

The Viscoelastic Behavior of Rubber Under a Complex Loading. II. The Effect Large Strains and the Incorporation of Carbon Black

N. Suphadon, A.G. Thomas, J.J.C. Busfield

Department of Materials, Queen Mary University of London, Mile End Road, London, E1 4NS, United Kingdom

Received 5 October 2009; accepted 16 December 2009

DOI 10.1002/app.31991

Published online 26 March 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Suphadon et al. (J App Polym Sci 2009, 113, 693) showed using small oscillations of less than 1% strain superimposed on a larger prestrain that the loss modulus, referred to the test piece dimensions after the application of the prestrain, did not vary with prestrain for unfilled rubber materials for a wide range of prestrains up to 100%. Also for unfilled rubbers it was observed that up to 100% prestrain that the loss modulus behavior was isotropic. This paper extends this previous work to larger prestrains for styrene butadiene rubber (SBR) compounds and natural rubber (NR) compounds some of which incorporate carbon black fillers. Both the storage modulus and the loss modulus are again calculated relative to the dimensions of the test piece after the application of the prestrain. These results show that for materials with 25

phr of carbon black filler, the loss modulus was still independent of the prestrain for normal engineering strains but at filler contents of 50 phr the loss modulus increases with prestrain at extension ratios less than 2. Even so over the typical engineering strains of below 50%, the loss modulus was still independent of strain. This increase in loss modulus at large prestrains can in part be explained by considering the molecular orientation of the polymer in combination with a consideration of the molecular slippage that takes place at the polymer filler interface. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 1290–1297, 2010

Key words: rubber; elastomer; large strain; mechanical properties; filler reinforcement; carbon black; viscoelasticity; anisotropy

INTRODUCTION

In engineering applications containing rubber such as tyres and vibration mounting systems the rubber part of the component is often subjected to a combination of complex dynamic loads. Therefore, the viscoelastic behavior of the materials under a combination of a static strain with an additional fluctuating strain is important. Busfield et al.¹ and Davies et al.² studied the dynamic behavior of prestrained strips of rubber subjected to tensile oscillations. Suphadon et al.³ adopted this approach to study the anisotropy in the viscoelastic behavior resulting from the application of the prestrain. For unfilled rubber, at preextension ratios less than two where the storage and loss modulus are both calculated relative to the prestrained dimensions of the test piece, the loss modulus is seen to be independent of the prestrain and the energy dissipation depends upon the loss modulus and the test piece geometry alone.

The physical background to this approach is to presume the visco-elastic properties of a rubber sam-

ple are determined by a single viscosity term and the geometry of the sample. Therefore, when a prestrain is applied, the viscosity remains constant. Any measured changes to the visco-elastic behavior must then result from the geometric changes alone. The amplitudes of the small additional oscillations applied in this work were small to ensure linear behavior, in the case of the torsional test the maximum engineering strain amplitude was 0.1% and for the tensile oscillations the maximum engineering strain amplitude was 0.75%. At these small oscillation amplitudes the frequency of the oscillation remained constant confirming that the behavior was linear.

In this work larger prestrains to an extension ratio above two were observed using both unfilled rubbers as well as conventional rubber compounds filled with carbon black. The anisotropy in the loss modulus with strain was examined by measuring the damped oscillations in a rubber sample prestrained in tension with either a superimposed torsion oscillation or an additional tensile oscillation.

The effects of carbon black on the dynamic behavior of rubber have been discussed by several researchers.^{4–15} Rubber compounds that contain carbon black exhibit a higher modulus than unfilled rubber, in part because the carbon black is much

Correspondence to: J.J.C. Busfield (j.busfield@qmul.ac.uk).

stiffer than the rubber. This simple geometric stiffening effect is known as the "hydrodynamic" effect. In addition, the deformation of the rubber matrix in a filled compound is larger than the bulk deformation, this is known as "strain amplification." Guth and Gold¹⁶ derived a power series equation for the increase in the small strain stiffness resulting from hydrodynamic effect based upon the Einstein equation for the viscosity, η , of a suspension of spherical particles. Truncated to the first three terms, this gives:

$$\eta = \eta_0(1 + 2.5\phi + 14.1\phi^2) \quad (1)$$

where η_0 is viscosity of the fluid, and ϕ is the volume fraction of filler. Their equivalent equation for the storage modulus, G' is given as

$$G' = G'_0(1 + 2.5\phi + 14.1\phi^2), \quad (2)$$

where G'_0 is the storage modulus of the unfilled rubber. Viscosity equations and small strain elasticity equations are identical except that the time derivative of the strain rather than the strain itself is used. Therefore, assuming that there is no slippage at the interface between the fillers and the rubber in both circumstances, it is apparent that the viscosity relationship, given in eq. (1), can also be used not only to describe the storage modulus given as eq. (2) but also to the time derivative equivalent equation for loss modulus, G'' :

$$G'' = G''_0(1 + 2.5\phi + 14.1\phi^2), \quad (3)$$

where G''_0 is the loss modulus of the unfilled rubber.

In this work, the viscoelastic behavior is measured using a small free oscillation technique and it is evaluated relative to the deformed dimensions of the test piece after the application of the prestrain using a range of different compounds. The observations are then discussed in detail.

EXPERIMENTAL

Six different compounds of styrene-butadiene rubber (SBR) and natural rubber (NR) were used in this investigation. The compositions and processing conditions are given in Table I. To allow the SBR compounds to be highly extensible they were only lightly cross linked. Carbon black was incorporated where necessary in a master batch using an internal mixer. The conversion was done on an open two roll laboratory mill. A compression molded rectangular rubber strip was used to examine a tension superimposed with small tensile oscillations. The typical dimensions for the strip were 80 mm in length, 5

mm in width, and 2 mm in thickness. A compression molded rubber cylinder was used to examine a tension superimposed with a small torsional oscillation. The cylindrical rod was bonded to metal end pieces. It had a diameter of 12.2 mm and a length of 75 mm.

For small strain additional oscillations where the behavior is in the linear range for small cycles, the dynamic behavior of rubber for a small additional strain can be represented by a complex shear modulus,

$$G^* = G' + iG'' \quad (4)$$

where G' is the storage shear modulus (elastic component) and G'' is the loss shear modulus (dissipated energy component). The values of G' and G'' for any given prestrain are calculated with reference to the deformed dimensions. All the experiments in this work were conducted by measuring the damping during a free vibration test, where the energy dissipation is expressed in terms of the log decrement,

$$\Delta = \frac{1}{n} \ln \left(\frac{x_i}{x_{i+n}} \right), \quad (5)$$

where x_i is the amplitude of the i th cycle and n is the number of free oscillations being measured. The log decrement was measured in each case from a first cycle when the oscillating engineering strain amplitude was 0.1% in torsion or 0.75% in tension.

The elastic behavior for each material was also measured using dumbbell shaped specimens of 2 mm thickness and 3 mm width in the gauge length using a screw driven Instron 5550 with an optical strain measuring device. To study the elastic behavior, the test specimens were loaded at a strain rate of 500 mm/minute until break.

The method whereby a sample prestrained in tension has an additional small torsion oscillation superimposed has been adopted previously by several researchers¹⁷⁻²¹ and again recently by Suphadon et al.³ A suitable schematic for the test is shown in Figure 1. The base of the rubber cylinder was fixed and the top was mounted to a torsion inertia bar. The cylinder was prestrained to a specified engineering prestrain by pulling an inelastic string attached above the inertia bar. After each prestrain has been applied the sample was allowed to relax for three minutes to minimize the effects of stress relaxation on the measurements.²² A torsion oscillation was established by tapping the torsion bar. The period of oscillation and the decay in the displacement amplitude of the oscillation were measured using a noncontacting displacement sensor and recorded on an oscilloscope. The period remained constant

TABLE I
Compound Formulations and Processing Conditions Used in this Work

Ingredients		Parts per hundred rubber					
NR	SMR CV-60	0	0	0	100	100	100
SBR	JSR#1500	100	100	100	0	0	0
Carbon black	N330 ¹	0	25	50	0	25	50
Stearic Acid		2	2	2	2	2	2
Zinc Oxide		3	3	3	5	5	5
Antioxidant	HPPD ²	1	1	1	1	1	1
Accelerator	CBS ³	0	0	0	1.5	1.5	1.5
Accelerator	DPG ⁴	1	1	1	0	0	0
Sulfur		1.5	1.5	1.5	0.5	0.5	0.5
Molding conditions							
Curing time		70 min	70 min	70 min	15 min	15 min	15 min
Temperature		160 °C	160 °C	160 °C	160 °C	160 °C	160 °C

HPPD², N-(1, 3-dimethyl butyl)-N-phenyl-p-phenylenediamine; CBS³, N-Cyclohexy-2-benzothiazole sulfenamide; DPG⁴, diphenyl guanidine; N330¹, High abrasion furnace (HAF) black, size 28–36 nm, surface area 73–91 m²/g, density 1.8 kg/m³

throughout the test, indicating that the small oscillations were of sufficiently small amplitude to ensure that the behavior was linear. The measurement of the log decrement was consistently measured from the cycle when the maximum shear strain in the sample was approximately 0.1%.

Expressed in terms of the deformed geometry G' and G'' can be derived as follows for the case of a damped torsion on a prestrained test piece assuming that the free oscillations are small in amplitude and that the materials exhibit linear viscoelastic behavior at these strains.

The free oscillation relationships for K'_θ , the in-phase component of the torsional stiffness (torque/rad) and K''_θ , the out-of-phase component of torsional stiffness, for a torsion pendulum are given by Brown²³ as,

$$K'_\theta = I\omega^2 \left(1 + \frac{\Delta^2}{4\pi^2} \right), \quad (6)$$

which for small strain oscillations reduces to

$$K'_\theta = I\omega^2, \quad (7)$$

and

$$K''_\theta = I\omega^2 \Delta / \pi \quad (8)$$

where I is the inertia of the oscillating mass and ω is the angular frequency. For linear elastic behavior the relationship between the static shear modulus (G) and the static torsional stiffness (K_θ) is derived from the formula for the torsion of a cylinder as,

$$K_\theta = \frac{\pi r_0^4 G}{2l}. \quad (9)$$

When the rubber rod is subjected the static pre-tension, eq. (9) can be expressed in terms of the undeformed geometry as,

$$K_\theta = \frac{\pi r_0^4 G}{2l_0 \lambda^3} \quad (10)$$

Similarly, the out-of-phase torsion stiffness is given as,

$$K''_\theta = \frac{\pi r_0^4 G''}{2l_0 \lambda^3}. \quad (11)$$

Linking the log decrement, Δ , to the loss modulus, G'' , can be achieved by equating eq. (8)–(11). This gives

$$\Delta = \frac{\pi^2 G'' r_0^4}{2I\omega^2 l_0 \lambda^3}. \quad (12)$$

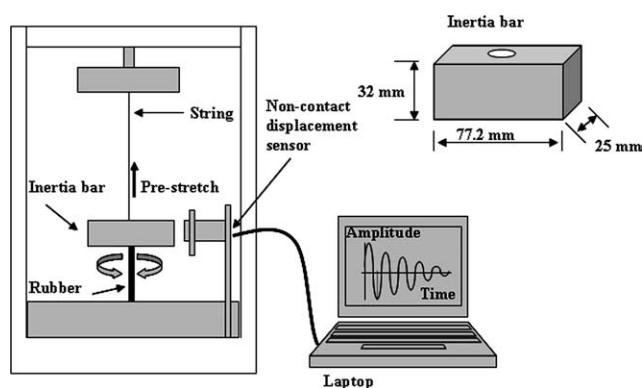


Figure 1 The apparatus used to measure a small torsion oscillation superimposed on a tensile prestrain.

Equation (12) can be rearranged to show that the loss shear modulus is given as

$$G'' = \left(\frac{2I\omega^2\Delta}{\pi^2} \right) \left(\frac{l_0}{r_0^4} \right) \lambda^3. \quad (13)$$

By equating eq. (7), (8), and (13), the storage modulus can similarly be given as

$$G' = \left(\frac{2I\omega^2}{\pi} \right) \left(\frac{l_0}{r_0^4} \right) \lambda^3. \quad (14)$$

A schematic for the apparatus used for the static tensile tests superimposed with an additional much smaller tensile oscillation is given in Figure 2. 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 and then also allowed to relax before testing for a minimum of 3 min. The beam was triggered by releasing an electromagnet. As the beam oscillates, the reduction in the oscillation amplitude was measured using the same method as during the torsion-tension experiment. In this case G' and G'' are expressed in terms of the deformed geometry as defined by Busfield et al.^{1,24} The derivation of the relevant expressions to relate the storage and loss modulus to the log decrement and the prestrained dimensions of the test piece are shown below. Once again this derivation assumes that the materials exhibit linear viscoelastic behavior during the small oscillations. This is possible if the oscillations are small in amplitude and this is confirmed by the frequency remaining constant throughout a test. In this case the log decrement measurement was triggered from when the maximum strain amplitude in the sample had reached 0.75% strain.

The equation of motion of this oscillating system is given by,

$$I \frac{\partial^2 \theta}{\partial t^2} + T = 0, \quad (15)$$

where I is again the inertia of the beam, θ is the angular displacement of the beam and T is the torque because of the force at the center of the strained specimen. T is given by,

$$T = f_v a = 2ka^2\theta, \quad (16)$$

where a the distance from the knife edge to the clamped rubber, f_v is the net vertical force on the cross-sectional area of the strained rubber, which can be represented by the sum of an upward force and downward force and k is the incremental stiffness of the specimen which can be defined as $k = \frac{df_v}{d\theta}$. Hence,

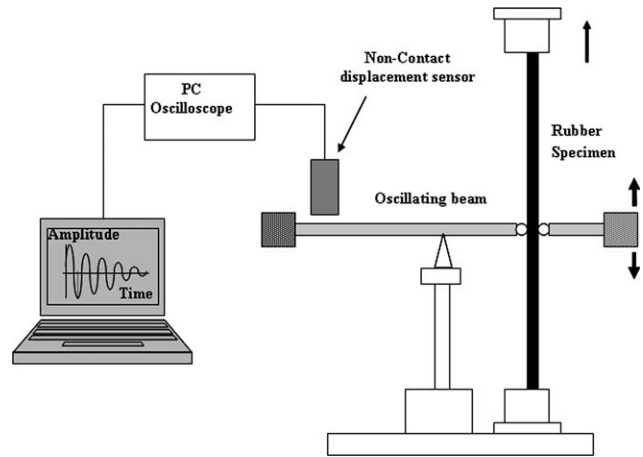


Figure 2 The apparatus used to measure a small tensile oscillation superimposed on a tensile prestrain.

$$I \frac{\partial^2 \theta}{\partial t^2} + 2ka^2\theta = 0. \quad (17)$$

The tensile modulus (E) referred to the actual cross section area of the strain specimen can be defined as,

$$E = \frac{t^*}{\varepsilon^*} = \frac{\lambda\sigma}{\Delta l/l} = \frac{\lambda\sigma}{\Delta l/\lambda l_0} = \lambda^2 \frac{(k\Delta l/A_0)}{\Delta l/l_0} = \frac{\lambda^2 k l_0}{A_0}, \quad (18)$$

where t^* is the true stress, ε^* is the true strain, σ is the engineering stress, l_0 is the original test piece length and A_0 is the undeformed cross-sectional area of the test piece. Hence,

$$k = E\lambda^{-2} \frac{A_0}{l_0} \quad (19)$$

Combining eq. (17) and (19) gives,

$$I \frac{\partial^2 \theta}{\partial t^2} + 2E\lambda^{-2} \frac{A_0}{l_0} a^2\theta = 0 \quad (20)$$

The equation describes the motion of the system and has the standard solution given by,

$$\theta = \theta_0 \cos(\omega t + \alpha), \quad (21)$$

where ω is the angular frequency of the beam. Combining eq. (20) and (21) gives,

$$\left[2E\lambda^{-2} \frac{A_0}{l_0} a^2 - I\omega^2 \right] \theta_0 \cos(\omega t + \alpha) = 0. \quad (22)$$

Since $\theta_0 \cos(\omega t + \alpha) \neq 0$, it is possible to deduce that

$$I\omega^2 = 2E\lambda^{-2} \frac{A_0}{l_0} a^2 \quad (23)$$

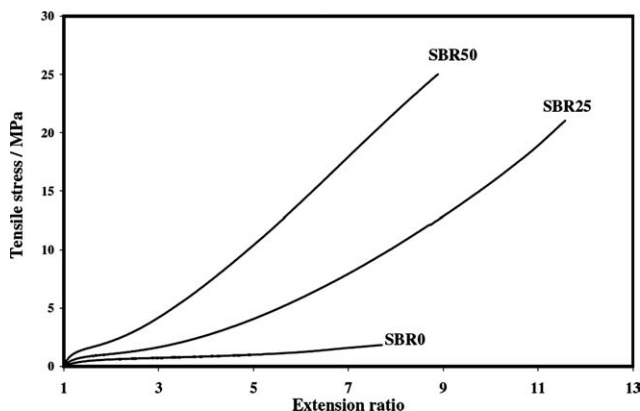


Figure 3 Stress versus strain plots for the three different SBR compounds.

Equation 23 can be arranged to give the elastic modulus E as

$$E = \frac{I\omega^2 l_0 \lambda^2}{2a^2 A_0} \quad (24)$$

For a viscoelastic material this can be resolved into storage and loss modulus terms and by assuming that rubber is an incompressible material, where $E = 3G$, eq. (24) can be written as,

$$G' = \left(\frac{I\omega^2}{6a^2} \right) \left(\frac{l_0}{A_0} \right) \lambda^2, \quad (25)$$

and the loss modulus can be given as,

$$G'' = \left(\frac{I\omega^2 \Delta}{6\pi a^2} \right) \left(\frac{l_0}{A_0} \right) \lambda^2. \quad (26)$$

The inertia bars were altered to ensure that the range of frequencies for all the tests was in the range of 0.5 and 1.5 Hz for the unfilled compounds and in the range of 1 and 2 Hz for the filled compounds.

RESULTS AND DISCUSSION

Suphadon et al.³ found for unfilled rubbers the loss modulus calculated with reference to the deformed dimensions of the test piece after prestraining was independent of prestrain for extension ratios less than 2 and was the same whether measured using the torsion oscillation (out of plane with the prestrain) or the tension oscillation (in plane with the prestrain). This work extends this earlier work to prestrains greater than two and also examines the behavior in filled rubbers.

The incorporation of fillers made the materials much stiffer and stronger as shown in Figures 3 and 4. The SBR compounds were specifically com-

pounded to have a low cross link density so that they could be prestrained to more than 500% without breaking. Equations (14) and (13) were used to determine G' and G'' respectively, expressed relative to the deformed dimensions, for the static prestrain superimposed with a small torsion oscillation. Equations (25) and (26) were used to calculate G' and G'' respectively, expressed relative to the deformed dimensions, for the static prestrain superimposed with a much smaller tensile oscillation.

Figures 5–7 show how the loss modulus G'' varies as a function of the prestrain measured using both small tension and torsion oscillations. The loss modulus is independent of prestrain within the bounds of the experimental accuracy at prestrain extension ratios below 3.0 for the unfilled compounds (NR0 and SBR0). These results are entirely consistent with the previous findings.

At larger prestrains an increase in the loss modulus with strain is observed. Suphadon et al.³ suggested at larger extension ratios, the molecular orientation and the finite extensibility effect of the rubber molecules might have started to have an effect on the viscoelastic behavior. The orientation of the monomer units, as distinct from the chain segments between crosslink, and the entanglement slippage at large prestrain were suggested to be the factors, which controlled the change in G'' with strain. The statistical theory suggests that the orientation of the chain segments between crosslink is modest until the polymer chains are extended by a substantial fraction of their contour length. However, the orientation of the monomer unit takes place at much lower global strains.

For SBR25 and NR25 with 25 parts per hundred of rubber filled with carbon black, the change in loss modulus with pre-extension is still modest up to extension ratios of two, but the upturn is clearly more marked than was the case for the unfilled

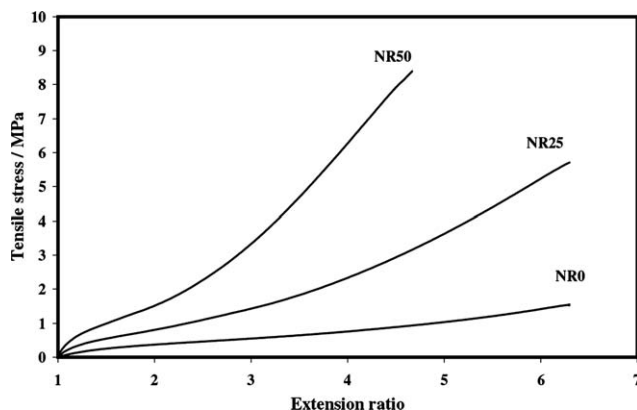


Figure 4 Stress versus strain plots for the three different NR compounds.

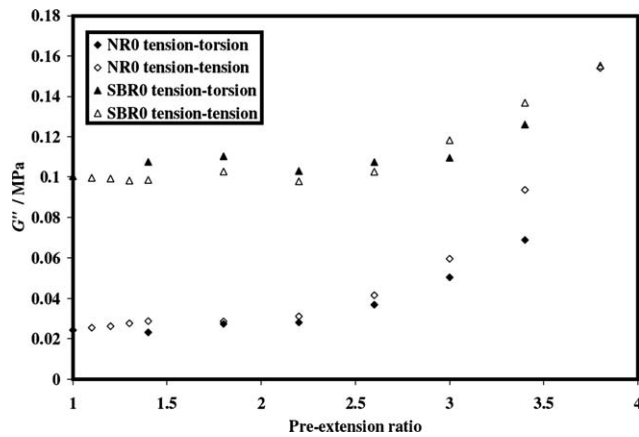


Figure 5 The loss modulus of NR0 and SBR0 based upon the deformed dimensions plotted against the tensile prestrain for both free oscillations.

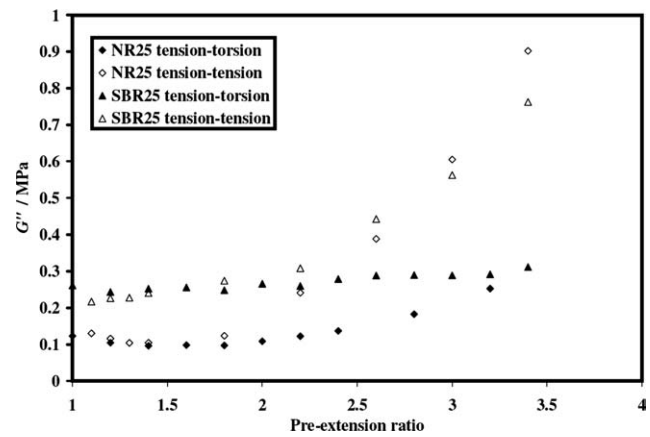


Figure 6 The loss modulus of NR25 and SBR25 based upon the deformed dimensions plotted against the tensile prestrain for both free oscillations.

rubber. For the more highly filled rubbers, NR50 and SBR50, the loss modulus is clearly dependent on the prestrain at comparably lower prestrains. However, the prestrain where the increase occurs is still significantly higher than the engineering strain range for most rubber components. This suggests that for most materials working under normal conditions there is hardly any prestrain dependence in the loss modulus expressed relative to the deformed dimensions.

It should be noted that at zero prestrain ($\lambda = 1$) $\tan \delta$ should not depend upon filler content if the rubber is firmly bonded to the filler and no other factors, such as unusual viscoelastic behavior of the rubber layer adjacent to the filler arises. However, when we consider both the storage and the loss modulus, where the tests were conducted in torsion-tension test at zero prestrain, it appears that both the storage and the loss modulus of the filled materials measured experimentally are not only slightly different to each other but they are significantly higher than those calculated using the unfilled rubber behavior modified by the Guth–Gold equation. For NR50 the measured loss modulus is 5 times greater than expected when compared to the Guth–Gold calculation, whereas the storage modulus is 4.5 times greater. For SBR50 the measured loss modulus is 3.75 times greater than expected and the storage modulus is 2.6 times greater. The reason that the measured data is much higher than predicted by Guth–Gold relationship results from the shape of the N330 fillers, which are not the perfect spheres assumed during the derivation of the equations. However, at small strains and with small additional oscillations, the deformation should be in the linear viscoelastic range, therefore both G' and G'' should both depend upon the volume fraction of the filler and the filler shape to the same amount. This is not

entirely true and therefore some other energy dissipation mechanism must take place.

It is known that fillers generate local strains in the rubber phase of the composite that are higher than the globally applied strains and this strain amplification^{16,25–27} reduces the strain at which the increase in loss modulus is felt with an increase in the filler volume fraction. However, it is not clear how this could produce a greater effect on the loss modulus compared with the storage modulus.

Figures 5, 6, and 7 allow a comparison of the loss modulus measured both in the direction of the prestrain as well as in the direction of a superimposed torsion. The similarity of the loss modulus measured in both directions indicates that the behavior is broadly isotropic for tensile prestrains that are in the normal working range for typical engineering components. The unfilled compounds are modestly anisotropic at the higher prestrains, with the loss modulus in the tension–tension test being slightly higher with prestrain. However, for the filled materials

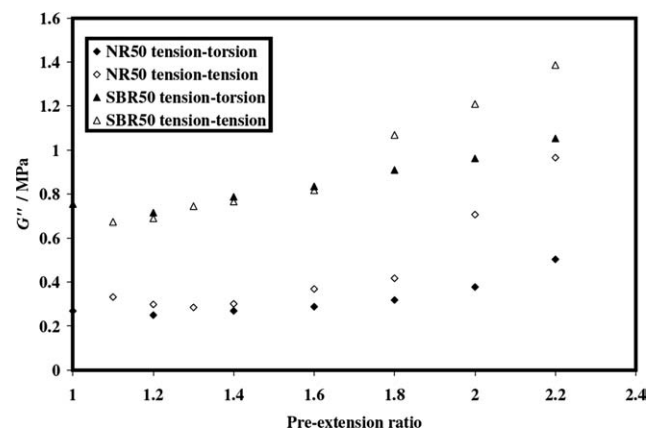


Figure 7 The loss modulus of NR50 and SBR50 based upon the deformed dimensions plotted against the tensile prestrain for both free oscillations.

greater anisotropy is observed in the loss modulus at larger prestrains, with the tension–torsion test showing a lower dependence of G'' with strain than the tension–tension test.

All the NR compounds have higher loss modulus dependence with prestrain than the SBR compounds. This might simply result from the differences in the extent of the cross linking, as the SBR compounds were all less tightly crosslinked than the corresponding NR compounds to allow them to be extended to large strains. As a result their molecules are less highly oriented under strain, and hence they have to be strained further before the effects of any finite extensibility are felt. The increase in the damping seen in the filled NR may also be a consequence of a difference in the interfacial slippage of labile bonds at the filler–rubber interface, which might have a greater role to play in NR. The bonds at the interface are secondary van den Waals and their magnitude might be slightly different between the two rubbers. The prestrains in all the NR materials were maintained below the threshold for the onset of complications arising because of strain induced crystallization.

In Figures 8 and 9 the previous data measured using the tension with superimposed torsion are replotted to examine more closely the loss factor (the ratio of loss modulus to the storage modulus) against the amount of prestrain. Examining the behavior at small strains, where you might expect the loss factor to be the same for both the filled and the unfilled elastomers, as both the storage and loss modulus should both be altered to the same extent by the presence of a filler, it is shown clearly that the loss factor is greater for the filled rubbers. This might be a result of the unpeeling of rubber from the carbon black or as a result of energy dissipation during frictional sliding of the rubber over carbon black surface under deformation.^{11,28,29} This may

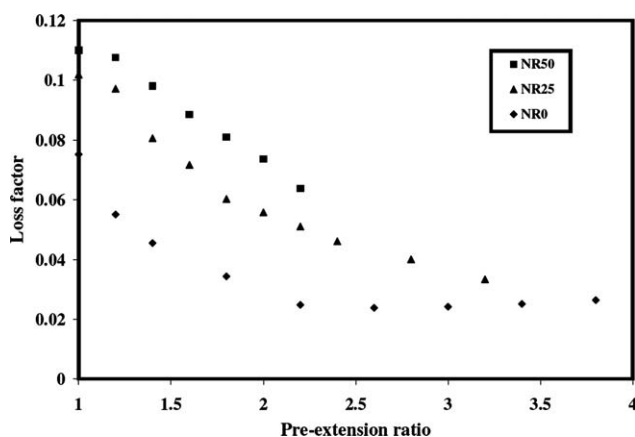


Figure 8 The ratio of loss modulus to storage modulus for the three NR compounds measured using tension superimposed with torsion oscillations.

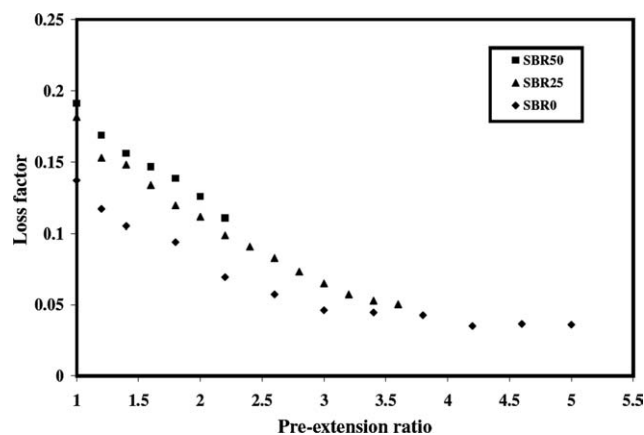


Figure 9 The ratio of loss modulus to storage modulus for the three SBR compounds measured using tension superimposed with torsion oscillations.

have the effect of relieving the stresses more in a filled material than is possible in the unfilled compound. In this case a small additional oscillation in the direction of prestrain may more readily result in slippage, and hence more energy dissipation than a small oscillation in another plane. The effect is also more significant at small volume fractions as the ratio between NR0 and NR25 as well as SBR0 and SBR25 is proportionally greater than that for NR50 and SBR50 compared to their unfilled counterparts.

CONCLUSIONS

The effect of a large prestrain on the dynamic behavior calculated with reference to the dimensions of the rubber sample after the application of the prestrain has been investigated using a free vibration test with measurements taken both in the direction of the tensile prestrain as well as in the plane of a superimposed torsion for a range of different unfilled and filled rubbers.

At lower prestrains and for the unfilled rubbers, NR0 and SBR0, the loss modulus when calculated in terms of the deformed test piece geometry is independent of the prestrain. This contrasts to the larger prestrains (which are typically beyond the working strain range for most rubbers) where there is a modest dependence with prestrain. The prestrain does not induce any anisotropy in G'' at lower prestrains. However, at larger prestrains it is possible that constraints on the monomer units in the rubber network might introduce some additional dissipation.

The loss modulus of filled rubbers is seen to depend to a larger extent on the prestrain especially at large prestrains and with the most highly filled rubbers. This is thought to arise from strain amplification effects and the molecular slippage over the carbon black surface. The anisotropy suggests that the frictional sliding at the filler boundaries depends

upon the direction of the stress field around the filler. However, for the entire working strain range the behavior is remarkably independent of the prestrain.

The significant result of this work is that a single value for the loss modulus defined in terms of the dimensions of the test piece after the application of a prestrain can be used for general engineering design for example when rubber is used in vibration damping applications where a complex loading is applied to a component and the designer wishes to predict the energy dissipation per cycle. The introduction of a single value for the loss modulus for a specific material for a wide range of geometries, prestrains and loading cycles means that it should be much easier to design components using analytical design approaches such as finite element analysis.

The author would like acknowledge Dr. Yoshi Fukahori for his thought provoking discussions. One of the authors, N. Suphadon, would also like to thank the Royal Thai Government for his scholarship.

References

1. Busfield, J. J. C.; Deeprasertkul, C.; Thomas, A. G. *Polymer* 2000, 41, 9219.
2. Davies, C. K. L.; Thomas, A. G.; Akutagawa, K. *Prog Rubber Plast Technol* 1996, 12, 174.
3. Suphadon, N.; Thomas, A. G.; Busfield, J. J. C. *J Appl Polym Sci* 2009, 113, 693.
4. Wolff, S.; Wang, M. J.; Tan, E. H. *Rubber Chem Technol* 1993, 66, 163.
5. Meissner, B. *Rubber Chem Technol* 1995, 68, 297.
6. Meissner, B. *Rubber Chem Technol* 1975, 48, 810.
7. Medalia, A. *Rubber Chem Technol* 1974, 47, 411.
8. Houwink, R. *Rubber Chem Technol* 1950, 23, 414.
9. Dannenberg, E. *Rubber Chem Technol* 1986, 59, 512.
10. Dannenberg, E. *Rubber Chem Technol* 1975, 48, 410.
11. Ulmer, J. D.; Hess, W. M.; Chiricp, V. E. *Rubber Chem Technol* 1974, 47, 729.
12. Dannenberg, E. *Rubber Chem Technol* 1952, 25, 843.
13. Wang, M. J.; Wolff, S. *Rubber Chem Technol* 1991, 64, 714.
14. Yamaguchi, K.; Busfield, J. J. C.; Thomas, A. G. *J Polym Sci Part B: Polym Phys* 2003, 41, 2079.
15. Jha, V.; Thomas, A. G.; Bennett, M.; Busfield, J. J. C. *J Appl Polym Sci* 2010, 116, 541.
16. Guth, E.; Gold, O. *Phys Rev* 1938, 53, 322.
17. Kuhn, W.; Kunzle, O. *Rubber Chem Technol* 1955, 28, 694.
18. Mason, P. *J Appl Polym Sci* 1959, 1, 63.
19. Mohsin, M. A.; Treolar, L. R. G. *Polymer* 1987, 28, 1893.
20. Mooney, M.; Gerke, R. H. *Rubber Chem Technol* 1941, 14, 35.
21. Suphadon, N.; Busfield, J. J. C. *Plastics Rubber Compos* 2009, 38, 337.
22. Asare, S.; Thomas, A. G.; Busfield, J. J. C. *Rubber Chem Technol* 2009, 82, 104.
23. Brown, R. P. *Physical Testing of Rubber*; Elsevier applied science publishers Ltd.: 1986.
24. Busfield, J. J. C.; Deeprasertkul, C.; Thomas, A. G. In *Constitutive Models for Rubber*; Dorfmann, A., Muhr, A., Eds.; 1999; pp 87–94.
25. Busfield, J. J. C.; Thomas, A. G.; Yamaguchi, K. *J Polym Sci Part B: Polym Phys* 2005, 43, 1649.
26. Wolff, S. *Rubber Chem Technol* 1990, 63, 32.
27. Jha, V.; Hon, A. A.; Thomas, A. G.; Busfield, J. J. C. *J Appl Polym Sci* 2008, 107, 2572.
28. Kumar, P.; Fukahori, Y.; Thomas, A. G.; Busfield, J. J. C. *J Polym Sci Part B: Polym Phys* 2007, 45, 3169.
29. Medalia, A. *Rubber Chem Technol* 1978, 51, 437.