

# Viscoelastic Behavior of Rubber Under a Complex Loading

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**ABSTRACT:** In the literature, the loss factor of an elastomer, expressed as  $\tan \delta$ , has been reported to decrease with strain. This has been interpreted as a lowering of the internal viscosity due to chain orientation under strain. This contrasts with experimental findings showing that up to large strains, loss modulus does not change with strain. These experiments show that, as measured,  $\tan \delta$  does decrease with strain. However, a simple analysis shows that this effect is due to geometric changes alone and that the essential viscoelastic behavior, expressed as the loss modulus, is constant with strain up to an extension of about 2 for the simple unfilled compounds investigated here. This article also shows that the prestrain does not induce any significant anisotropy in the loss modulus, at

least up to an extension ratio of 2. This was measured by the stretching of a rubber sample by simple extension and then the subsection of the sample to free vibrations in either torsion or tension. By the measurement of the damping in this way, the anisotropy induced by the preextension was measured. The experiments in this work were all conducted on unfilled natural rubber or styrene-butadiene rubber compounds, with 2 different natural rubber compounds being used to investigate the effect of the crosslink density. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 693–699, 2009

**Key words:** biaxiality; elastomers; mechanical properties; rubber; viscoelastic properties

## INTRODUCTION

The viscoelastic behavior of rubber is very important during the design of rubber engineering components, particularly those that are used for vibration damping, such as rubber suspension bushes used in vehicle suspensions or bearings used to protect buildings during earthquakes. Some components are difficult to design because of their complex loading. A rubber suspension bush, for example, is subjected to both shear and compression loading as well as a combination of torsion and tension loading. The aim of this work was to study the strain dependence and anisotropy of the dynamic loss modulus ( $G''$ ) as a function of a tensile prestrain.

Torsion oscillations superimposed on a simple extension were studied previously by Kuhn and Kunzle,<sup>1</sup> Gaydon,<sup>2</sup> Mason,<sup>3</sup> and Mohsin and Treloar.<sup>4</sup> The hysteresis and viscoelastic behavior were considered to result from changes in the molecular structures and the slippage of the molecular chains. However, in this work, the viscoelastic losses are examined in terms of the geometric changes. The free torsion oscillation experiment was originally described by Mooney and Gerke<sup>5</sup> to characterize the

dynamic properties of a rubber strip. The effect of a prestrain on the viscoelastic behavior of rubber was studied under tensile oscillations by Busfield et al.<sup>6</sup> and Davies et al.<sup>7</sup> Their experimental setup allowed a static tensile prestrain to be applied to a rubber strip, which then was superimposed on a small tensile oscillation. These two approaches have been combined in this study to allow both free tensile and torsional oscillations to be superimposed on a tensile prestrained sample. Measurements of the logarithmic decrement and frequency have been used to calculate the dynamic properties with the equations derived next.

## THEORY

The assumption proposed here is that under conditions of a small oscillation superimposed on a large static deformation (which has previously been measured with several different experiments by, for example, Mason<sup>8</sup> and Nakatani et al.<sup>9</sup>), the fundamental dissipative process is itself little affected by the static prestrains. Presumably, the prestrain is insufficient to cause substantial orientation of the monomer units in a chain. This seems a reasonable assumption because up to 100% strain, the statistical theory of rubberlike elasticity suggests that the amount of orientation should not be substantial for a moderately crosslinked rubber. On this basis, the energy dissipation, which is shown in terms of the logarithmic decrement ( $\Delta$ ), will depend on the strained dimensions of the rubber cylinder and

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the square of the oscillated frequency.  $\Delta$  is expressed as the reduction of the amplitude of oscillation  $x$  from cycle  $i$  to cycle  $i + n$ , where  $n$  is the number of free oscillations being measured:

$$\Delta = \frac{1}{n} \ln \left( \frac{x_i}{x_{i+n}} \right) \quad (1)$$

$$\tan \delta \approx \frac{\Delta}{\pi \left( 1 + \frac{\Delta^2}{4\pi^2} \right)} \quad (2)$$

If  $\Delta$  is very small, then  $\left( 1 + \frac{\Delta^2}{4\pi^2} \right) \approx 1$ . The free oscillation relationships were given by Brown<sup>10</sup> as follows:

$$K'_\theta = I\omega^2 \left( 1 + \frac{\Delta^2}{4\pi^2} \right) \quad (3)$$

$$K''_\theta = I\omega^2 \Delta / \pi \quad (4)$$

where  $K'_\theta$  is the in-phase component of the torsional stiffness (torque/rad),  $K''_\theta$  is the out-of-phase component of the torsional stiffness,  $I$  is the moment of inertia of the system, and  $\omega$  is the angular frequency. The relationship between the static shear modulus ( $G$ ) and the static torsional stiffness ( $K_\theta$ ) is derived with the formula for the static torsion of a cylinder:

$$K_\theta = \frac{\pi r^4 G}{2l} \quad (5)$$

where  $r$  is the radius of the cylinder and  $l$  is the height of the cylinder. When a rubber rod is subjected to static pretension, eq. (5) can be expressed in terms of the undeformed geometry and becomes

$$K_\theta = \frac{\pi r_0^4 G}{2l_0 \lambda^3} \quad (6)$$

where  $\lambda$  is the extension ratio for the static tensile prestrain. Similarly, we can express the static formulation in terms of  $K''_\theta$ :

$$K''_\theta = \frac{\pi r_0^4 G''}{2l_0 \lambda^3} \quad (7)$$

We can obtain  $\Delta$  in terms of the loss shear modulus ( $G''$ ) by equating eqs. (4) and (7). Hence

$$\Delta = \frac{\pi^2 G'' r_0^4}{2I\omega^2 l_0 \lambda^3} \quad (8)$$

where  $r_0$  is the initial radius and  $l_0$  is the initial height of the specimen. This equation is used to examine the relationship between  $\Delta$  and  $1/\omega^2 \lambda^3$ . If the graph has a constant slope, it implies that  $G''$  is independent of  $\lambda$ .

The torsional stiffness for a perfectly elastic material was given by Rivlin and Saunders<sup>11</sup> as follows:

$$\frac{M}{\theta} = \frac{Nr_0^2}{2\lambda(\lambda - \lambda^{-2})l_0} \quad (9)$$

where  $M$  is the torque and  $N$  is the axial force. This relation is at first sight surprising as it is independent of the shear modulus.

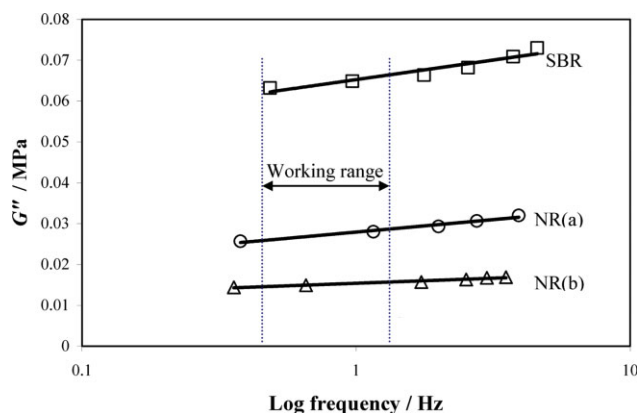
When a free torsion experiment is conducted,  $\Delta$  gives the energy dissipation per cycle and indicates that this should vary with  $1/\lambda^3$  and  $\omega^2$ . The loss factor is expressed as  $\tan \delta$ , which is given by the ratio of  $G''$  to the storage modulus ( $G'$ ); the latter, being influenced by the torsional stiffness, is obtained from the extension ratio in accordance with eq. (9). Thus, the variation of  $\tan \delta$  with strain is dependent on the form of the stress-strain curve and the extent to which eq. (9) is applicable to an imperfectly elastic material. Equation (8) can be used when eq. (9) is no longer valid because of excessive hysteresis.

## EXPERIMENTAL

Two different experimental setups have been used in the work. They are described throughout the article as follows:

- A static tensile prestrain superimposed with a torsional oscillation.
- A static tensile prestrain superimposed with an additional tensile oscillation.

Both techniques measure the amplitude reduction of free oscillations. In these experiments, the test frequency is determined by the inertia and the effective spring stiffness of the system. Experimentally, these are hard to adjust to conduct all the experiments at the same test frequency. Fortunately, the materials used in this experiment have only a modest amount of damping, and they also exhibit only a modest frequency dependence. All the experiments were completed in frequency range of 0.4–1.32 Hz. Of the three materials used in this work, the most frequency-dependent was found to be styrene-butadiene rubber (SBR). Over the typical test frequency range, this represents a change in the measured  $G''$  value of less than 2.5%, as shown in Figure 1. As this is considered small, the effect of the test frequency at different prestrains and hence stiffness values is ignored in this work.  $\Delta$  of a rubber material is typically strain-dependent, and this dependence was investigated first. A test of the static tensile prestrain superimposed with an additional tensile oscillation was used to observe this effect over the entire range of amplitudes encountered in this investigation. The range of oscillation amplitudes used in this work was determined by the sensitivity and range of the noncontacting displacement transducer.



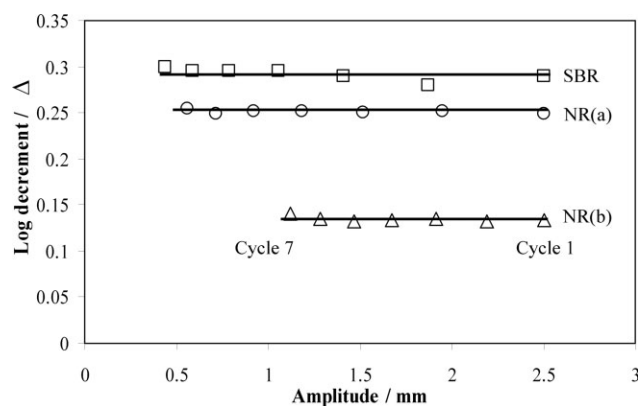
**Figure 1**  $G''$  plotted against the log frequency for the free tension experiment.

This range was approximately 0.3–2.5 mm; with a sample length of 40 mm, this corresponded to strains of approximately 0.75–6.25%. To verify that  $\Delta$  was not significantly changed by the strain amplitude, the  $\Delta$  values were determined for different cycles. These values are plotted against the strain amplitude in Figure 2. The figure shows that  $\Delta$  is independent of the amplitude over this range.

Three different unfilled elastomer materials were used in this work. The formulations and the curing conditions are outlined for each material in Table I. All samples were compression-molded.

#### Static tensile prestrain superimposed with a torsional oscillation

The viscoelastic behavior of the elastomer was observed in the direction perpendicular to the initial prestrain with a technique by which a static tensile prestrain was superimposed with a torsional oscillation. This approach was used previously by Mooney and Gerke,<sup>5</sup> Plazek et al.,<sup>12</sup> and Zerbini.<sup>13</sup> A bonded cylindrical rubber specimen with a diameter of 12.2



**Figure 2**  $\Delta$  plotted against the amplitude for the free tension experiment.

**TABLE I**  
Rubber Formulations

	SBR	NR(a)	NR(b)
Ingredient			
NR (SMR CV-60)		100	100
SBR (JSR 1500)	100		
Stearic acid	2	2	2
Zinc oxide	5	5	5
HPPD (antioxidant)	3	3	3
CBS (accelerator)	0	1.5	1.5
DPG (accelerator)	1.3	0	0
MBTS (accelerator)	1	0	0
Sulfur	1.5	0.5	1.5
Molding condition			
Curing time	15 min	15 min	15 min
Temperature	160°C	160°C	160°C

CBS = *N*-cyclohexy-2-benzothiazole sulfenamide; DPG = diphenyl guanidine; HPPD = *N*-(1, 3-dimethyl butyl)-*N*-phenyl-phenylene diamine; MBTS = 2,2'-dibenzothiazyl disulfide.

mm and a length of 75 mm was fixed to a rigid frame, as shown in Figure 3. The upper end of the cylinder was attached to both a torsional inertia bar and a multifilament inextensible cord by a bolt. A stretched string was used so that the rubber specimen could be extended independently of the mass of the inertia bar. This setup allowed both the torsional moment of inertia and the static prestrain to be altered. The rubber cylinder could be stretched through the cord. The torsional oscillation was triggered manually by the tapping of the torsion bar. The decay of the amplitude of the oscillation was measured with a noncontacting displacement sensor. The oscillation amplitude ranged from 0.3 to 2.5 mm and was limited by the maximum range and minimum sensitivity of the displacement sensor. The maximum amplitude was set at 2.5 mm for all specimens. This corresponded to a maximum shear strain of 3.3%. Seven successive damped amplitudes were used to calculate  $\Delta$ . The signal was recorded with a personal computer based oscilloscope.

A servohydraulic biaxial torsion tension test machine (model MTS 858) with a very sensitive torque load cell (model TQM 202-0.175, Omegadyne, Sunbury, OH) with a working range of 0.001–0.175 N m was used to measure the static stiffness of a series of tensile prestrained elastomer cylinders for comparison with the results of the free oscillation tests. The output of this test was used as an independent measure of the torque versus the rotational angle as the prestrain was increased for comparison with the stiffness results calculated from the damped free oscillation tests.

The behavior of linear viscoelastic materials can be represented by the complex shear modulus ( $G^*$ ):

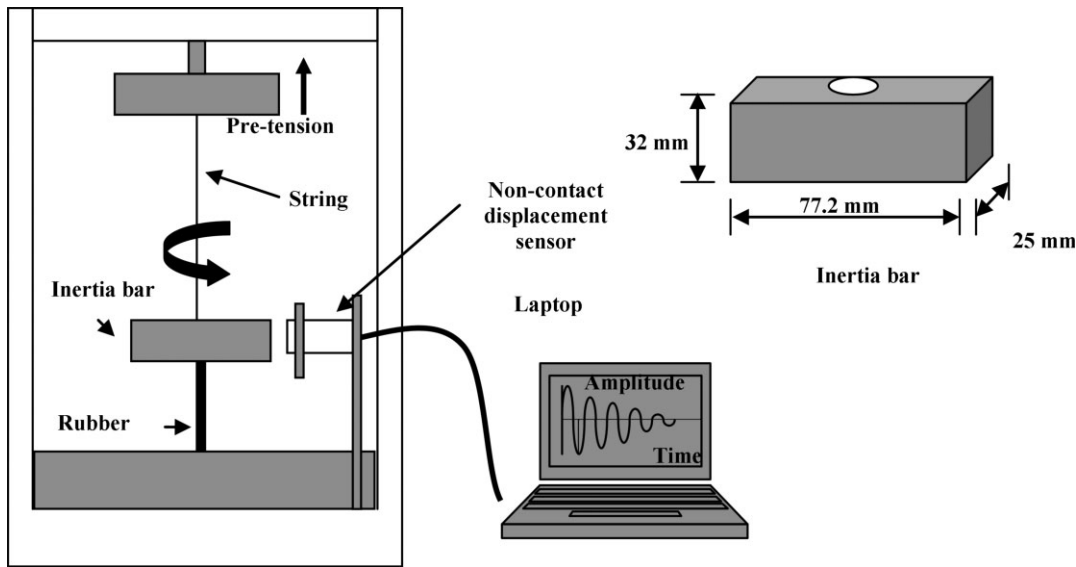


Figure 3 Schematic of the experiment of pretension superimposed with free torsion.

$$G^* = G' + iG'' \quad (10)$$

$$G'' = \left( \frac{I\omega^2\Delta}{6\pi r^2} \right) \left( \frac{l_0}{A_0} \right) \lambda^2 \quad (14)$$

where  $G'$  is the storage shear modulus (elastic component) and  $G''$  is the loss shear modulus (dissipated energy component). In our case, the definitions of  $G'$  and  $G''$  are expressed in terms of the deformed geometry:

$$G' = \left( \frac{2I\omega^2}{\pi r^4} \right) \lambda^3 l_0 \quad (11)$$

$$G'' = \left( \frac{\Delta}{\pi} \right) G' \quad (12)$$

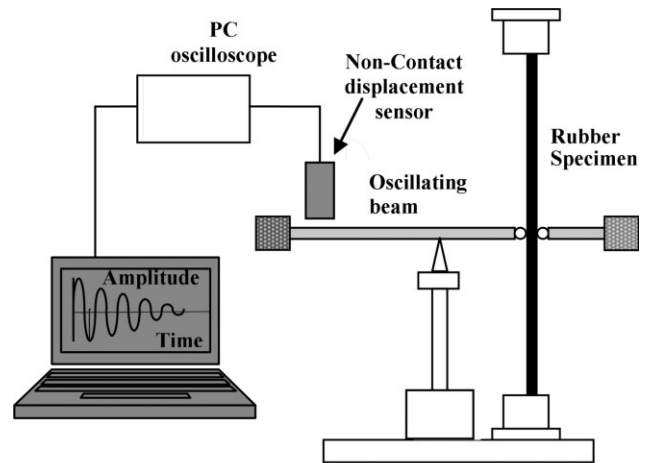
**Static tensile prestrain superimposed with an additional tensile oscillation**

A schematic for the apparatus used for the static tensile tests superimposed with an additional tensile oscillation is given in Figures 4(a,b).<sup>14</sup> The inertia bar in this case was supported by a knife edge and was also clamped at the center of a rubber specimen. The specimen was extended to a specified prestrain. The beam was set in motion by the release of an electromagnet. As the beam oscillated, the period of oscillation and the decay in the oscillation amplitude were measured with a noncontacting displacement sensor and recorded on a personal computer oscilloscope. In this case,  $G'$  and  $G''$  are also expressed in terms of the deformed geometry as defined by Davies et al.<sup>7</sup>:

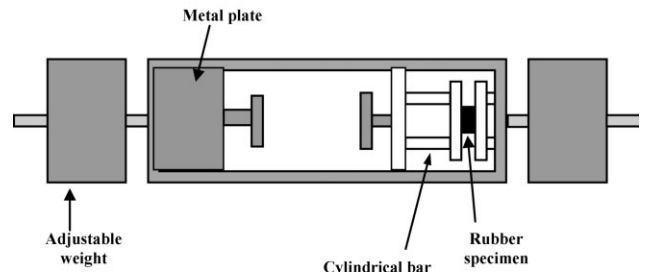
$$G' = \left( \frac{I\omega^2}{6r^2} \right) \left( \frac{l_0}{A_0} \right) \lambda^2 \quad (13)$$

$G''$  can be determined by the combination of eqs. (12) and (13):

where  $I$  is the moment of inertia of the beam,  $r$  is the distance from the knife edge to the clamped



(a)



(b)

Figure 4 (a) Apparatus used for dynamic mechanical measurements of strained rubber in tension and (b) the oscillating beam viewed along the axis of the specimen.



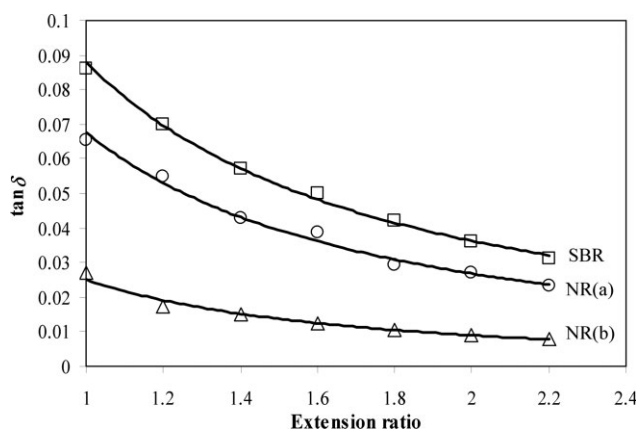
rubber,  $l_0$  is the original test piece length, and  $A_0$  is the original cross-sectional area of the test piece (which is  $10 \text{ mm}^2$ ). Equation (14) shows the relationship between  $G''$  and a specified prestrain. This was used to calculate  $G''$  from the static tensile prestrain superimposed with an additional tensile oscillation so that its value could be compared with  $G''$  in eq. (12) measured with the static tensile prestrain superimposed with a torsional oscillation. Rectangular samples for this test were cut from a molded flat sheet with approximate dimensions of  $80 \times 5 \times 2 \text{ mm}^3$ . The moment of inertia of the beam was measured experimentally with a bifilar suspension system. To do this, the beam was supported by vertical strings at both ends, and the oscillating frequency ( $f$ ) was measured. The moment of inertia was given by

$$I = \frac{mga^2}{4l\pi^2 f^2} \quad (15)$$

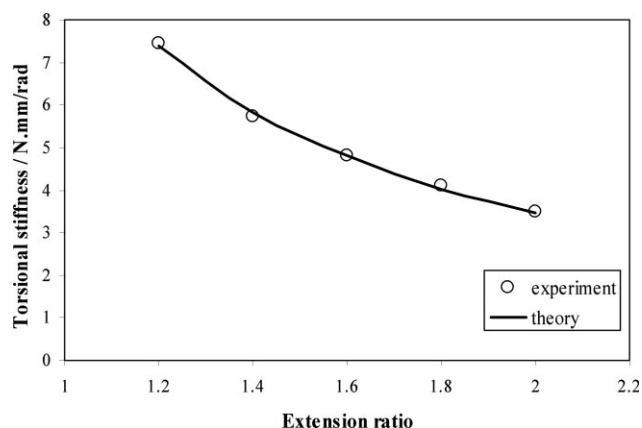
where  $m$  is the mass of the beam,  $a$  is the half-length of the beam, and  $l$  is the length of the strings.<sup>15</sup>

## RESULTS AND DISCUSSION

$\tan \delta$  can be calculated from the ratio of  $G''$  to  $G'$ . It is plotted as measured by a test of the static tensile prestrain superimposed with a torsional oscillation against the pre-extension, as shown in Figure 5. The result shows that  $\tan \delta$  decreases as a function of the pre-extension, as reported earlier by Kuhn and Kunzle.<sup>1</sup> The unfilled SBR shows a higher  $\tan \delta$  value than both unfilled natural rubber (NR) compounds, and NR(a) shows a higher  $\tan \delta$  value than NR(b) because of the difference in the crosslink density.<sup>16</sup> In this work, it is, however, important to reconsider the plot in terms of the original dimensions.  $G'$ , measured with a servohydraulic test machine, is shown in Figure 6. It decreases with an increase in



**Figure 5** Plots of  $\tan \delta$  against the extension ratio measured in the test of the pretension superimposed with a torsion oscillation.

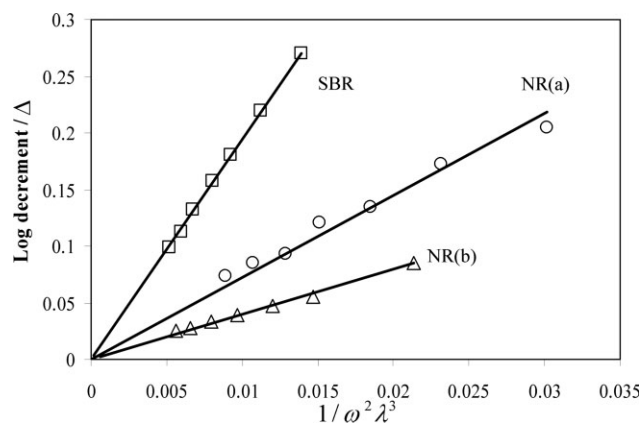


**Figure 6** Comparison of the experiment and Rivlin's equation [eq. (9)] for torsional stiffness at different pretensions for NR(a).

the static pretension. As anticipated from the theory of Rivlin and Saunders,<sup>12</sup> the stiffness depends on the deformed dimensions, as shown in eq. (9).

$\Delta$  of the free oscillations can be related to  $G''$  with eq. (8). A graph of  $\Delta$  versus  $1/\omega^2\lambda^3$  is shown for the torsional experiments in Figure 7. The graph shows that for all three materials considered here,  $G''$  is independent of the amount of the prestrain.

The results of the tests of the static tensile prestrain superimposed with an additional tensile oscillation were used to calculate  $G''$  with eq. (14) and were plotted against the extension ratio, as shown in Figure 8. Again,  $G''$  is only a modestly increasing function of the prestrain, at least up to an extension ratio of about 2. The earlier results measured in the tension torsion tests are also replotted on Figure 8, with eq. (12) used to calculate  $G''$  for each of the three materials. However, the modest increases in  $G''$  at an extension ratio above 2 arise at lower extension ratios than the finite extensibility effects seen in the curves of the stress versus the extension ratio



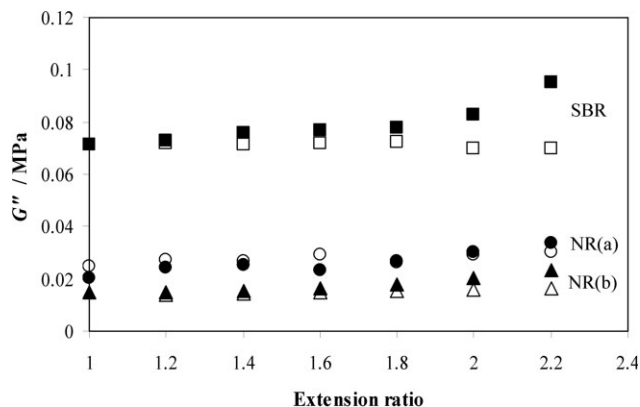
**Figure 7** Comparison of the experiment and theory for  $\Delta$  against  $1/\omega^2\lambda^3$ . The lines are the theoretical predictions from eq. (8), and the points are the experimental data.

shown in Figure 9. It appears at least for the SBR materials that  $G''$  is more sensitive to the polymer chain orientation than the stress-strain behavior. NR(a) has a lower sulfur content and hence a lower crosslink density than NR(b), as can be seen from both the lower stress-strain behavior and higher  $G''$  values. Figure 9 shows that the extension ratio at which the finite extensibility effects are observed is greater for NR(a) than NR(b). The strain for the observed increase in  $G''$  is also greater in NR(a), which has virtually no increase in  $G''$  over the range of experimental strains described in this article.

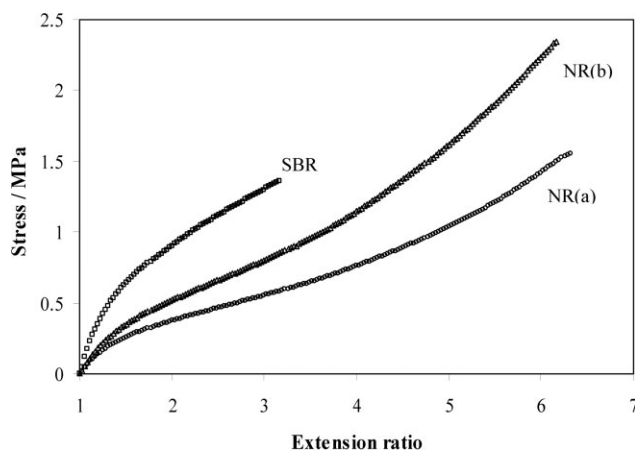
The results show the same trends for both types of deformation. This indicates that the prestrain has virtually no effect on  $G''$ , at least up to an extension ratio of 2, and that the behavior is broadly isotropic, with similar data being measured with strain within the accuracy of the experiment, for both types of deformation.

This work confirms the previous findings of Busfield et al.<sup>6</sup> and Davies et al.<sup>7</sup>: up to about 100% strain,  $G''$  is approximately independent of strain. At an extension ratio greater than 2, the curves start to show a modest increase in  $G''$ . It is likely that this strain represents the point at which the elastomer network begins to depend on pre-extension. Above an extension ratio of 2, it is possible that molecular orientation might have an effect on the viscoelastic behavior. The orientation of the monomer units, as distinct from the chain segments between crosslinks, is probably the controlling factor in any change in  $G''$  with strain. The statistical theory suggests that the orientation of the chain segments between crosslinks is modest until the polymer chains are extended by a substantial fraction of their contour length.

The next stage of this investigation is to measure the behavior for common engineering compounds. If



**Figure 8** Comparison of the  $G''$  values (measured with the test of the pretension superimposed with a torsion oscillation) plotted as a function of the pretension (the hollow symbols are from the torsion-tension test, and the solid symbols are from the tension-tension test).



**Figure 9** Curves of the tensile stress versus the extension ratio measured at a rate of 500 mm/min.

it applies there as well then it will be, from an engineering design point of view, an important discovery because for situations in which the working extensions are below 2, the viscoelastic behavior may be independent of the strain. Also, the energy dissipation should be easy to calculate for any simple oscillation (in any direction) applied to a prestrained component, with only a relatively simple material characterization being required.

## CONCLUSIONS

With these experiments, we have investigated how the dynamic behavior of a prestrained rubber sample changes with the extension ratio. The results have been measured from small dynamic oscillations, and they show that  $\tan \delta$  decreases with strain. However, a simple analysis shows that this effect is due to geometric changes alone and that the essential viscoelastic behavior, expressed as  $G''$ , is approximately constant with strain up to an extension ratio of about 2 for both unfilled SBR and NR compounds. The results from small oscillations in tension and torsion on prestrained samples also show that the prestrain does not induce any significant anisotropy in  $G''$ , with very similar values of  $G''$  being found. Above an extension ratio of 2, it is possible that constraints on the molecular orientation of the monomer units in the polymer chain might have an effect on the viscoelastic behavior. This is a worthwhile finding that might have potential applications in engineering applications, even though these will be for filled rubbers. As for most engineering applications, for which the working extensions are below 2, it appears that the viscoelastic behavior is independent of the extent of the strain, and the energy dissipation should be easy to calculate with a relatively simple characterization.

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