

Effect of Vulcanization on the Low-Strain Dynamic Properties of Filled Rubbers

A. R. PAYNE, R. E. WHITTAKER, *Shoe and Allied Trades Research Association, Kettering, Northants, England*
and J. F. SMITH, *Natural Rubber Producers Research Association, Welwyn Garden City, Herts, England*

Synopsis

A change in the degree of vulcanization in a carbon black-filled rubber is shown not to affect the change of in-phase shear modulus with strain amplitude, provided the amount of filler is kept constant. Similar results are found with the change of out-of-phase modulus and phase angle with strain amplitude. A similar value of change of in-phase shear modulus with strain amplitude ($G'_0 - G'_\infty$) is found for a vulcanized and unvulcanized tire tread rubber; this behavior is attributed for the breakdown of the secondary three-dimensional carbon black aggregated network. Detailed consideration is given to other factors such as hydrodynamic, shape factor, and relaxation effects which contribute to the difference between the shear modulus of the gum rubber and the filled rubber when all the carbon black structure has been broken down. The consequence of the breakdown of the secondary aggregated structure of carbon black are considered in terms of factors affecting heat build-up in tires.

INTRODUCTION

Numerous studies¹⁻⁶ in recent years have shown that the dynamic properties of filled-rubber vulcanizates are dependent on strain amplitude. It has been found that the in-phase shear modulus for filled-rubber vulcanizates (G'), decreases from a high value (G'_0) at very low strains to a low modulus plateau (G'_∞) when there is no further change in modulus with strain amplitude. The hysteresis measured by the phase angle between the sinusoidal stress and strain oscillations also reaches a maximum value near the point of inflexion on the in-phase modulus-strain amplitude graph.

This type of behavior has also recently been found in other composite systems such as carbon black in oil⁷ and clay in rubber⁸ or water.⁹ The behavior in carbon black-filled rubbers has been ascribed to the breakdown of the three-dimensional carbon black aggregated structure.

The general level of the modulus and phase angle is known to be dependent on the nature and degree of crosslinking. If, however, the magnitude of the modulus decrease with strain amplitude, ($G'_0 - G'_\infty$) is affected by the degree of crosslinking; then the effect cannot entirely be due to the

carbon black aggregated structure but must also reflect changes that occur in the rubber phase of the filled vulcanizate. If the effect, however, is independent of the level of vulcanization of the rubber, then the suggestion that it is due entirely to the carbon black particles is confirmed.

This paper presents the results of a study into the effect of changing the degree of vulcanization on the low-strain dynamic properties of carbon black-filled natural rubber vulcanizates.

EXPERIMENTAL

Conventional sulfur-cured natural rubber gum vulcanizates were prepared with 0.20, 0.75, 1.65, and 4.17 phr sulfur and are referred to as mixes 1-4, respectively, in the paper. Each gum mix was also filled with 30, 50, and 70 phr ISAF black. The mix details and cure times are given in the Appendix. The cylindrical test specimens, 1.80 cm in diameter and 2.54 cm in height, were cured in a multicavity mold and were handled with a minimum deformation when removed from the mold.

The samples were tested on the sinusoidal strain dynamic tester, a machine which has been described in earlier publications.^{1,2,10} Two test pieces were bonded to either side of a central metal plate which applied the oscillating movement and the other sides of the specimen to restraining static plates. The temperature of the test was 21°C, and frequency of oscillations, 0.2 cycles per second.

After setting up and resting overnight, the specimens were first tested at displacements of 10^{-4} to 10^{-2} cm, where it was experimentally convenient to apply a chosen stress and record the strain. They were then all tested at successively higher strains by selecting the strain and observing the stress up to total displacements of 3.20 cm.

The experimental measurements made were the maximum straining force, the resulting amplitude of strain, and the phase angle between the sinusoidal stress and strain oscillations at each individual setting of the dynamic tester. The variation of the complex shear modulus G^* and phase angle δ with increasing amplitude of dynamic oscillation could then be determined.

The relationship^{1,11} between the moduli are shown by eqs. (1) and (2):

$$G^* = G' + iG'' \quad (1)$$

$$\tan \delta = G''/G' \quad (2)$$

where G' is the in-phase modulus with the strain or elastic component of the shear modulus and G'' is the out-of-phase or viscous component of the shear modulus. A correction¹¹ can be applied to take account of the bending factor; but as all the moduli data are relative, this was considered unnecessary.

EXPERIMENTAL RESULTS

In-Phase Shear Modulus

The variation of in-phase shear modulus G' with strainwork for the gum and 50 phr carbon black-filled vulcanizates is shown in Figure 1, and for the 30 phr and 70 phr ISAF-filled vulcanizates, in Figure 2. The modulus has been plotted against strain work, which is defined here as the product of double stress amplitude and double strain amplitude instead of strain amplitude, as earlier studies have shown that the dynamic parameters are much more dependent on strain work.

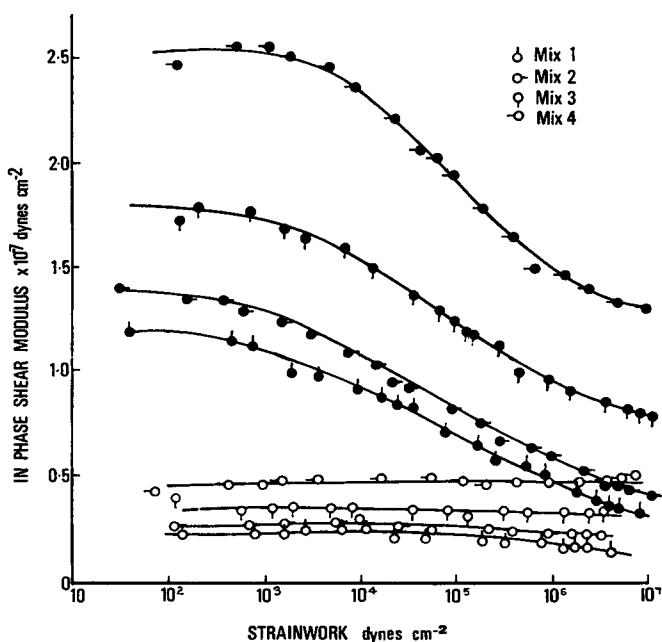


Fig. 1. Variation of in-phase shear modulus G' with strain work of oscillation. Open circles, gum vulcanizates; filled circles, vulcanizates filled with 50 phr ISAF black.

The typical sigmoidal change of in-phase modulus with strain work is apparent in all the filled vulcanizates, the effect increasing with increasing concentration of the carbon black as found previously. It has been found in earlier work that the shear modulus of filled rubbers has a limit, G'_0 , at low strains and a second limit, G'_∞ , which occurs at high strains when there was no further change of modulus with strain. These values for the vulcanizates considered in this paper are listed in Table I. A very small dependence of modulus on amplitude is observed in the unfilled rubbers shown in Figure 1, especially the very low crosslinked rubber (mix 1). This is probably due to the slippage of entanglements and motion of chains with free ends, a secondary effect which is discussed in the next section.

Considering the data for the 70 phr ISAF black vulcanizates in Figure 2, the curves through the points appear to be approximately parallel although the degree of crosslinking varied widely from 0.20 phr sulfur for mix 1 to 4.17 phr sulfur for mix 4. The total modulus change, $G'_0 - G'_\infty$, is also

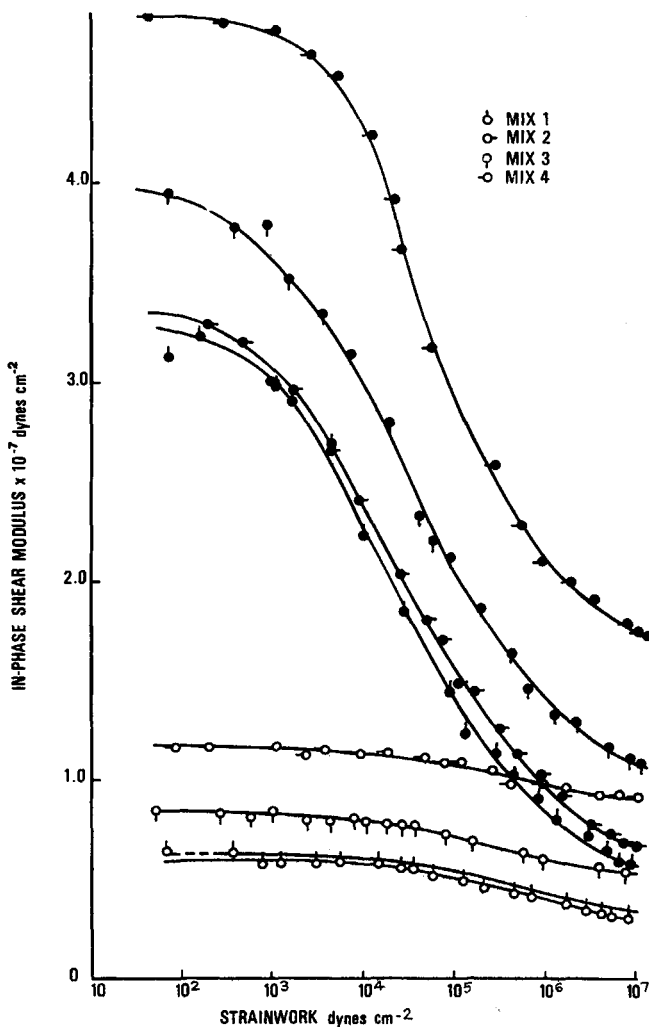


Fig. 2. Variation of in-phase shear modulus G' with strain work of oscillation. Open circles, vulcanizates filled with 30 phr ISAF black; filled circles, vulcanizates filled with 70 phr ISAF black. Points not shown for mix 2 vulcanizate with 30 phr ISAF.

similar, 2.81×10^7 and 3.14×10^7 dynes/cm² for mixes 1 and 4, respectively. Although values of $G'_0 - G'_\infty$ are similar, the values of G'_0/G'_∞ vary markedly for the 70 phr filled vulcanizates, from 6.51 for mix 1 to 2.86 for mix 4 over the same strain work ranges.

TABLE I
Derived In-Phase Shear Modulus Parameters

Mix no.	Carbon black, phr	G'_0 , (dynes/cm ²) $\times 10^{-7}$	G'_∞ , (dynes/cm ²) $\times 10^{-7}$	$G'_0 - G'_\infty$, (dynes/cm ²) $\times 10^{-7}$	G'_0/G'_∞	$G'_{\infty f}/G'_{\infty g}$
1	—	0.23	0.12	0.11	1.92	—
2	—	0.26	0.22	0.04	1.18	—
3	—	0.36	0.33	0.03	1.09	—
4	—	0.46	0.46	0.00	1.00	—
1	30	0.56	0.26	0.30	2.15	2.17
2	30	0.60	0.33	0.27	1.82	1.50
3	30	0.83	0.54	0.29	1.54	1.64
4	30	1.18	0.90	0.28	1.31	1.96
1	50	1.20	0.28	0.92	4.29	2.33
2	50	1.40	0.40	1.00	3.50	1.82
3	50	1.70	0.77	0.93	2.21	2.33
4	50	2.50	1.30	1.20	1.92	2.83
1	70	3.32	0.51	2.81	6.51	4.25
2	70	3.45	0.65	2.80	5.31	2.95
3	70	3.93	1.02	2.96	3.90	3.09
4	70	4.84	1.70	3.14	2.85	3.70

Table I lists the values of the dynamic parameters, G'_0 , G'_∞ , $G'_0 - G'_\infty$, and G'_0/G'_∞ for all the vulcanizates studied. It is also seen that in the case of the 30 and 50 phr filled vulcanizates, values of $G'_0 - G'_\infty$ remain fairly constant while G'_0/G'_∞ values vary considerably.

These experimental results lead to the conclusion that the modulus change $G'_0 - G'_\infty$, which occurs when the rubber is strained, remains approximately constant for a particular loading of black, irrespective of the degree of cure, even though G'_∞ varies three- or fourfold. If G'_∞ reflected the degree of crosslinking and G'_0 was only a multiplicative function of the modulus of the matrix (and therefore of G'_∞), $G'_0 - G'_\infty$ would increase in the same ratio as the G'_∞ values increase with the degree of crosslinking, but this is not the case, and therefore $G'_0 - G'_\infty$ must essentially be additive to G'_∞ which alone reflects the crosslink density changes. The mechanism responsible for the modulus change with strain work of oscillation must therefore be substantially independent of the curative level of the rubber matrix.

In a separate experiment, an attempt was made to obtain $G'_0 - G'_\infty$ for a completely unvulcanized filled rubber. This led to some experimental difficulty because of porosity in the unvulcanized sample; therefore the samples were prepared by careful milling and degassing, warmed gently to 75°C, and then left for about 150 min at this temperature in the mold. Samples which did not have the correct specific gravity or shape of end-pieces were rejected. Figure 3 shows the variation of the in-phase shear modulus with strain work for a normal tire tread NR vulcanizate vulcanized with 2.5 phr sulfur and containing 45 phr HAF black. The $G'_0 - G'_\infty$ values were 7.2×10^6 dynes/cm² and 6.8×10^6 dynes/cm² for vulcanized

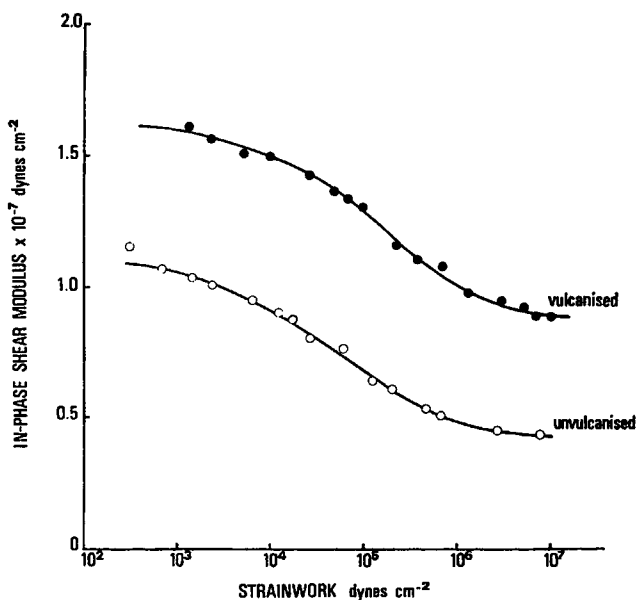


Fig. 3. Variation of in-phase shear modulus G' with strain work of oscillation for typical NR tire tread compound vulcanized and unvulcanized.

and unvulcanized samples, respectively, a small change in value with crosslinking, whereas G'_{∞} varied from 8.8×10^6 to 4.2×10^6 dynes/cm², respectively, a twofold change.

Phase Angle

Figure 4 shows the variation of the tangent of the phase angle ($\tan \delta$) with strain work for the gum and 50 phr mixes, and Figure 5, for the 30 and 70 phr filled mixes. The curves for the filled vulcanizates appear similar in shape, and peak values occur at similar strain work values for all the vulcanizates. Increasing crosslinking progressively reduces the general level of phase angle at a particular strain work. In order to compare the phase angle graphs, the $\tan \delta$ values were subtracted from the value at the peak ($\tan \delta_{\max}$) so that

$$\Delta \tan \delta = \tan \delta - \tan \delta_{\max}. \quad (3)$$

$\Delta \tan \delta$ is plotted against strain work for the 70 phr filled vulcanizates in Figure 6. This shows more clearly that the degree of crosslinking does not alter the value of strain work at which the peaks coincide, although the $\tan \delta_{\max}$ values decrease with increasing crosslinking. The curves in the positive-slope portion of the graph show a small effect due to crosslinking, while at high strainworks, the lightly crosslinked rubber (mix 1) shows smaller $\Delta \tan \delta$ values than the high crosslinked mixes.

The phase angle-strain work curve for the highest crosslinked rubber (mix 4) is probably solely attributable to the breakdown of the carbon

black aggregates, while the curve for the lightly crosslinked mix also reflects some additional losses at high strain work due to amplitude effects in the rubber matrix, thereby giving slightly higher $\tan \delta$ values than expected from carbon black-carbon black effects alone. This is to some extent also shown in Figure 1 by the slight dependence of the in-phase modulus of the gum rubber on strain amplitude.

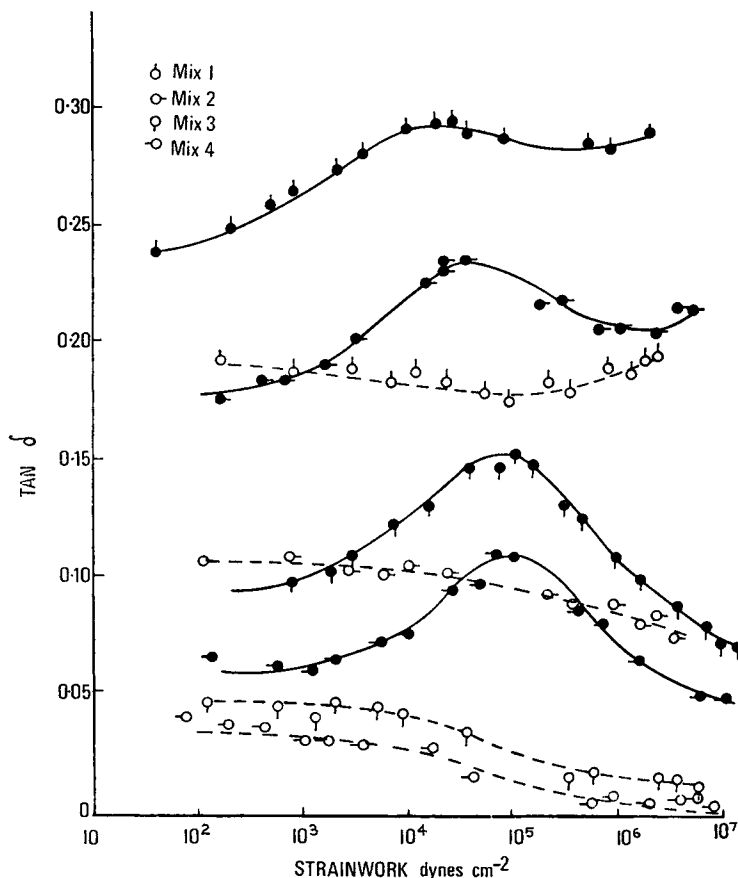


Fig. 4. Variation of the tangent of the phase angle with the strain work of oscillation. Open circles, gum vulcanizates; filled circles, vulcanizates filled with 50 phr ISAF black.

A number of investigators¹²⁻¹⁴ have shown that finite values of $\tan \delta$ in the rubbery elastic plateau region of viscoelastic behavior firstly are due to the slippage of entanglements of the long polymer chains, and secondly the losses are associated with the motion of strands with free ends. It would be expected therefore that an increase in the degree of crosslinking would decrease the effect of the entanglements and hence decrease the values of $\tan \delta$, as shown in Figures 4 and 5.

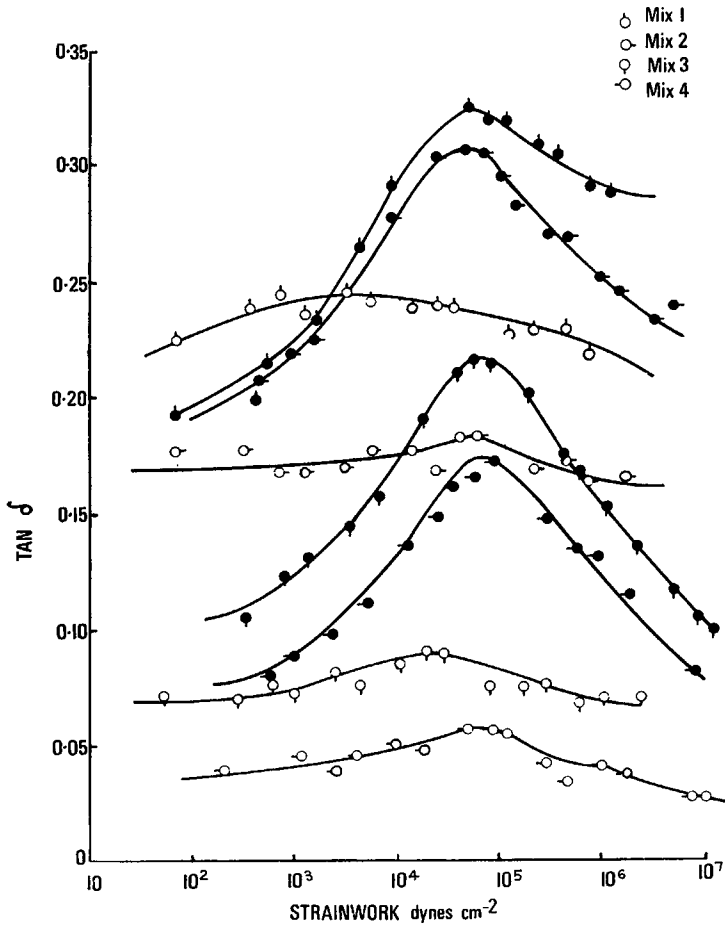


Fig. 5. Variation of the tangent of the phase angle with strain work of oscillation. Open circles, vulcanizates filled with 30 phr ISAF black; closed circles, vulcanizates filled with 70 phr ISAF black.

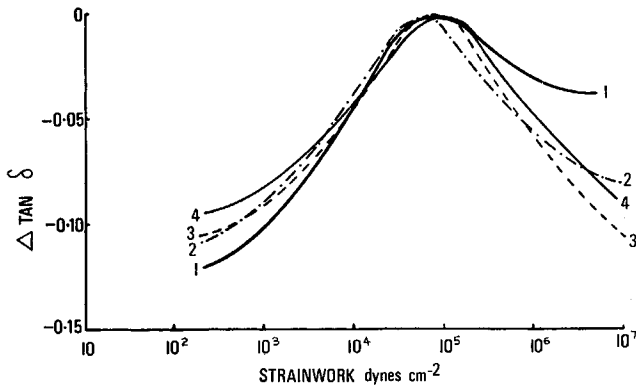


Fig. 6. Variation of $\Delta \text{tan } \delta$, defined in eq. (3), with strain work of oscillation for vulcanizates filled with 70 phr ISAF black.

Out-Of-Phase Shear Modulus

Figure 7 shows the variation of the out-of-phase shear modulus G'' with strain work of oscillation for the gum and 50 phr filled vulcanizates, and Figure 8, for the 30 phr and 70 phr filled vulcanizates. At low strain work, G'' appears to decrease systematically with increasing crosslink density, while at intermediate strain work, the 50 and 70 phr data show small G'' difference due to crosslink levels. The results in the negative slope portion of the curve are, however, remarkably similar.

In general, the out-of-phase modulus appears to change with strain in a similar manner to the phase angle graphs shown in Figures 4 and 5.

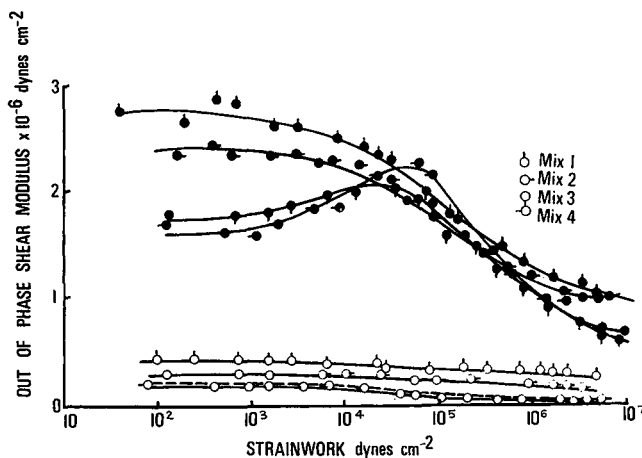


Fig. 7. Variation of out-of-phase shear modulus G'' with strain work of oscillation. Open circles, gum vulcanizates; filled circles, vulcanizates filled with 50 phr ISAF black. Points not shown for mix 3 gum vulcanizate.

NORMALIZATION OF IN-PHASE MODULUS

The in-phase component of shear modulus G' is associated with energy storage, while the out-of-phase component of shear modulus G'' is associated with energy dissipation. If the difference between G'_0 and G'_∞ values for a carbon black-filled vulcanizate are due to the breakdown of aggregates of carbon black, as has been suggested previously, $G'_0 - G'_\infty$ is then a measure of the total energy storage potential of the carbon black structure in the filled vulcanizate. The function $G' - G'_\infty$ therefore represents the energy storage capacity of the carbon black structure remaining after the vulcanizate has been strained sinusoidally to an amplitude corresponding to the particular value of G' .

The normalized modulus Z , defined by

$$Z = \frac{G' - G'_\infty}{G'_0 - G'_\infty} \quad (4)$$

therefore represents the fraction of the total of energy storage capacity remaining after straining at each particular amplitude. The variation of this parameter with the logarithm of strain work has been found in earlier work¹⁻⁹ to follow a Gaussian curve. This relationship was also found for

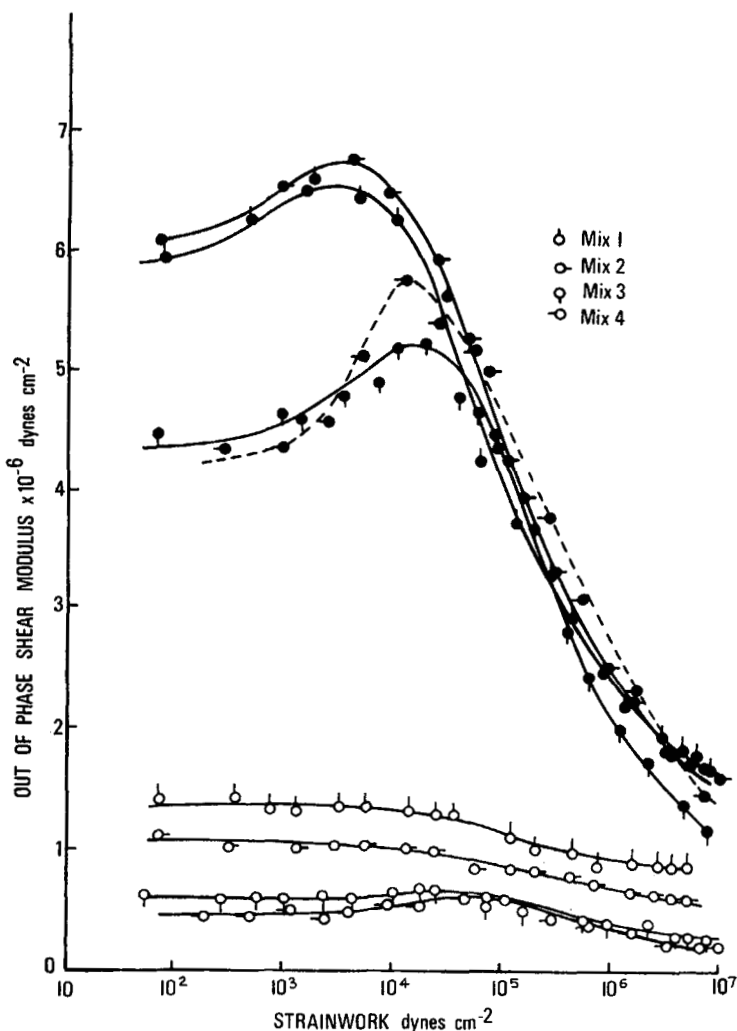


Fig. 8. Variation of out-of-phase shear modulus G'' with strain work of oscillation. Open circles, vulcanizates filled with 30 phr ISAF black; filled circles, vulcanizates filled with 70 phr ISAF black.

the vulcanizates used in this investigation, as shown in Figure 9, where normalized modulus is plotted on probability paper against the logarithm strainwork for vulcanizates filled with 70 phr ISAF carbon black. The linear relationships obtained indicate that the modulus decreases sig-

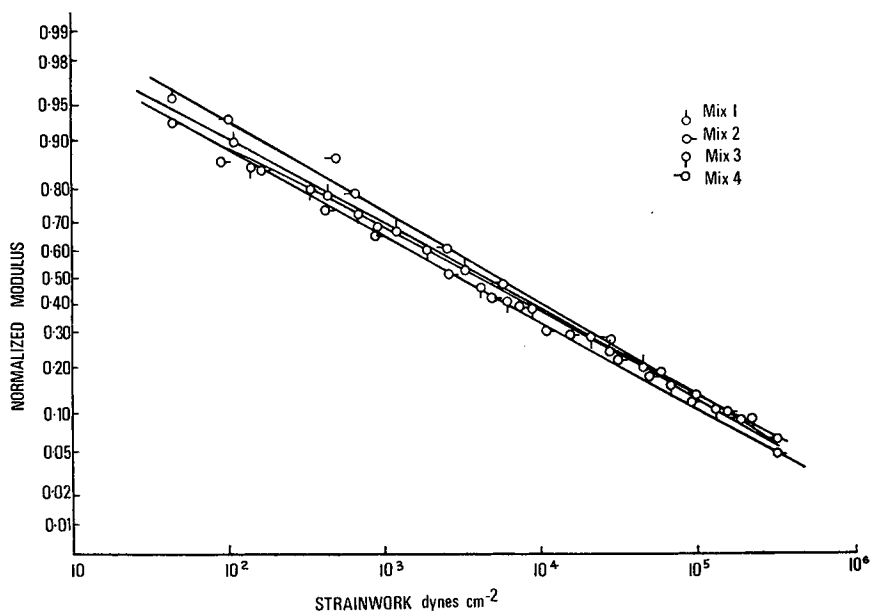


Fig. 9. Variation of normalized modulus with strain work of oscillation on probability paper for vulcanizates filled with 70 phr ISAF black.

modally with strain work of oscillation and hence implies a Gaussian curve relationship of the following type¹⁻⁹:

$$Z = 1 - \frac{1}{\sigma\sqrt{2\pi}} \int_{\infty}^x \exp \frac{(x - \mu)^2}{2\sigma^2} dx \quad (5)$$

where $x = \log X$, X being the strain work, and $\mu = \log_{10} X_{0.50}$, where $X_{0.50}$ is the value of strain work at $Z = 0.50$. It can also be shown that

$$\sigma = \frac{X_{0.10} - X_{0.90}}{2.56} \quad (6)$$

where $X_{0.10} - X_{0.90}$ is referred to as the width of the distribution and is the difference between values of the logarithms of the strain work corresponding to $Z = 0.10$ and $Z = 0.90$.

This type of Gaussian distribution is frequently encountered in materials science,¹⁵ although quite often a theoretical explanation is not clear or even available. A simple model, to interpret the relationship shown in Figure 9, is to assume the energy storage carbon black structure as composed of storage elements which are similar except that they are destroyed at different levels of strain work. The total storage capacity of the structure, $G'_0 - G'_\infty$, is then proportional to the initial number of these elements and $G' - G'_\infty$ is the number remaining at the appropriate value of strainwork. Figure 9 therefore represents a number-energy distribution of these storage elements.

The important feature noticed with the results shown in Figure 9 is the little effect that changing the degree of crosslinking has on the position and slope of the normalized graphs. It would appear therefore that the decrease in modulus is due to the properties of the carbon black alone and is little affected by crosslink density changes. The model discussed above of energy storage elements is therefore appropriate.

ANALYSIS OF G'_∞

Introduction

As shown in Figures 1 and 2, the value of G'_0 for the 70 phr ISAF-filled vulcanizates is approximately 15 times larger than the shear modulus of the unfilled rubbers. Although the modulus of the filled rubber decreases markedly with an increase in strain amplitude, it is still much higher than the unfilled rubber at the lower limit of modulus, G'_∞ , at high strain work.

Some of this difference is undoubtedly due to hydrodynamic effects of the filler particles embedded in a viscous medium. A number of other contributions to the modulus of filled rubbers have also been suggested, and this section of the paper discusses some of these various factors.

One interesting feature noticed with the results shown in Table I is that the ratio of G'_∞ of the filled rubber to the modulus of the unfilled rubber increases with increasing crosslink density at the same carbon black content for mixes 2, 3, and 4. Mix 1 appears to have enhanced amplitude-dependent properties in the gum rubber, and a satisfactory value for modulus of the unfilled rubber was not obtained.

Hydrodynamic Equations

The study of colloidal suspensions and emulsions by hydrodynamic analysis, the results of which were later applied to filler particles in rubber, was initiated by Einstein^{16,17} in 1906. For rigid spheres suspended in a liquid at concentrations sufficiently small for interactions between the particles to be neglected, he obtained the equation

$$\eta = \eta_0(1 + 2.5c) \quad (7)$$

where η and η_0 are the viscosities of the suspension and liquid, respectively, and c is the volume fraction of the particles.

Smallwood¹⁸ in 1944 used an approach essentially similar to that of Einstein to explain the reinforcement of rubber by a filler particle. He obtained the relationship

$$G'_r = G'_g(1 + 2.5c) \quad (8)$$

where G'_r was the modulus of the filled rubber and G'_g was that of the rubber matrix. The equation had certain limitations; the assumptions on which it was founded were (a) the filler particles were spherical, (b) complete adhesion existed between rubber and filler, (c) elongation was small,

(d) the filler particles were completely dispersed, (e) volume loading was small, and (f) the filler particles were sufficiently large that the molecular structure of the rubber could be neglected.

In an attempt to extend the Smallwood equation, eq. (8), to take account of higher loadings of filler, Guth and Gold^{19,20} added a term involving the square of the concentration of the filler. By considering the hydrodynamic interaction between pairs of particles, they obtained the relationship

$$G'_f = G'_g (1 + 2.5c + 14.1c^2). \quad (9)$$

A number of other hydrodynamic equations have been suggested, and these have been extensively reviewed by Rutgers.^{21,22} Other more important equations with regard to rubber reinforcement include the empirical formula suggested by Eilers²³:

$$G'_f/G'_g = \left(1 + \frac{1.25c}{1 - 2.8c}\right)^2, \quad (10)$$

a similar type of equation due to Brinkman,²⁴

$$G'_f/G'_g = \frac{1}{(1 - c)^{3/2}}, \quad (11)$$

and an equation due to Kerner,²⁵

$$G'_f/G'_g = \frac{1 + 2.5c}{1 - c}. \quad (12)$$

Van der Poel,²⁶ when studying bitumen-mineral aggregates, obtained a much more complicated yet more exact equation than any of the above theoretical equations at higher concentrations of filler by determining directly the rigidity of a concentration of elastic spheres in an elastic medium. For the typical moduli obtained in rubber-filler composites, the values of the ratio of moduli of the filler rubber to the unfilled are shown in Table II.

The variation of the six equations discussed above with volume concentration of filler is shown in Figure 10. Experimental values of the ratio $G'_{\infty f}/G'_{\infty g}$ from Table I are also shown in Figure 10. None of the equa-

TABLE II
Ratio of Moduli of Filled and Unfilled Rubbers (after Van der Poel²⁶)

Concentration c	G'_f/G'_g
0.10	1.3
0.20	1.7
0.30	2.5
0.40	4.1
0.50	8.1
0.60	21.4
0.65	42.5
0.70	78.7

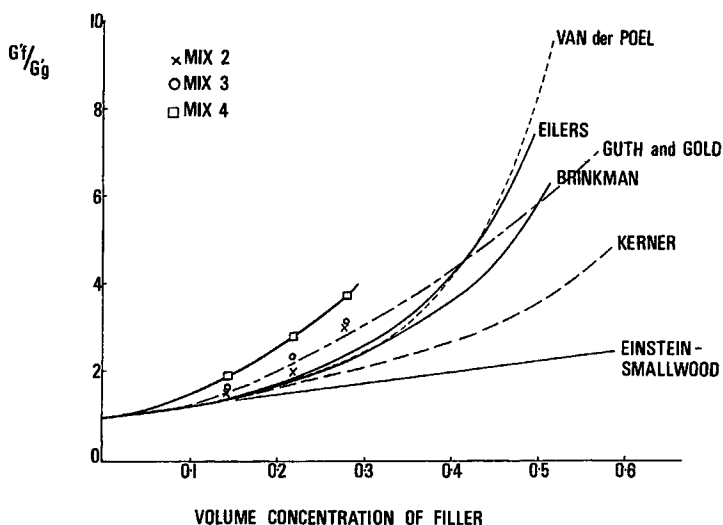


Fig. 10. Comparison of experimental values of $G'_{\infty}f/G'_{\infty}g$ from Table I with the various theoretical hydrodynamic equations.

tions appears to satisfactorily describe the results, the best equation, however, being the Guth and Gold equation. This equation has been found in other investigations to fit tensile results²⁷⁻³⁰ at high strains, provided that the data are expressed independently of time or temperature.

An earlier investigation³¹ showed that Eilers, Van der Poel, and Guth and Gold's equations predicted reasonably satisfactory results from glass spheres in natural rubber up to volume concentrations of 0.25, but at higher concentrations none of the equations predicted the results satisfactorily. In rubber containing glass beads, the main contribution to modulus enhancement would be hydrodynamic effects only, and hence it must be concluded that although hydrodynamic effects cause the major part of the increase in modulus at high strains of a carbon black-filled rubber, above that of the unfilled rubber, it does not completely account for the whole increase in modulus.

Other factors which are likely to be involved are discussed in the next three sections.

Shape Factor Effects

A number of early investigators using electron microscopy^{32,33} and other methods suggested that carbon black did not exist as single spherical particles but fused into a chain-like structure. This chain-like structure can be considered as a rodlet. Recent studies³⁴⁻³⁶ on electron microscopes having much better resolution than the instruments used by the earlier investigators have confirmed that this type of structure is evident.

A number of hydrodynamic equations have been suggested which include "shape factor" terms, the shape factor being defined as the length-to-

breadth ratio of the rodlet. The most well-known and used equation in rubber reinforcement studies is due to Guth³⁷ and is given as

$$G'_f = G'_g (1 + 0.67fc + 1.62f^2c^2) \quad (13)$$

where f is the shape factor.

Cohan³⁸ found that up to about 25% volume concentration, eq. (13) could be shown to apply to chain-like carbon particles within normal testing accuracy if the value of f was taken as the ratio of chain length to the average diameter of the ellipsoid units composing the chain.

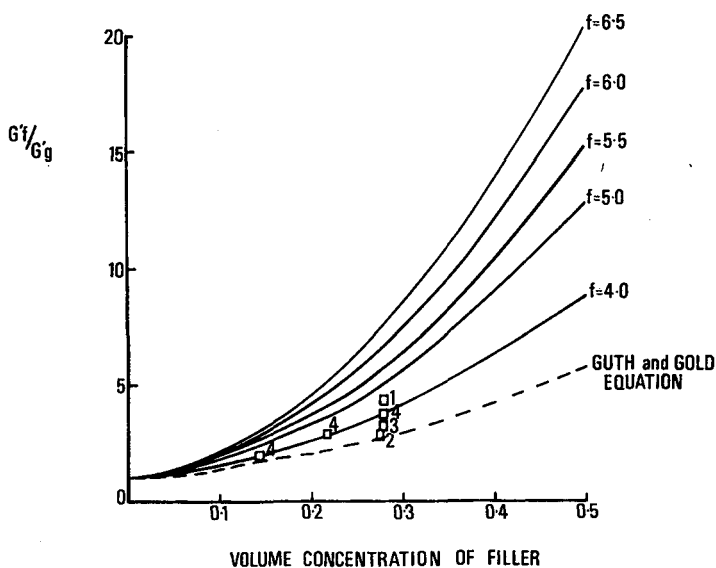


Fig. 11. Variation of G'_f/G'_g with volume concentration of filler calculated for different values of shape factor f from the Guth shape factor equation, eq. (13). Experimental values of $G'_{\infty f}/G'_{\infty g}$ from Table I are also shown.

Figure 11 shows the theoretical values of G'_f/G'_g derived from eq. (13). Also plotted are some of the experimental values of $G'_{\infty f}/G'_{\infty g}$ from Table I. It is shown that the curve $f = 4.0$ reasonably fits the data. The line from eq. (9) is also plotted on the figure.

By determining equivalent ellipsoids for carbon black chains from electron microscopy photographs, Dannenberg et al.³⁹ have recently shown that the shape factor taken as the ratio of the lengths of the major and minor axes of an ellipse for ISAF black of the type used in this investigation is about 1.8.

The value of $f = 4$ given by the Guth equation would appear therefore to be too large, and hence it must be concluded that although shape factor effects probably contribute to the modulus of filled rubbers, the addition of hydrodynamic and shape factor effects still does not account for the total increase in modulus of filled rubbers above that of the unfilled rubbers.

Effect of Carbon Black on Viscoelastic Properties

It is well known that the viscoelastic properties of filled rubbers depend upon the amount and type of carbon black, and many investigations have been undertaken into this phenomenon.

The hydrodynamic equations discussed in the two previous sections consider only the case where the matrix is either a Newtonian liquid or a Hookean solid. None considers that the matrix is in fact a viscoelastic material and that the presence of hard particles will give rise to "additional" relaxation and retardation times because of the shear rate gradients from the surface of the black which is not sheared to the maximum shear conditions, as in the rubber matrix removed from the filler surface. As the relaxation or retardation response of most rubbers covers such a wide range of relaxation or retardation times, it is to be expected that the measured response must reflect the perturbed relaxation behavior of the rubber matrix.

A number of investigations by swelling,⁴⁰ electron microscopy,⁴⁰⁻⁴² glass transition temperature,⁴² modulus,⁴³ and tensile measurements^{27-30,44} have indicated that there exists a shell of immobilized rubber around carbon black particles in a filled rubber vulcanizate.

Some workers^{45,46} have identified this immobilized rubber with "bound rubber" measured by solvent extraction, whereas others^{47,48} have recently suggested that some immobilized rubber is occluded within the carbon black aggregates.

This immobilized rubber will, however, cause a perturbed relaxation response of the rubber matrix, as discussed quantitatively by Radok and Tai,⁴⁹ and could account to some extent for the reinforcing effect of carbon black. This mechanism therefore could contribute to the increase in G'_{∞} when carbon black is added. The change in ratio of the modulus of the filled rubber to the unfilled rubber with degree of crosslinking shown in Figure 10 and Table I indicates that viscoelastic effects are evident. Valentine et al.⁵⁰ have shown that the relaxation spectrum of polybutadiene vulcanized with both sulfur and dicumyl peroxide changes remarkably with an increase in the degree of crosslinking. Mancke and Ferry⁵¹ have also shown that the storage compliance-time curve for styrene-butadiene copolymer is also dependent on the degree of crosslinking.

Harwood et al.²⁷⁻³⁰ have recently shown that if tensile failure data on filled and unfilled rubber are expressed independently of time or temperature by using bulk energy or hysteresis as the parameters, the results from the gum and filled rubbers can be unified by use of a correction factor predicted by the Guth and Gold equation, eq. (9). If however the failure data were expressed using time or temperature as one of the parameters, then the correction required was far larger than predicted by any of the hydrodynamic equations, hence reflecting the perturbed relaxation response of the rubber matrix.

An immobilized layer of rubber can therefore affect the relaxation response of a rubber vulcanizate. This could therefore be a major reason for

the large difference between the filled and unfilled dynamic modulus G'_{∞} values.

Other Contributions

Some investigators^{52,53} have suggested that strong linkages occur between the filler particles and the rubber. This could contribute to the increased modulus of filled rubber vulcanizates, but this is thought unlikely as the majority of the hydrodynamic equations discussed above are based on the assumption that there is complete wetting of the filler particles by the rubber. The existence of strong linkages connecting filler particles to the rubber matrix would therefore contribute little to the increased modulus of the filled rubber above that accounted for by the hydrodynamic equations.

Porter⁵⁴ has suggested that an increase in the level of vulcanization can occur in the rubber phase of a filled rubber which arises from the modification to the nature of the cure due to the presence of the carbon black, e.g., the acidic surface of the carbon black may accelerate or retard the rate of curing. This phenomenon only occurs in polysulfide-crosslinked natural rubber vulcanizates. Dynamic test results⁵⁵ on an efficiently vulcanized rubber at degrees of crosslinking similar to those used in this investigation showed that the maximum difference in $G'_{\infty f}/G'_{\infty g}$ between the efficiently vulcanized and the polysulfide mixes was only 5%. Hence it can be concluded that this mechanism would only produce a small contribution to the modulus of the filled vulcanizate.

FACTORS AFFECTING HEAT BUILD-UP IN TIRES

One of the practical consequences of the decrease of in-phase shear modulus of carbon black-filled rubbers with strain amplitude is increased heat build-up. In tires, for example, energy absorption during running causes a rise in temperature. The amount of heat generated will depend on the physical circumstances; in large lorry tires, for example, the heat build-up can cause ply separation and ultimate failure of the tire.

Kainradl et al.⁵⁶ have recently quantitatively analyzed the problem of heat build-up in tires. Some difficulty arises because the amount of heat generated, ΔT , is dependent on the mode of deformation, and this is different in each part of the tire. It is firstly necessary therefore to consider the heat generated under different deformations: (a) at constant deformation, the heat rise ΔT is proportional to G''/λ ; (b) at constant alternating force, ΔT is proportional to

$$\frac{G''}{\lambda/G^*/2} \cong \frac{G''}{\lambda G'^2}; \quad (14)$$

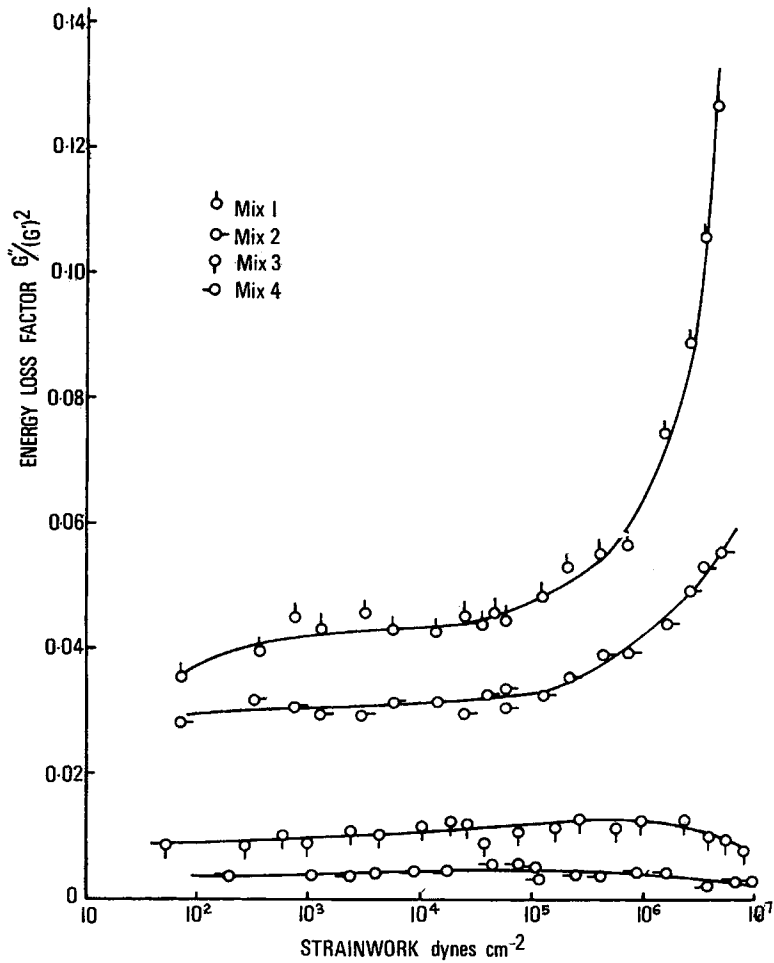


Fig. 12. Variation of energy loss factor $G''/(G')^2$ with strain work of oscillation for vulcanizates filled with 30 phr ISAF black.

(c) at constant elastic deformation energy, ΔT is proportional to

$$\frac{G''}{\lambda G^*} \cong \frac{G''}{\lambda G'} \quad (15)$$

where λ is the thermal conductivity.

Kainradl et al.⁵⁶ have shown that in the shoulder of a lorry tire

$$\Delta T = \frac{C_1 G''_L}{\lambda_L} + \frac{C_2 G''_L}{G'^2_L \lambda l} + \frac{C_3 G''_K}{\lambda k} + \frac{C_4 G''_K}{G'^2_K \lambda k} + C_5 \quad (16)$$

tread topping compound chord

where the indices L and K refer to either tread or carcass of the tire and C_1 to C_5 are constants involving dimensions.

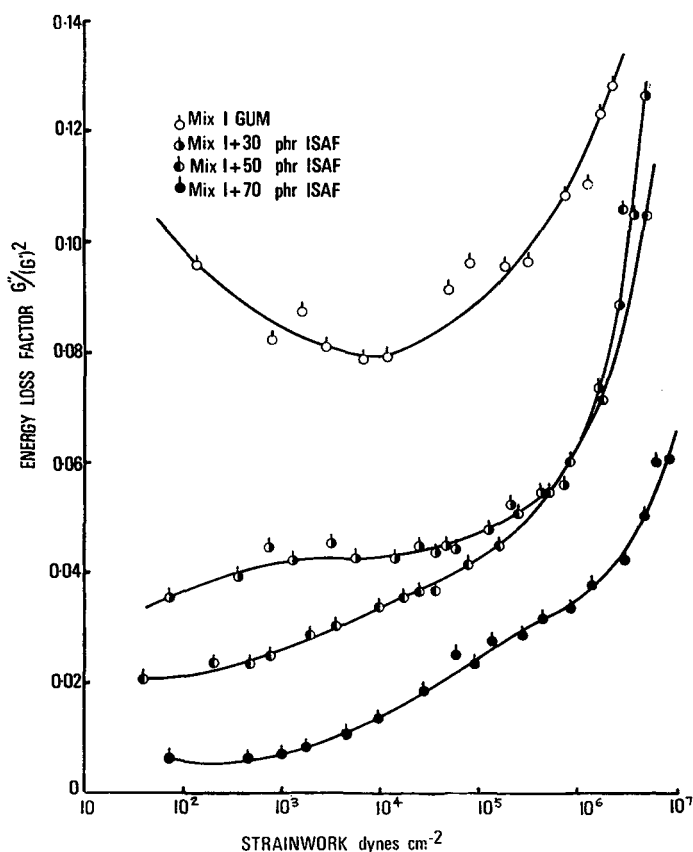


Fig. 13. Variation of energy loss factor $G''/(G')^2$ with strain work of oscillation for mix 1 vulcanizates containing various concentrations of carbon black.

The important viscoelastic parameters, therefore, that contribute to heat build-up in a tire are: (a) G'' , the out-of-phase shear modulus, and (b) G''/G'^2 or $\tan \delta/G'$.

It has already been shown that G'' is very dependent on the amount of carbon black but is not very dependent on the degree of crosslinking. Values of $\tan \delta$, however, are dependent both on carbon black content and degree of crosslinking. Figure 12 compares $\tan \delta/G'$ data for different crosslink densities for vulcanizates containing 30 phr ISAF black, and Figure 13, for mix 1 filled with increasing amounts of ISAF black. The function is plotted against energy or strain work of oscillation, as the earlier sections have shown that all the dynamic parameters are dependent on this quantity. It is seen that the function $\tan \delta/G'$ is dependent on both carbon black loading and crosslink density in a rather complex manner. The complexity obviously arises from the various changes brought about by crosslinking on both modulus and hysteresis properties, as discussed in the earlier sections. Typical results have been presented in this section because of the im-

portance of the function of $\tan \delta/G'$ in governing the heat-build-up properties generally.

Kainradl et al.⁵⁶ have shown that the heat build-up in the shoulder of a lorry tire is correctly predicted when the dynamic parameters obtained at 10% precompression with a plus-and-minus oscillation of 8% strain at 120°C are substituted in eq. (16). Although the measurements presented in this section have been obtained under different conditions of test, it must be concluded that in order to predict the heat build up in tires, a thorough knowledge of how the dynamic parameters vary with filler loading, crosslinking, and strain work of oscillation is essential.

CONCLUSIONS

An increase in the degree of crosslinking of an unfilled rubber increases the in-phase modulus and decreases values of $\tan \delta$, as shown by the early sections of this chapter. The most interesting feature, however, of the in-phase shear modulus curve is that values of $G'_0 - G'_\infty$ appear to be similar for a particular loading of carbon black irrespective of the degree of vulcanization of the rubber. This was confirmed by the small difference found between modulus values of the unvulcanized and vulcanized tire tread rubber shown in Figure 3 and the similarity of the normalized modulus-strain work graphs shown in Figure 9.

The results in this paper therefore confirm the hypothesis that the decrease of the in-phase shear modulus with strain amplitude is due to the breakdown of carbon black aggregates in the filled vulcanizate and is little affected by changes that take place in the rubber phase of the filled vulcanizates.

When the carbon black structure has been completely broken down at high strain work, the modulus of the filled vulcanizate is still higher than that of the corresponding gum rubber. This difference has been considered in detail in this paper, and the more likely factors that contribute to the difference appear to be hydrodynamic, shape factor, and relaxation effects.

The apparent breakdown of the carbon black structure at low strains causes a number of practical consequences. One particular feature is the complex manner in which the breakdown of structure affects the heat rise in a tire on running, as discussed in the last section.

A recent paper⁵⁷ has shown that a general domain theory of hysteresis can be applied to the low-strain dynamic behavior of carbon black-filled rubber vulcanizates. This would suggest that the secondary carbon black aggregated structure breaks down on stressing and reforms when the stress is removed. The results presented in the paper support this conclusion. The breakdown of a three-dimensional aggregated structure has now been observed in a number of other composite systems such as clay in both rubber⁸ and water,⁹ carbon black in oil,⁷ and crystal structures in rubber.⁵⁸

Appendix

Mix no.	Compounding details			
	1	2	3	4
RSS (SMR 5) phr	100	100	100	100
Zinc oxide phr	5	5	5	5
Lauric acid phr	1	1	1	1
CBS phr	0.048	0.18	0.40	1.00
Sulfur phr	0.20	0.75	1.65	4.17

Mixes 1 to 4 also vulcanized with 30, 50, and 70 phr ISAF black. All cured for 40 min at 140°C.

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