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A Note on the Conductivity and Modulus of Carbon Black-Loaded Rubbers

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Synopsis

Electrical conductivity and dynamic shear modulus measurements were made simultaneously on carbon black-filled natural rubbers. G', the in-phase shear modulus, and the electrical conductivity, C, were shown to vary in an approximately similar way as the amplitude of dynamic oscillation was increased. Both G' and C altered sigmoidally from a high value at low amplitudes of oscillation to very much reduced values at high amplitudes of oscillation. Recovery curves for conductivity were shown to be parallel with respect to the logarithm of the time (in minutes), even though the initial deforming amplitudes varied widely.

Recent studies[1-6] of the effect of the dynamic amplitude of oscillation on shear modulus of carbon black-loaded rubbers have shown that considerable changes in modulus occur at low strains, in the manner depicted in Figure 1. Bulgin and others[6] had shown, in an earlier study, that there is a correspondence between conductivity changes and modulus changes with the dynamic amplitude of oscillation. It is the purpose of this paper to pursue this study further, that is, to show how the conductivity does alter with the amplitude of oscillation, and to study the recovery of the conductive structure with the elapsed time after a previous large strain oscillation.

Experimental

Figure 2 is a schematic diagram of the jig used on the RAPRA dynamic testing machine to measure both the electrical conductivity and the dynamic shear modulus of carbon black filler-loaded rubbers. For the higher amplitudes of oscillation, the clamp from the driving center of the machine is attached to the center plate of the rubber sandwich. The outer plates of the rubber sandwich are bonded to insulating blocks of polyethylene. In order to impose very small strain oscillations on the rubber, the clamp is removed, so then the rubber is stressed by the springs only, the displacement of the rubber being measured by a displacement transducer. The

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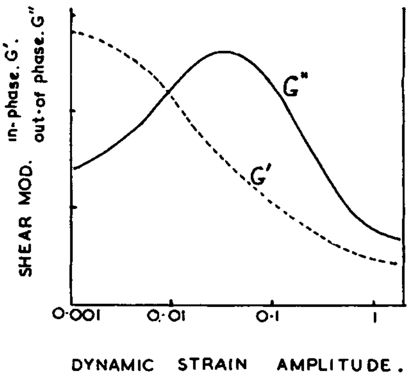

Fig. 1. Nature of the change of shear modulus G' and G'' with the amplitude of dynamic oscillation.

method of testing rubber over a wide strain amplitude range has been discussed in previous publications.[2–5]

Figure 3 is a schematic diagram of the electrical circuit which was adopted to measure the conductivity. The voltmeter was used to measure the voltage across a fixed known resistance in order to determine the current flow in the circuit. A constant voltage d.c. source was used to supply the potential to the circuit. Knowing the voltage across the rubber and the current in the circuit, the resistance or conductivity was determined.

Rubber stocks were mixed on a warm laboratory mill, and the formulation used is given in Table I.

TABLE I

	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5	Mix 6
RSS1	100	100	100	100	100	100
ZnO	4	4	4	4	4	4
CBS	1.24	1.24	1.24	1.24	1.24	1.24
Stearic acid	1	1	1	1	1	1
PBN		1	1	1	1	1
HAF black	50	60	70	80	90	100
Sulfur	3	3	3	3	3	3

From curometer traces of time to reach 90% crosslinks gave a cure time of 20 min. at 145°C. The rubber was cured in molds and bonded to brass plates during the curing process to form a shear sandwich type of test piece.

The sinusoidal strain tester has been described previously. It was convenient to apply a chosen stress by means of the springs and to record the displacements produced between 0.1 to 100 μ, and then to select the displacement and observe the force for displacements from 100 μ to 1.25 cm. The frequency of test was 0.1 cycles/sec.

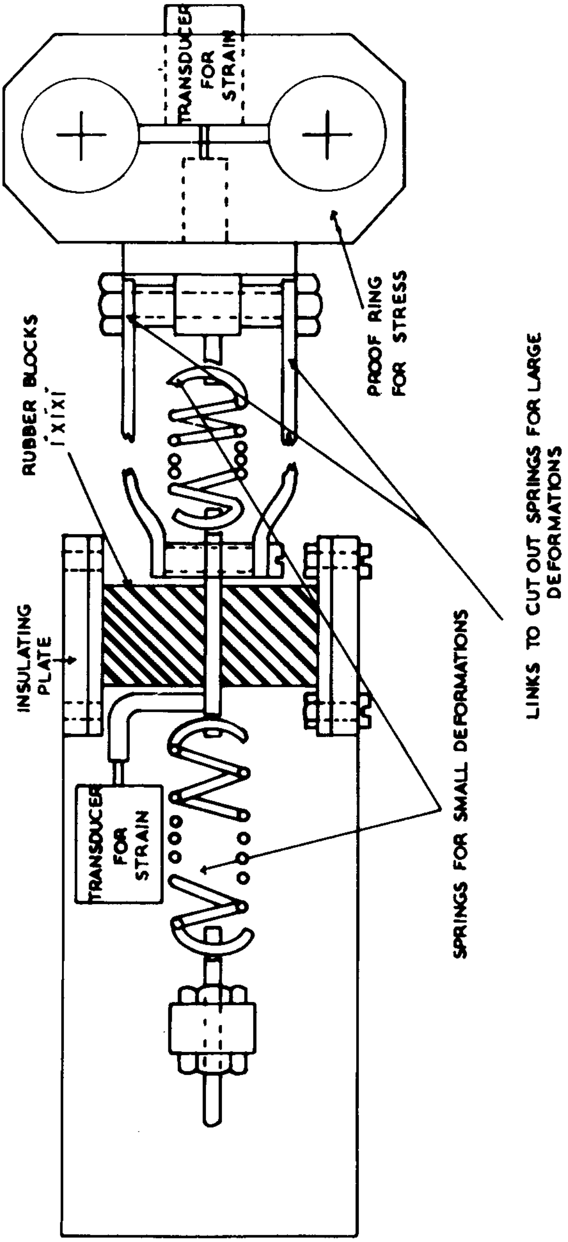

Fig. 2. Schematic drawing of the RAPRA dynamic stressing jig.

After setting up and resting overnight, the rubbers were tested first at the lowest strains and measurements continued to successively higher strains. The experimental measurements were of the maximum straining force, the amplitude of strain oscillation, and the phase angles. From these measurements, the components of the modulus in phase with the stress, G', and out of phase with the stress, G'', were readily calculated from the relationships

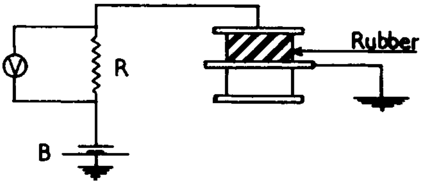

Fig. 3. Schematic diagram of the electrical circuit: (V) voltmeter; (R) fixed known resistance ≪ resistance of the rubber; (B) constant d.c. supply voltage.

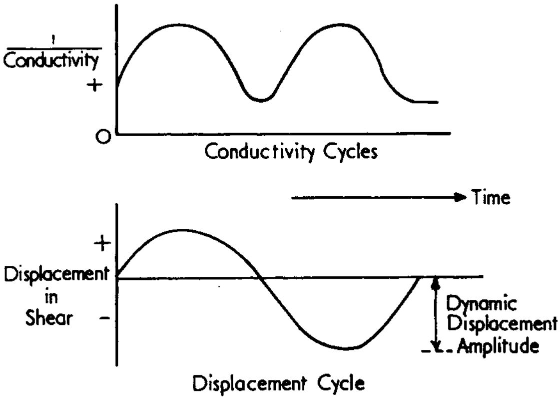

Fig. 4. Relationship between conductivity and displacement cycles.

$$\tan \delta = G''/G'$$

and

$$G^* = G' + iG''$$

where δ is the phase angle in degrees and G^* is the complex shear modulus.

The conductivity measurements were made simultaneously to the modulus measurements. As the experimental method involves straining the rubber sample in shear about the zero shear strain position, two cycles of conductivity changes were recorded for each dynamic strain cycle, (Fig. 4), so it was necessary to record the maximum and minimum conductivities observed. ΔC was noted as the difference between the maximum and minimum conductivities recorded.

Results

Figures 5–10 show both the dynamic results, G', G'', and tan δ, and the conductivity results, C_{max}, C_{min}, and ΔC plotted on each figure for a single concentration of carbon black.

Inspection of Figures 5–10 shows that C_{min} changes approximately in the same manner as the shear modulus G' with the amplitude of oscillation.

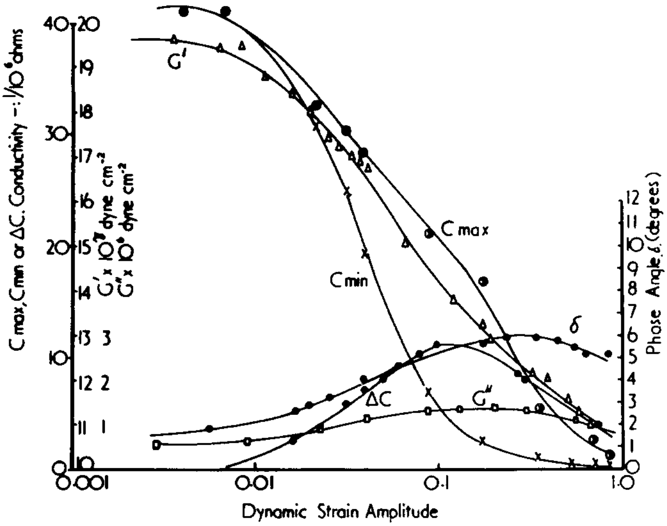

Fig. 5. G', G'', δ, and C_{min}, C_{max}, and ΔC vs. dynamic strain amplitude of test; 50 phr HAF black.

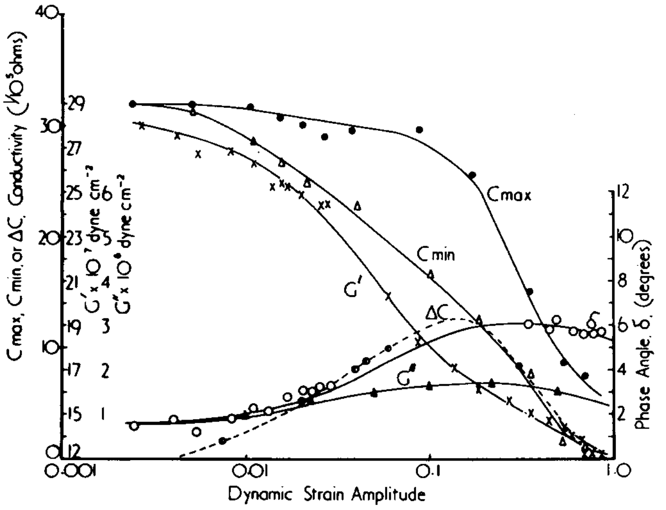

Fig. 6. G', G'', δ, and C_{min}, C_{max}, and ΔC vs. dynamic strain amplitude of test; 60 phr HAF black.

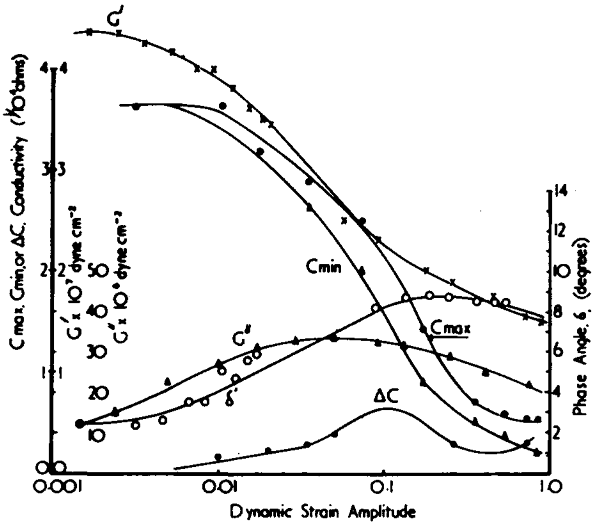

Fig. 7. G', G'', δ, and $C_{\min}$, $C_{\max}$, and ΔC vs. dynamic strain amplitude of test; 70 phr HAF black.

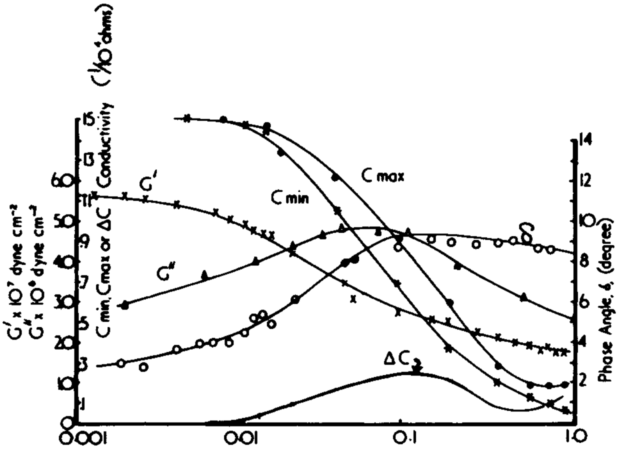

Fig. 8. G', G'', δ, and $C_{\min}$, $C_{\max}$, and ΔC vs. dynamic strain amplitude of test; 80 ph HAF black.

The change is not quite the same because the $C_{\min}$ curves for the higher concentrations of carbon blacks in Figures 8 and 9, show that the commencement of decrease in $C_{\min}$ occurs at higher strain amplitudes than does the commencement of decrease in G'. If the conductive mechanism between two particles of black is by a tunnel process,[7] this process may not be as sensitive as changes in shear modulus which according to the theory of van den Tempel[8,9] varies as the increase of the distance between the particle surfaces to the power 3.5. Apart from this observation, it is ap-

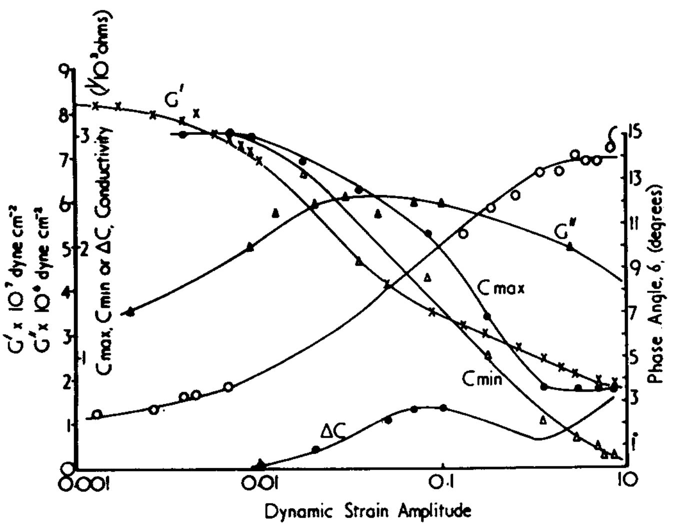

Fig. 9. G', G'', δ, and $C_{\min}$, $C_{\max}$, and ΔC vs. dynamic strain amplitude of test; 90 phr HAF black.

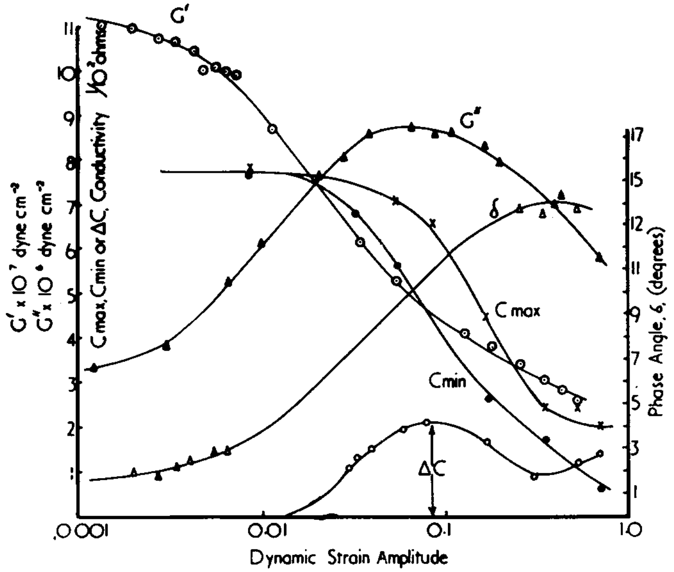

Fig. 10. G', G'', δ, and $C_{\min}$, $C_{\max}$, and ΔC vs. dynamic strain amplitude of test; 100 ph HAF black.

parent that conductivity and modulus alters in a roughly similar way when subjected to increasing dynamic strain.

The ΔC values show a maximum at approximately the same dynamic strain amplitude value as the maximum in G'', again stressing the similarity between modulus and conductivity changes. It is to be noticed that the

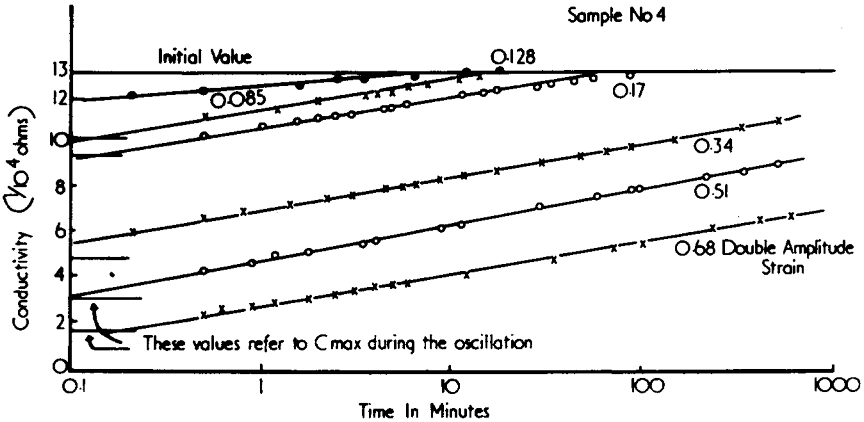

Fig. 11. Conductivity recovery curves. The figures noted on the curves refer to the dynamic strain amplitude of test to which the rubber has been subjected prior to recovery at zero shear strain.

out-of-phase component of the modulus, G'', increases to a maximum in the middle region of the strain range where the in-phase component is changing most rapidly. The interpretation of the G' change has been of a structure which remains substantially constant on repeated straining to the chosen amplitude. This simple picture does not provide the energy dissipation mechanism reflected in the increase in G''. To account for this it seems necessary to invoke the postulate that to some extent there is both structure reformation and breakdown during the strain cycle. At small amplitudes, little structure is breaking down and hence G'' is small even though reformation is probably most easy at the small separations of the black particles which occurs. At large amplitudes, the structure is largely broken down but so extensively that reformation of structure is very much slower than the cycle time and G'' is lower again. A maximum G'' is expected somewhere in the middle region where considerable structure breakdown occurs but reformation is rapid. These changes are obviously also reflected in the ΔC values. The relationship between G' and G'' has been discussed in previous publications.[1,5]

Figure 11 plots the conductivity at zero strain against the logarithm of the time (in minutes) after the oscillation has stopped. The strain amplitude of the dynamic test has been noted on the appropriate curve. The surprising feature of this plot is the fact that the recovery curves are parallel to each other, that is that the rate of recovery of conductivity is independent of the dynamic strain amplitude of oscillation. Within the accuracy of the measurements it is difficult to decide whether or not there is an asymptotic approach to the unstrained value of the conductivity, nevertheless it is certain that the time to reach the initial value is very dependent on the previous history of the rubber sample, i.e., it takes longer time to recover the larger the prestrain, these results suggest that the recovery process is controlled by the viscosity of the rubber stock. Hine and Whorlow[9] and others[10,11] have previously shown that a long time is necessary for complete recovery to take place after a sample has been highly strained, and they also demonstrated that the recovery time is considerably reduced by heating the rubber above ambient temperature conditions. It would be necessary to repeat these experiments over a temperature range in order to derive the energy of activation of flow, and this is a subject of a further proposed program of work.

Conclusions

The experimental results discussed above confirm that the conductivity alters in a similar fashion to the modulus changes in the rubber when it is subjected to an increasing dynamic strain amplitude. Bearing in mind that the conduction process is probably due to a tunnel effect, and that the modulus is probably controlled by the nature of the van der Waals forces of attraction between carbon black particles, it is not to be expected that the changes of conductivity and modulus are to be exactly similar in nature when the distance between the carbon black particles is increased when the rubber is strained, nevertheless it is clear that both physical measurements are dependent on the carbon black network, that is to say that a rubber compounded with a reinforcing carbon black possesses high conductivity and modulus when the carbon black network is intact, and possesses lower conductivity and modulus when the carbon black network has been broken down by a large amplitude mechanical oscillation.

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Résumé

On a mesuré simultanément la conductivité électrique et le module de cisaillement dynamique sur des caoutchoucs naturels chargés de noir de fumée. On a montré que G', le module de cisaillement dans la phase et C, la conductivité électrique varient à peu près de la même manière lorsqu'on augmente l'amplitude de l'oscillation dynamique. G' ainsi que C changent suivant une courbe sigmoïde depuis les valeurs élevées pour de faibles amplitudes d'oscillation jusqu'à des valeurs très faibles pour des amplitudes élevées. On a montré que les courbes correspondant au retour à la conductivité initiale étaient parallèles par rapport au logarithme du temps (en minutes) malgré la grande variation des valeurs des amplitudes de déformation initiales.

Zusammenfassung

An mit Russ gefülltem Kautschuk wurden gleichzeitig Messungen der elektrischen Leitfähigkeit und des dynamischen Schubmoduls angestellt. G', der Schubmodul in Phase, und die elektrische Leitfähigkeit C, ändern sich annähernd gleichartig bei Erhöhung der Amplitude der dynamischen Oszillation. Sowohl G' als auch C zeigen einen s-förmigen Übergang von hohen Werten bei niedriger Oszillationsamplitude zu sehr stark herabgesetzten Werten bei hohen Oszillationsamplituden. Die Erholungskurven der Leitfähigkeit sind in Bezug auf den Logarithmus der Zeit (in Minuten) parallel, sogar wenn die anfänglichen Deformationsamplituden stark schwanken.

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