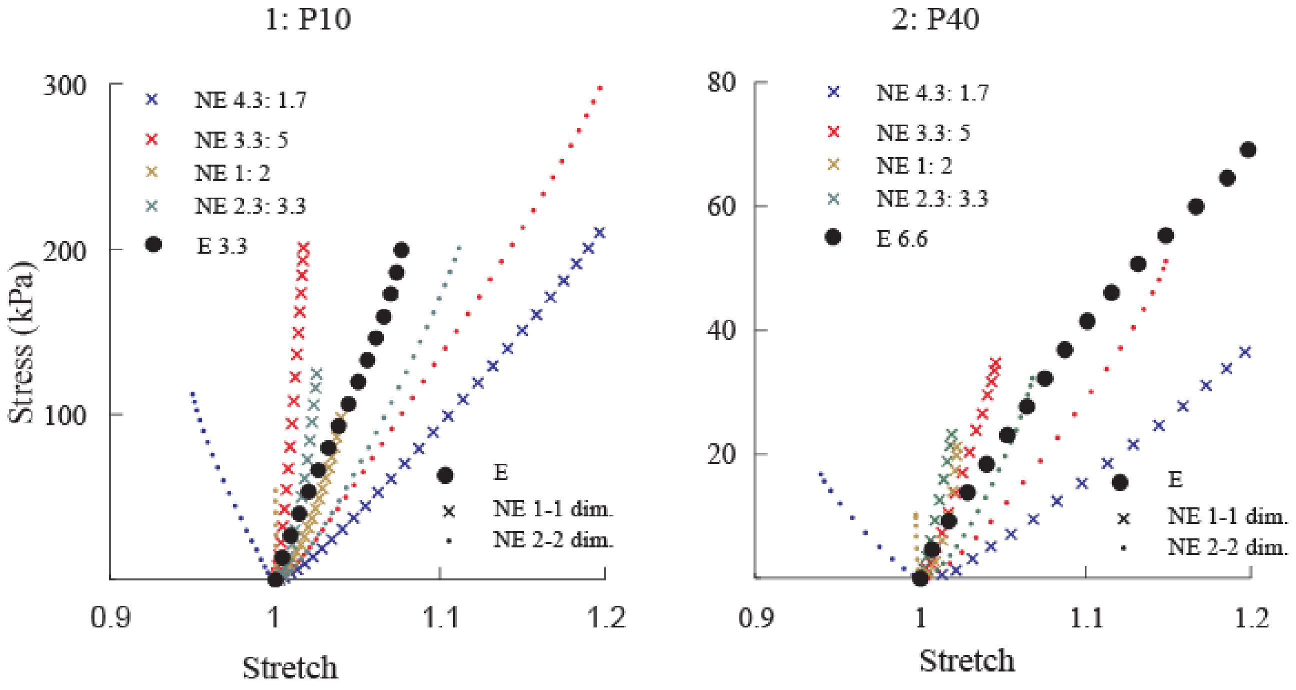

Figure 3. Equibiaxial (E) and nonequibiaxial (NE) stress-stretch results for P10 and P40 samples [10] obtained by differential stretching of samples in two orthogonal directions denoted 1-1 and 2-2 in the figure. The maximum load in the P10 sample was 600 gram whereas that in the P40 was 60 gram. The different ratios in NE experiments were normalized with respect to these maximum loads.

To clearly distinguish between the entanglements and crosslinks, we use methods to swell the elastomers and assess changes in network microstructures using DMA measurements. P10 and P40 samples in the unswollen state and that obtained by swelling and drying the elastomers were subjected to cyclic sinusoidal loading as described earlier (Figure 4).

Higher values of E' as compared to E'' with corresponding low values for tanδ demonstrate the dominance of elastic behavior contributing to the measured viscoelastic property of P10 and P40 samples. In general, E' and E'' for PDMS increases with an increase in frequency. Although entangled chains can slide freely at low frequencies, they are unable to loosen at higher frequencies that result in restriction in the motion of the polymer chains and a corresponding increase in modulus. The trend of frequency dependent response of storage and loss modulus of swollen P10 is however different as compared to that of unswollen specimen due to the presence of xylene. A similar frequency dependent response for dried samples following swelling and unswollen P10 specimens suggests that the chemical crosslinking of networks was not altered due to swelling. In contrast, there is a large variation in the storage modulus of unswollen and swollen, dried specimen for P40 specimens. Thes differences may arise due to the presence of trapped entanglements in the highly crosslinked P10 samples leading to lower rearrangements in the entanglements during swelling as compared to P40 specimens that also shows loss of sol fraction of uncrosslinked material and a corresponding lower molecular weight. The rate of increase in E' for the P40 specimens with respect to increase in frequency was however high compared to P10 specimens.

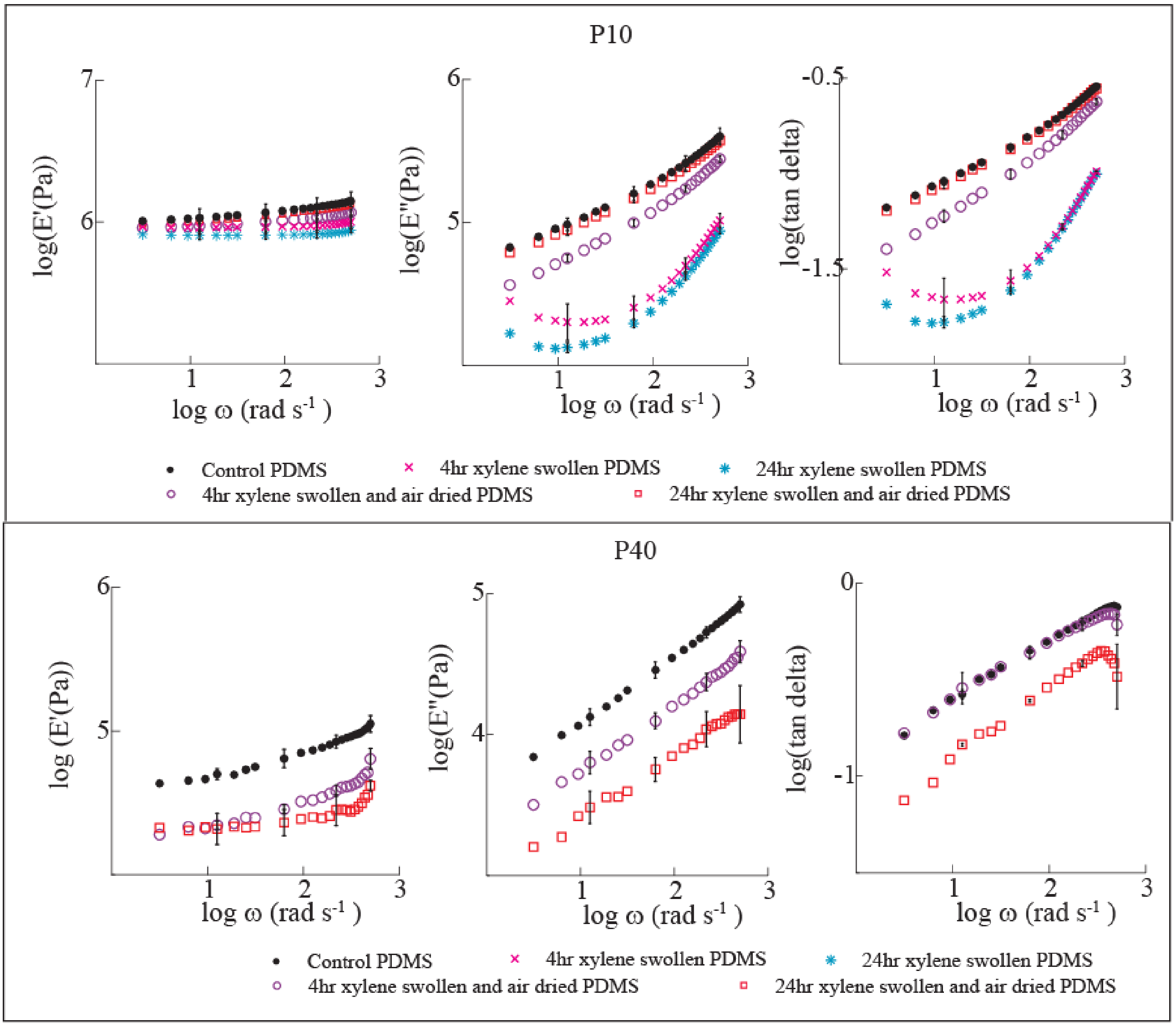

Figure 4. Effect of swelling in xylene on storage modulus (E'), loss modulus (E'') and damping factor (tan δ) for (a) P10 and (b) P40 specimen.

Table 3. Percentage increase E' of P10 and P40 when frequency varies from 1to 80Hz

	Control	Xylene for 4hr, drying	Xylene for 24hr, drying	Xylene for 24hr	Xylene for 4hr
P10	38.09±0.85	28.05±1.39	39.10±1.31	8.15±1.48	7.87±0.01
P40	159.60±10.29	239.35±71.02	103.42±18.62		

4. Conclusions

To study the effect of entanglements and crosslinks in the macroscopic behavior we performed swelling measurements and mechanical characterization of PDMS prepared with different weight ratios of base polymer to crosslinker, denoted as P10 and P40, in this study. Tensile, compression and biaxial mechanical tests show that P10 specimens demonstrate a stiffer response as compared to P40 specimens. Results from biaxial experiments were fit to the Edward-Vilgis slip link model using a nonlinear least squares fit method. Our results show that the mechanical response of elastomers demonstrate individual contributions from chemical crosslinks and physical entanglements. To delineate the effect of crosslinking and entanglements we performed DMA measurements on unswollen control material and those swollen in xylene, and dried in air for the P10 and P40 samples in the study. Our study shows that the P10 specimens have higher values of Young’s modulus and storage modulus and a corresponding low swelling ratio due to the higher degree of crosslinking and hence presence of trapped entanglements. In contrast, a low degree of crosslinking in P40 samples demonstrated a higher viscous contribution as compared to the elastic behavior of the P10 elastomers. Our results also show that both P10 and P40 exhibit an increase in rigidity and loss modulus at high frequencies. Dynamic mechanical experiments also show that the elastic and loss moduli decrease due removing of uncrosslinked polymer and locking the chains in different configurations produced by swelling. Ongoing stress relaxation experiments are envisaged to characterize the effects of swelling on the mechanical properties that will lead to a better understanding of the effects of entanglement in the on viscous properties of PDMS.

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6. References

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