

Transient Effects in Dynamic Modulus Measurement of Silicone Elastomers 1. Zero Mean Strain Measurements

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ABSTRACT: The strain-dependent dynamic storage modulus of a poly(dimethyl-siloxane-co-methylvinyl-siloxane-co-methylphenyl-siloxane) based silicone elastomer, which is reinforced with fumed silica and crosslinked with peroxide, is investigated. The dependence of the resulting dynamic storage modulus on the duration of cycling at a particular test condition is investigated and compared to static stress relaxation measurements in the same strain range. The dynamic modulus results are shown to depend on the time of cycling at the current test conditions as well as the time of cycling at prior conditions of lower strains. The relaxation is

shown to be related to the time of cycling rather than the number of cycles performed. The pattern of behavior of the relaxation of the dynamic modulus with respect to peak strain amplitude is different than that observed in a static stress relaxation test, both of which show significant nonlinear effects in strain. The observed phenomena are interpreted in terms of the role of the polymer phase on the dynamic behavior of the elastomer material. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1001–1009, 2005

Key words: silicones; elastomers; modulus; relaxation

INTRODUCTION

It is well established^{1,2} that the dynamic mechanical properties of particulate reinforced elastomers depend on the strain used to make the measurement. This reduction in modulus with increasing strain, (in the small strain region), is commonly referred to as the Payne effect. This phenomenon has been most thoroughly investigated¹ for carbon black reinforced organic elastomers. Even though this phenomenon has been well established in experimental trials, a fundamental understanding is still incomplete. Recently, silica-filled silicone elastomers have been investigated,^{3,4} yielding further insight into the role of the polymer phase as it affects this phenomenon.

The strong dependence of $G'(\gamma)$ on strain can be interpreted in terms of a filler interparticle interaction theory¹ in which the assembly of particles in the matrix interacts through an interparticle potential. Since an interparticle potential would be a strong function of the separation distance, this induces a steep dependence of the energy stored in the network of particles on the macroscopic strain. The particles are viewed as being assembled into a network in which interparticle distances are small enough that significant surface forces act between particles. Recently the complete-

ness of this interpretation has come into question.^{6–8} The role of entanglements in the polymer and the perturbation in the state of entanglement induced by the presence of high specific surface area particles has been proposed to explain the unusual behavior of the Payne effect in both elastomers and thermoplastic polymers above the glass transition.⁷ This work further investigates the complexities involved in the behavior of silica-filled silicone elastomers.

The common practice used for dynamic testing of elastomers is to use a sequence of increasing strains to measure strain-dependent modulus. The number of cycles performed at any condition is usually determined based on criteria such as signal-to-noise ratio, minimization of temperature increase during cycling, economy of testing time, and instrument control requirements.

Recently, cycling to a so-called fully equilibrated modulus has been advocated⁴ based on observation of the relaxation that occurs at a single dynamic test condition. In the current work we explore this relaxation to increase our understanding of the peculiarities of filled elastomers. In addition we seek an estimate of the magnitude of changes in dynamic modulus as well as the transient response to enable specification of meaningful test protocols.

EXPERIMENTAL

Raw materials

The polymer used was SE-54 PVMQ silicone gum (GE Silicones, Waterford, NY) and the silica was TS-500-

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treated silica (Cabot Corp., Cab-O-Sil Div., Tuscola, IL). The peroxide was Dicap 40C (Hercules, Inc., Wilmington, DE), which is 40% dicumyl peroxide ($C_{18}H_{22}O_2$) dispersed on an inert filler. All materials were used as received.

Masterbatch and compound preparation

The formulations in terms of parts per hundred (phr) of polymer by weight were:

SE-54 100;

TS-500 various (20–75);

Dicap 40C 1.4.

The peroxide level was chosen to be typical of a practical formulation that might be used to manufacture mechanical goods. The masterbatches were mixed in a 95-L Baker-Perkins sigma blade mixer by adding proportions of the TS-500 to the SE-54 at a mixer temperature of 150 °C followed by mixing for 1 h under vacuum after all of the silica was incorporated. The mixing procedures used in this work were typical of what would be used to produce commercial silicone elastomer bases. Three of these 30-kg masterbatches were prepared with silica loadings of 20, 50, and 75 phr of TS-500. Total mixing times were 2, 4.5, and 6 h, respectively. The masterbatches were aged for a minimum of 3 weeks (maximum of 10 months) prior to adding peroxide on a two-roll mill at room temperature in approximately 1-kg batches. These correspond to silica volume fractions (ϕ) of 0.080, 0.179, and 0.247, respectively, assuming a polymer density of 0.96 g/cm³ and a silica density of 2.2 g/cm³. Other silica loadings were obtained by blending these masterbatches on a two-roll mill at room temperature. Producing intermediate formulations by this blending technique is justified since a smooth curve results when material properties are plotted versus ϕ .

Dynamic modulus measurement

Dynamic property measurement was done using a double-lap, simple shear test specimen that consists of two layers of rubber approximately 5 mm in thickness bonded to steel supporting members using a silane adhesive during molding and vulcanization. The correction for the bending component of the deformation⁹ in this specimen is only 0.52% and is neglected. In this work all strains are stated in terms of single strain amplitudes (SSA) and are taken to be the magnitude of the strain cycle from zero to the maximum strain in the cycle. Thus the extremes of all dynamic strain cycles are \pm SSA.

Prior to molding, the rubber was freshened on a two-roll mill to remove crepe hardening. Identical milling procedures were used throughout the work. The specimens were molded in a six-cavity steam-heated transfer mold that fills each side of the speci-

men with a separate sprue with a gate approximately 1.6 mm in diameter. Specimens were cured for 20 min at 163 °C followed by a 24-h postcure in a circulating air oven at 177 °C. The time to fill the mold cavity was on the order of 20 s and the pressure in the transfer pot was approximately 13.5 MPa. The specimens are inserted in a servohydraulic test stand by attaching the inner member to a 22-kN load cell through a barrel nut. The outer members are clamped symmetrically to a fixture attached to the hydraulic actuator. The rubber wall thickness is thus constrained to remain constant throughout the test.

The periodic force and displacement time domain signals are decomposed through an FFT algorithm. The complex dynamic modulus (G^*) is calculated as the ratio of the amplitudes of the fundamental force and displacement sinusoids, and δ is defined as the phase angle between the force and displacement fundamental sinusoids. The other dynamic properties follow by calculation from these measured quantities. A common method of characterizing filled elastomers is to use some variation of an increasing strain sweep perhaps with an initial large strain conditioning cycle. In this work, however, samples with no prior strain history are employed unless specifically noted. Unless otherwise specified, each specimen was tested only once and discarded.

Stress relaxation measurement

The same apparatus and test sample geometry were used for the stress relaxation measurements. The deformation was applied within 0.1 s with no detectable overshoot.

RESULTS AND DISCUSSION

Figures 1 and 2 show the typical strain dependence of $G'(\gamma)$ and $G''(\gamma)$ for the materials used in this work. The range of the silica volume fractions employed in this work approximately covers the range used in typical practical elastomers. Most of the work, however, is done with the highest silica loading (75 phr, $\phi = 0.247$) since the nonlinear effects are the most pronounced at the higher loadings. A low strain plateau,⁵ where the dynamic properties are independent of strain, is present at strains lower than those used in this experiment (0.1–50% SSA).

The dynamic modulus $G'(\gamma, t)$ is a function of time of cycling as shown in Figure 3, which gives the time dependence of $G'(\gamma, t)$ for several values of dynamic strain γ_d . This temporal variation in $G'(\gamma, t)$ has been previously recognized⁴ and led the researchers to use a significant period of cycling prior to making a measurement. The magnitude of the changes in $G'(\gamma, t)$ with time at a prescribed value of γ_d are much smaller than changes induced by changing γ_d in a simple

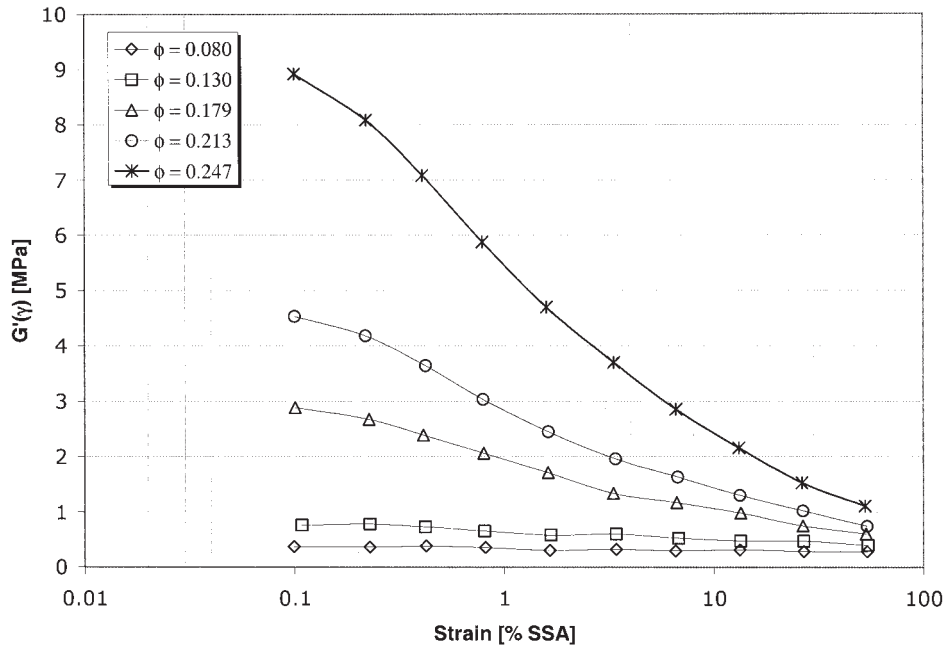


Figure 1 Dynamic storage modulus $G'(\gamma)$ (23 °C, 10 Hz) versus strain amplitude (% SSA) for various volume fractions of silica.

strain sweep type of experiment. Included in Figure 3 is a curve for a steel coil spring with approximately the same spring constant as the bonded rubber specimens to verify the stability of the test equipment over the time scale of this testing. The data in Figure 3 were plotted as $G'_{rel}(\gamma,t) = G'(\gamma,t)/G'(\gamma,0)$ to remove the dependence on γ_d and to put each specimen on a consistent basis for comparison. Note that two different specimens were tested at $\gamma_d = 2.7\%$ with very

good agreement. The range of the values for the steel coil spring in Figure 3 is (0.9994–1.0005), which is quite good compared to the accuracy needed to have confidence in the time dependence of the rubber specimens. Each point in the plot is the average of the same number of sinusoidal strain cycles with cyclic deformation being performed continuously during the test. It is observed that the larger the value of γ_d , the larger the fraction of the original $G'(\gamma,t)$ that is lost. This is

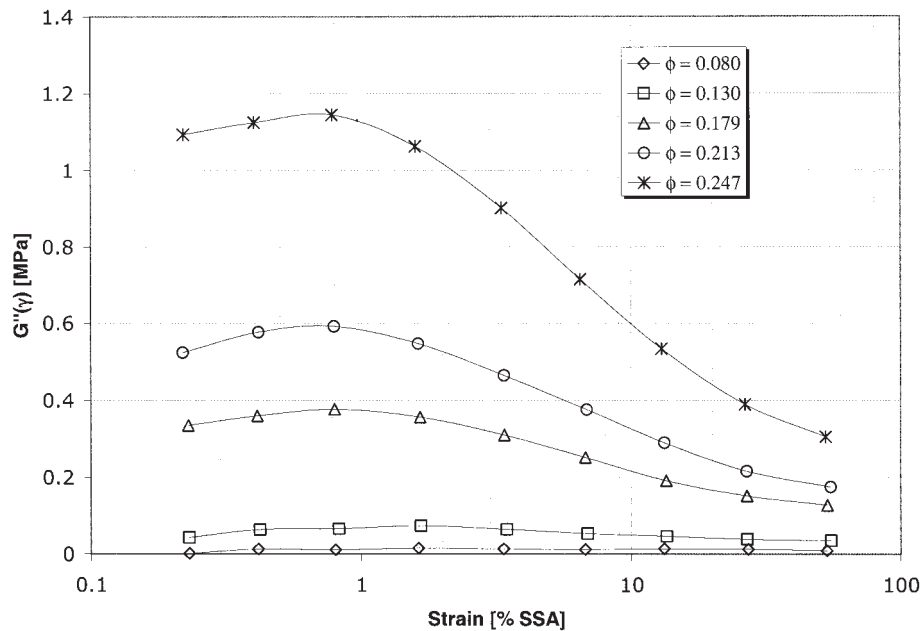


Figure 2 Dynamic loss modulus $G''(\gamma)$ (23 °C, 10 Hz) versus strain amplitude (% SSA) for various volume fractions of silica.

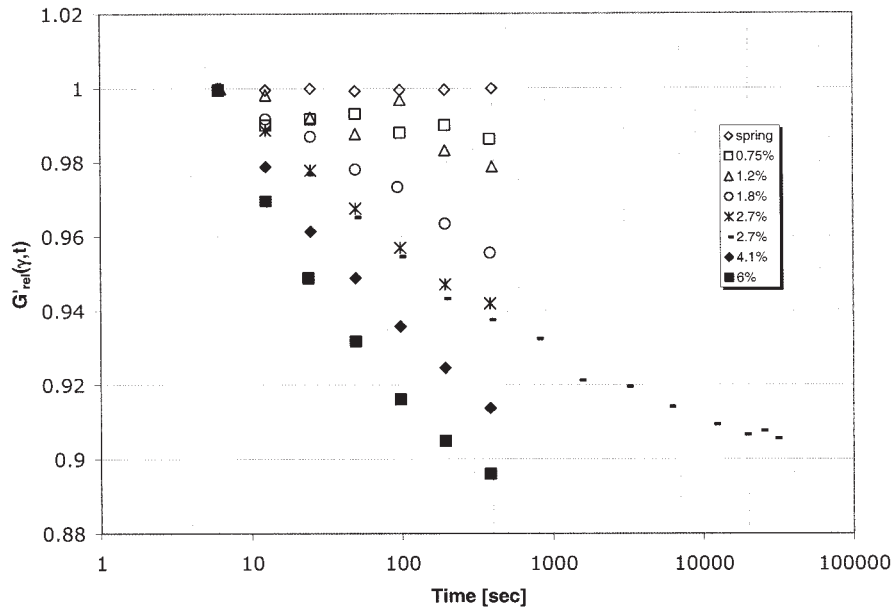


Figure 3 Normalized dynamic storage modulus $G'_{rel}(\gamma,t)$ versus time of dynamic cycling at γ_d (23 °C, 1 Hz). Silica loading is $\phi = 0.247$ (75 phr).

true even though $G'(\gamma,0)$ decreases significantly as γ_d increases.

This is the opposite of the behavior seen in static stress relaxation (Fig. 4), where the relaxation is most pronounced at lower values of static strain γ_s . The change in $G(\gamma,t)$ with γ_s is quite similar to the change in $G'(\gamma,t)$ with γ_d as seen in Figure 5. It is interesting that the application of a single-step strain yields a similar plot of $G'(\gamma,t)$ versus γ_s as the dynamic data,

yet the change in modulus with test time for the two different experiments is quite different. This also indicates that the change in the material leading to the pronounced decrease in $G'(\gamma,t)$ with γ_d occurs in the first loading cycle and does not require reversal of the deformation. The faster relaxation of the $G(\gamma,t)$ at low strains in the static experiment is evident in Figure 5. It has been suggested,⁴ based on comparison of constant strain rate tests with dynamic cycling tests, that

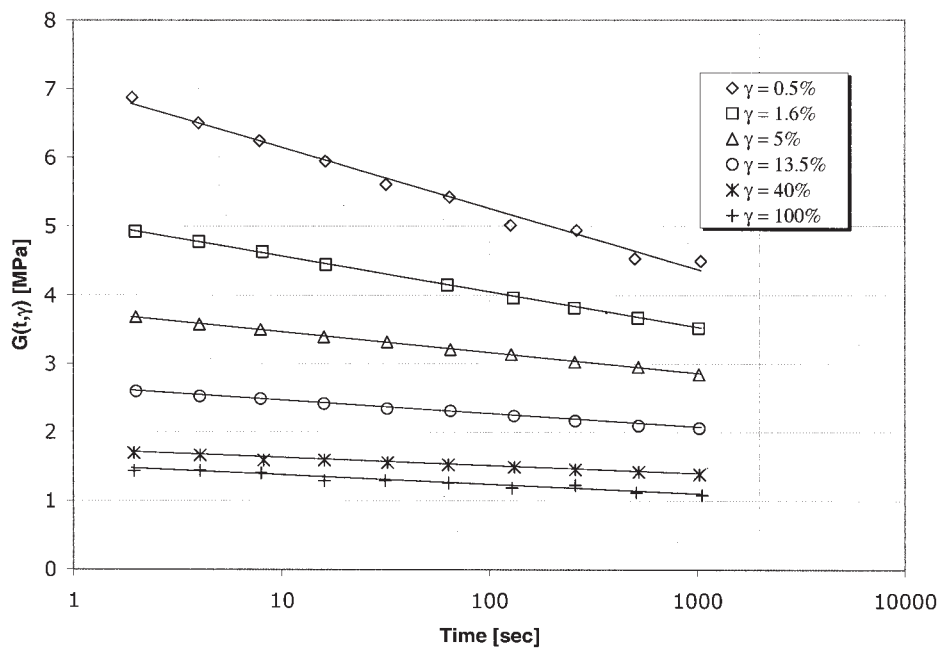


Figure 4 Stress relaxation modulus $G(\gamma,t)$ versus time since deformation γ_s was applied at 23 °C. Deformation was applied within 0.1 s, silica loading is $\phi = 0.247$ (75 phr).

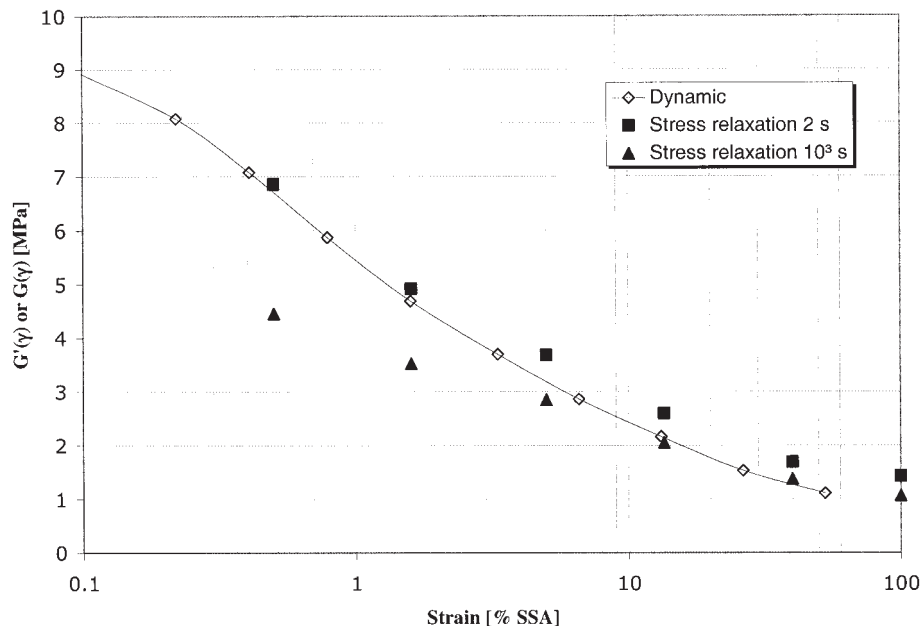


Figure 5 Comparison of dynamic storage modulus $G'(\gamma)$ (10 Hz) and stress relaxation modulus $G(\gamma, t)$ at (2 and 10^3 s) versus deformation at 23 °C. Silica loading is $\phi = 0.247$ (75 phr).

the dependence of $G'(\gamma, t)$ might disappear or be substantially diminished at sufficiently low frequencies or sufficiently long time scales. The static stress relaxation curves in Figure 4 would not extrapolate to a single value of modulus at a unique time, however. Using the 40% strain curve as the basis and extrapolating the lower strains to coincidence with the 40% curve yields 6.23×10^6 , 1.48×10^8 , 4.35×10^{10} , and 2.26×10^{10} s corresponding to the curves for $\gamma_s = 0.5$, 1.6, 5, and 13.5% strain, respectively. The hypothetical point of coincidence does not occur at a unique time of relaxation based on this approximation. The 40% strain curve was selected as the baseline since the slopes of the stress relaxation curves from Figure 3 continuously decrease with increasing γ_s up to 40% strain but the 100% strain curve shows an increase in slope above that for the 40% curve.

The difference between the stress relaxation processes when the deformation is applied in static and cyclic modes is evident in Figure 6. The reduction in modulus of rubber due to deformation history is usually thought of in terms of the Mullins¹⁰ effect. In Mullins softening an initial stretch to a relatively large deformation reduces the modulus markedly at strains less than that of the initial stretch. This softening process is usually observed mainly in the first few cycles (three to five cycles are typically used) of a deformation history and affects that behavior of a material only at strains less than the previous deformation. The process operative in Figure 6 is a time-dependent relaxation that is significantly slower than what one would expect if the modulus reduction were due to a Mullins type of softening. Enhanced creep and stress

relaxation have been reported as a result of cyclic application of a uniform stress or strain in both elastomers¹¹ and thermoplastics.¹²

That the softening noted in this work is dependent on the time of cycling and not the number of cycles is evident in Figure 7. Since the slopes of the plots are essentially identical for the different frequencies of cycling, it is the time of cycling and not the number of cycles that determines the decrease in $G'(\gamma, t)$. The vertical displacement of the three curves is due to the increase in dynamic modulus with increasing frequency. This leads to the conclusion that the softening is due to a relaxation process with a long time scale. The time scale is evidently long enough that all of the frequencies considered appear "static" to the process that is proceeding; otherwise a dependence on the number of cycles would be present. Presumably at a sufficiently low frequency, where the time scale for a single cycle is on the order of the time constant for the relaxation process, a dependence on the number of cycles would be found. Data¹³ on a filled butyl rubber in cyclic creep at high tension strains ($\sim 300\%$) at very low frequencies (~ 0.01 Hz) show a mixed time and cycle dependence.

If the cycling is stopped for a time and the sample is allowed to remain at $\gamma = 0$ there is a slow recovery from the decrease in $G'(\gamma, t)$ with cycling as shown in Figure 8. The sample was not removed from the test machine fixture during the recovery period to minimize the possible differences in modulus due to uncontrolled factors. The time scale is linear in this case to allow better visual inspection of the magnitudes of the modulus and also the moduli are not normalized. There is very slow recovery followed by an approach

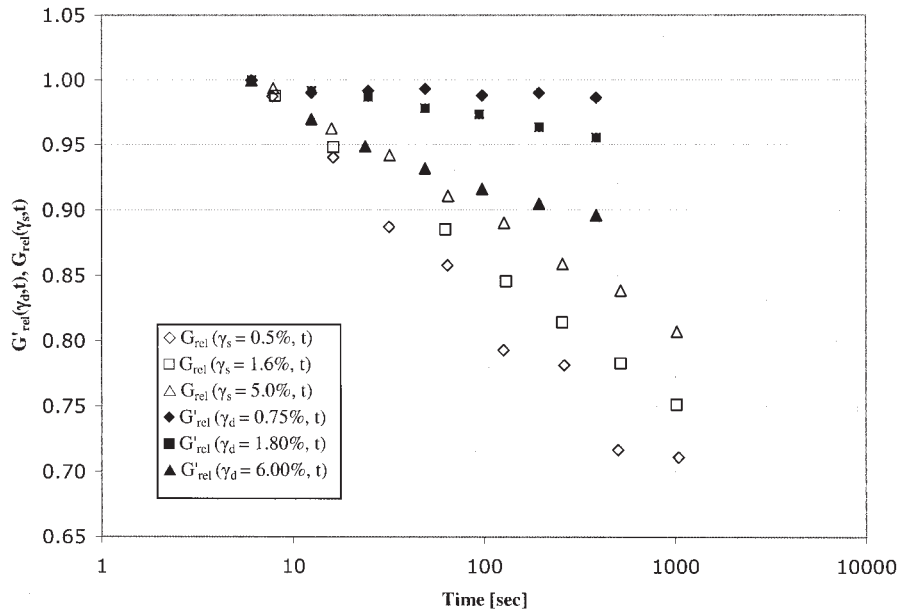


Figure 6 Comparison of dynamic storage modulus $G'(\gamma, t)$ (10 Hz) and stress relaxation modulus $G(\gamma, t)$ versus time at 23 °C. Silica loading is $\phi = 0.247$ (75 phr).

to the initial curve on continuation of cycling of the recovered specimen. Longer term recovery data are not possible in the apparatus used to generate these data since retention of the specimen in the fixture is critical to being able to detect a recovery from a relatively small change in terms of magnitude of $G'(\gamma, t)$. Experiments were attempted on a longer time scale by removing the specimens from the fixture during the recovery time but the uncertainty in the $G'(\gamma, t)$ values

generated by the removal/re-insertion made interpretation very difficult. Recovery from cycling at much larger strains than the measurement strain is reported to occur on a significantly shorter time scale.¹⁴

Deformation at a lower strain prior to cycling at $\gamma_d = 4\%$ changes the time dependence of $G'(4\%, t)$ (Fig. 9). In this experiment, the cycling at the previous strain (γ_p) was continued for 8 h to ensure that relaxation was essentially complete with respect to the time

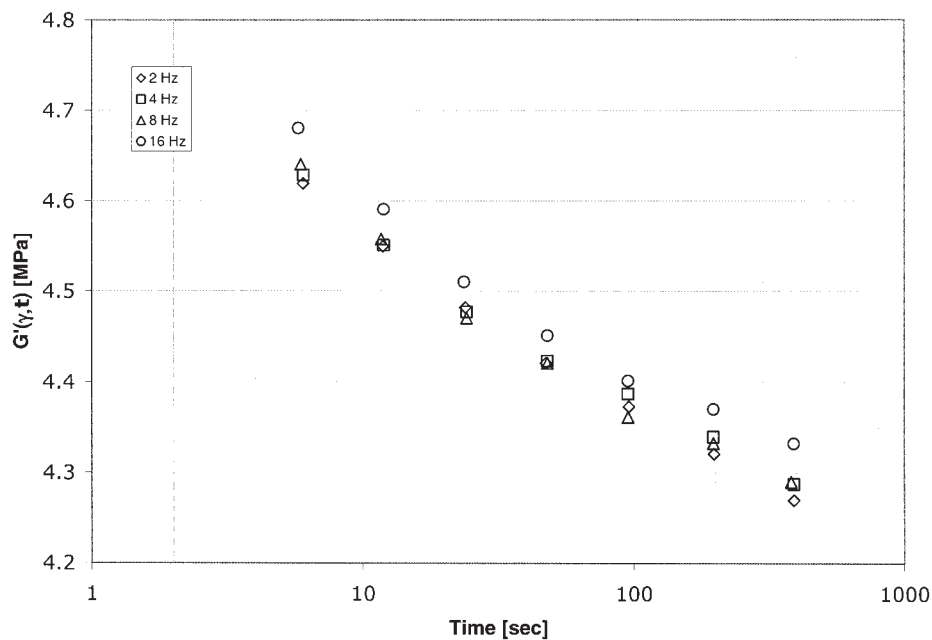


Figure 7 Dynamic storage modulus $G'(\gamma, t)$ versus time of cycling (23 °C, $\gamma_d = 3.3\%$) for various frequencies of cycling. Silica loading is $\phi = 0.247$ (75 phr).

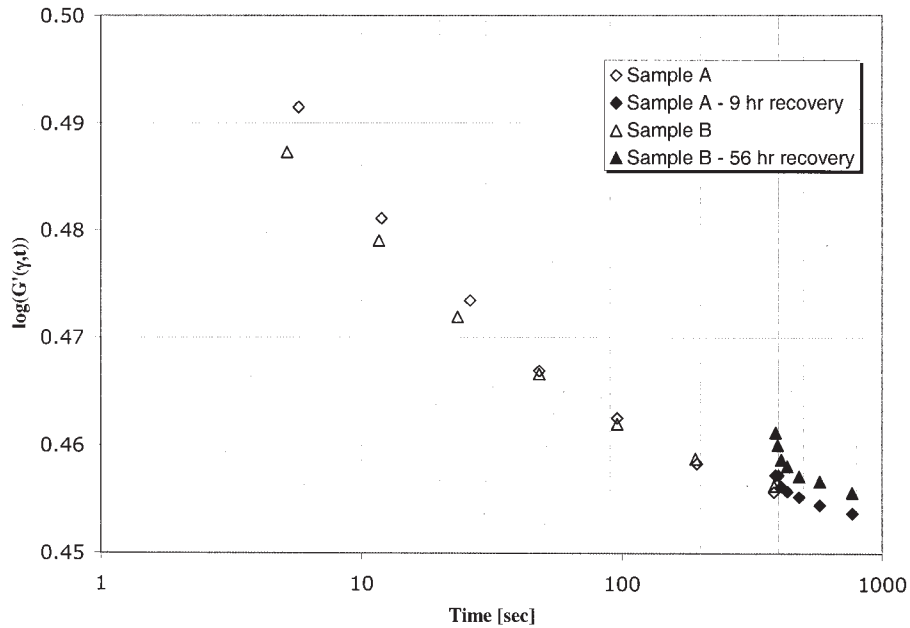


Figure 8 Dynamic storage modulus $G'(\gamma, t)$ versus time of cycling ($23\text{ }^\circ\text{C}$, $\gamma_d = 6\%$) with differing recovery times after initial cycling. Silica loading is $\phi = 0.247$ (75 phr)

scale of the subsequent measurements. The final value of $G'(4\%, t)$ is the same within experimental error for all of the different initial strains (as would be expected). The difference between the curves lies in the initial value of $G'(\gamma, t)$ immediately after the precycling is completed. Thus, an increasing strain sweep does not generate unique materials data unless extensive cycling is done since the results will depend on the spacing of the strain increments.

More importantly, it appears that the transient behavior can be described by the difference $\Delta\gamma = \gamma_d - \gamma_p$ between the precycling strain γ_p and the final strain γ_d (Fig. 10). The data for this plot are a combination of the data of Figures 3 and 9. Thus, the curve for $\gamma_d = 0.8\%$, where the strain history is uniform, coincides with the curve for $\Delta\gamma = 0.8\%$ where the specimen was first cycled to $\gamma_d = 3.2\%$ and then to $\gamma_d = 4.0\%$ during the measurement. The time scale for all of the curves

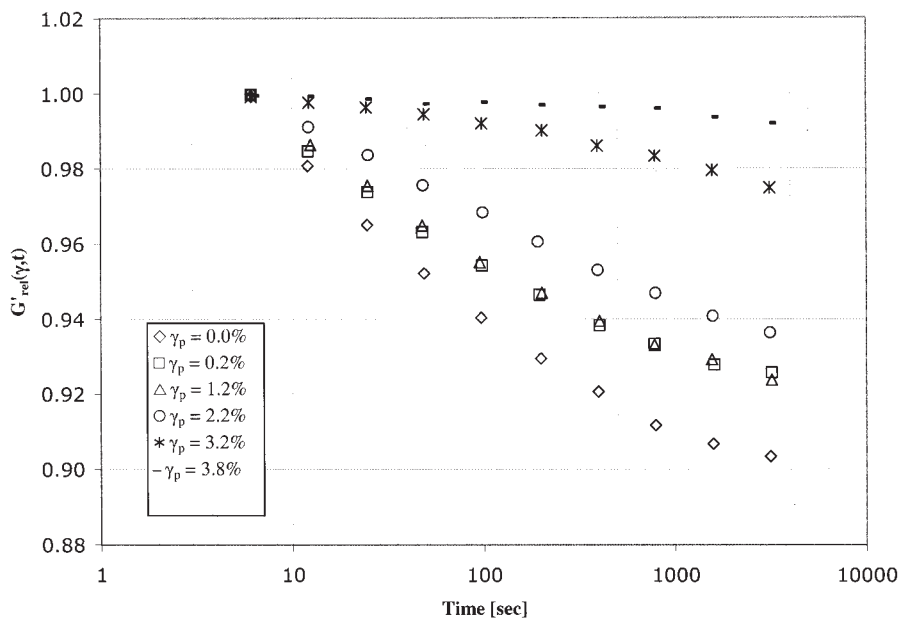


Figure 9 Normalized dynamic storage modulus $G'_{rel}(\gamma, t)$ versus time of dynamic cycling at $\gamma_d = 4\%$ ($23\text{ }^\circ\text{C}$, 1 Hz) for various levels of initial cycling at γ_p . Silica loading is $\phi = 0.247$ (75 phr).

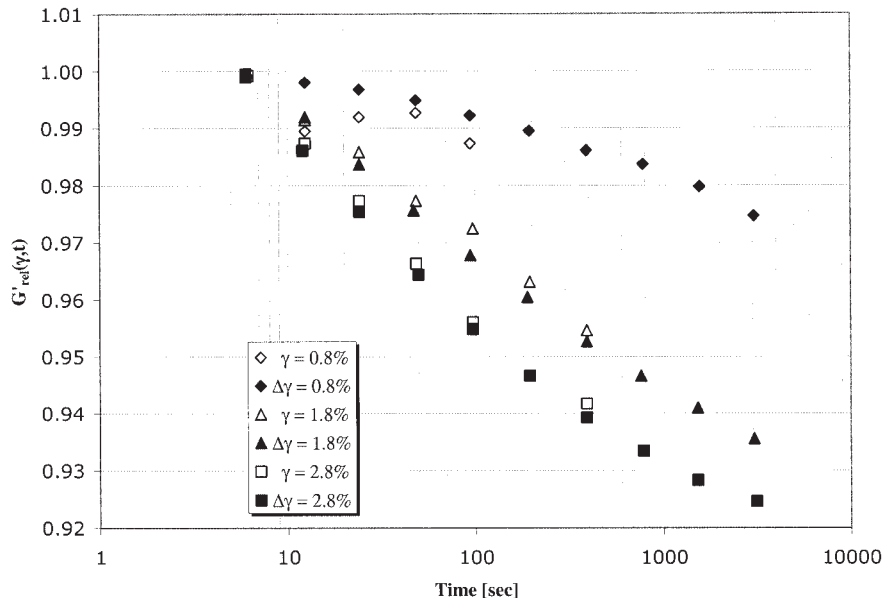


Figure 10 Normalized dynamic storage modulus $G'_{rel}(\gamma, t)$ versus time of dynamic cycling at a single strain γ compared to cycling at a change in strain $\Delta\gamma = 4\% - \gamma$ from a lower initial value to $\gamma = 4\%$ (23 °C, 1 Hz) for various levels of initial cycling at γ_p . Silica loading is $\phi = 0.247$ (75 phr).

begins when the cycling at the final strain is started. Similar agreement at other strains is shown in Figure 10. This behavior indicates a degree of linearity even though $G'(\gamma, t)$ depends on γ_d in the same strain range. This is analogous to the observation⁴ that hysteresis loops are essentially linear at a given γ_d in the region where $G'(\gamma, t)$ varies significantly with γ_d . This means that both the magnitude and the time scale of relaxation of $G'(\gamma, t)$ depend only on the difference in strain $\Delta\gamma$ when precycling has been done. This is true even though the trend of the relaxation with a single uniform strain appears to depend on γ_d in a nonlinear way. This is consistent with the observation⁴ that the $G'(\gamma, t)$ versus γ_d curve is essentially independent of γ_s (up to moderate values of γ_s) when dynamic measurements are made in the presence of a static offset.

The magnitude and transient behavior of $G'(\gamma, t)$ are significantly related to the volume fraction of silica in the rubber (Fig. 11). The phenomenon does not occur to any measurable extent when the silica volume fraction is relatively low.

CONCLUSIONS

The results presented in this work are consistent with the idea that entanglements present due to the adsorption of a proportion of the polymer on the highly active silica surface are important in the response of filled elastomers. In the discussion that follows it is supposed that entanglements are a significant contributor to the dependence of $G'(\gamma, t)$ and $G(\gamma, t)$ on γ .

The difference in behavior of the static stress relaxation data and the cyclic stress relaxation data can be

rationalized in terms of constraints to disentanglement imposed by the applied deformation. In the static deformation case there is a single application of the deformation so only those entanglements that are energetically able to release do so. As the initial imposed deformation increases so does the driving force to disentangle. However, the constraints may also increase with increasing applied deformation due to a larger perturbation of the location of neighboring chain segments. In the cyclic stress relaxation case the environment of an entanglement may change with each application of the deformation due to the possibility of disentanglement that may have occurred and due to random fluctuation of the topology of the network since the last deformation cycle. In this way it is possible to envision a faster decrease in $G'(\gamma, t)$ at higher γ_d and a faster decrease of $G(\gamma, t)$ at lower γ_s .

The dependence of the cyclic stress relaxation on time rather than on the number of cycles indicates that the recovery process following a deformation cycle is slow relative to the disentanglement that occurs due to the application of a displacement. There must be some opportunity for recovery during the reversal; otherwise the static stress relaxation data would overlay the cyclic curve.

Practical implications for the design of testing protocols are apparent from these data. Consideration of the transient effects is quite important if dynamic modulus information is needed in a very precise manner. Just as the response of reinforced elastomers in the displacement domain is quite complex, the response in the time domain is similarly perplexing. Any attempt at generation of a constitutive relation

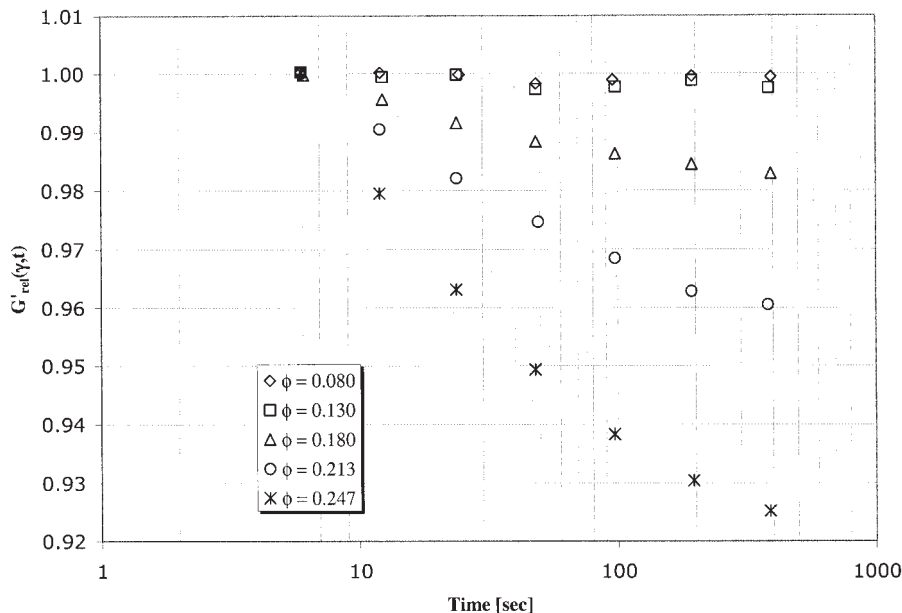


Figure 11 Normalized dynamic storage modulus $G'_{rel}(\gamma,t)$ versus time of dynamic cycling (23 °C, 1 Hz, $\gamma_d = 6\%$) for various silica loadings ϕ .

will need to include the time domain effects if it is to model the behavior accurately. Further work is required to fully characterize the behavior of these materials toward dynamic characterization experiments.

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