Dynamic Properties of Natural Rubber Containing Heat-Treated Carbon Blacks

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Synopsis

The dynamic properties of a series of carbon black-filled natural rubber vulcanizates have been studied for their amplitude dependence.   The HAF blacks studied possessed low, normal, or high structure, and one series of the high structure blacks was subjected to heat treatment up to 2700°C.   The effect of heat treatment of the black was to increase the low amplitude dynamic shear modulus and hysteresis but to reduce the high strain tensile modulus.   These effects were studied with respect to the dispersion of the black.

INTRODUCTION

Recently there has been considerable technological activity which has led to the commercial development of several families of carbon blacks possessing low, normal, or high structure, as well as blacks with different types of surface material and activity.   It is intended, in this paper, to discuss the results of a study of the dynamic properties of natural rubber vulcanizates containing one of these families of blacks, as well as a range of blacks, of the same particle size and structure, which have been heat-treated to various high temperatures in order to change mainly the nature of the surface.   The carbon blacks included in this study were: (A) low structure HAF;   (B) normal structure HAF;   (C) high structure HAF; (D) high structure HAF, experimental type;   (E) high structure HAF, type D heat-treated at 850°C.;   (F) high structure HAF, type D heat-treated at 1050°C.;   (G) high structure HAF, type D heat-treated at 1800°C.; (H) high structure HAF, type D heat-treated at 2700°C.

These were incorporated in a natural rubber mixing in a concentration of 70 parts by weight per 100 parts of rubber.

The compounding formulation was natural rubber (RSS1), 100 parts; zinc oxide, 5 phr; stearic acid 2.5 phr; Dutrex R, 4.5; CBS, 0.6 phr; carbon black, 70 phr; sulfur, 2.5 phr; cure was for 40 min. at 141°C.

EXPERIMENTAL

The dynamic measurements were carried out at 0.1 cycles/sec. on a modified sinusoidal strain dynamic tester.[1-3]   All the dynamic tests were

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made in shear initially at the lowest stain amplitude possible and then with strains increasing incrementally to the maximum. This sequence ensured that the rubber had not been overstrained before a particular test, as the dynamic properties of filler-loaded vulcanizates are very sensitive to prior mechanical treatment. Details of the equipment and test methods have appeared in the literature.[1]

RESULTS

In-Phase Modulus Measurements

Figure 1 shows the dynamic shear modulus G' plotted against twice the strain amplitude of oscillation. All the curves show the typical sigmoidal shape. The modulus–amplitude curves of compounds A, B, C, and D,
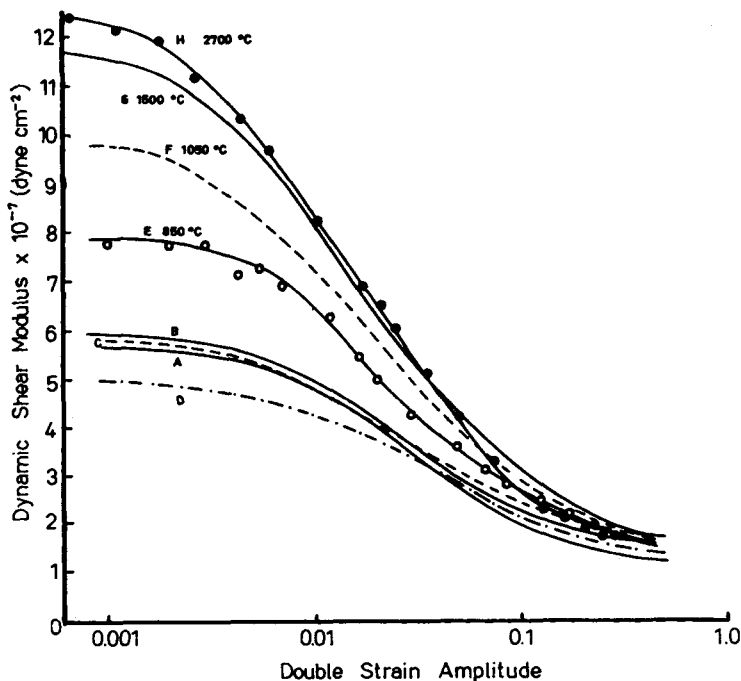

Fig. 1. Dynamic shear modulus vs. double strain amplitude. See introduction for details of vulcanizates.

those belonging to the blacks that have not been heat-treated, are very similar and show the smallest change with the amplitude of oscillation of all the compounds studied. On the other hand, increasing the temperature of heat treatment of the black (compounds E–H) increases the dynamic modulus at low amplitudes of oscillation.

Out-of-Phase Modulus Measurements

Figure 2 shows the out-of-phase shear modulus G'' plotted against twice the strain amplitude of oscillation.   The difference in behavior between the blacks is here quite evident, the heat-treated blacks (compounds E–H) possessing higher values of G'' than the other "normal" blacks; G'' increases with the temperature of the heat treatment.
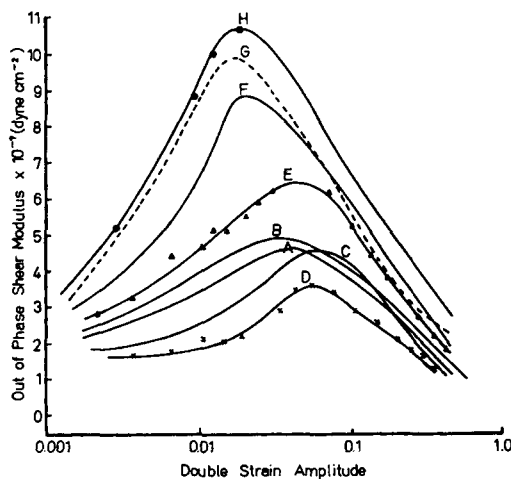

Fig. 2. Dynamic out-of-phase shear modulus vs. double strain amplitude.   See introduction for details of vulcanizates.

Phase Angle Measurements

Figure 3 shows the phase angle values.   The non-heat-treated blacks possess the lowest phase angle values, the normal and low structure blacks have intermediate values, whereas the increasing temperature of heat
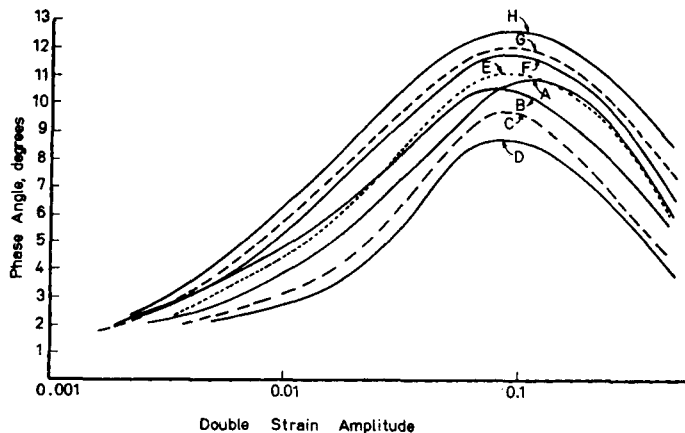

Fig. 3. Phase angle (degrees) vs. double strain amplitude.

treatment increases the phase angle values at all amplitudes of oscillation. All the compounds possess low phase angle values, 2°, at low strains, even though the vulcanizates contain 70 phr carbon black.

Normalization of the Modulus

It has been shown in previous papers[1-4] that a convenient method of comparing the modulus changes with the amplitude of oscillation is to "normalize" the data between the modulus limits at very high and very low strains. Consider the shear modulus G'; let G'_0 represent its values at strains approaching zero and G'_∞ its value at very high strains where there is no further change in G' with increase in strain amplitude. The normalized modulus is defined as[4]

$$Z = (G' - G'_\infty)/(G'_0 - G'_\infty)$$

and is shown in Figure 4 plotted on probability paper against the energy or strain work of oscillation. The G'_0 and G'_∞ values used in this normalization are given in Table I. It will be appreciated that there is some latitude in estimating a value for G'_∞, but the variation is too small to influence the position of the plot on probability paper.
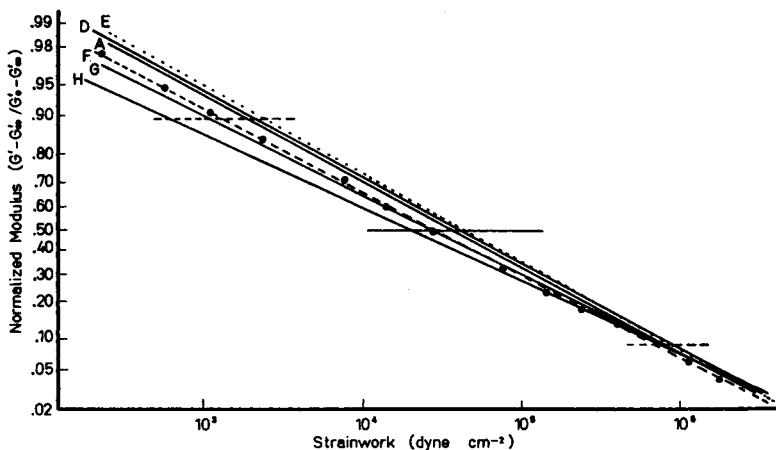

Fig. 4. Normalized modulus $(G' - G'_\infty)/G'_0 - G'_\infty)$ vs. strain work (double stress amplitude × double strain amplitude).

It has been shown in previous papers[1-4] that neither stress nor strain is the independent parameter which governs the variation of the dynamic modulus with strain but the product of double stress amplitude and double strain amplitude, which is referred to as strain work. It is useful to consider the strain work corresponding to $Z = 0.5$, and Table I gives these values for the different vulcanizates. It is apparent that the strain work decreases significantly for the blacks that have been subjected to high heat treatment (compounds F, G, and H). This parallels the change in strain

TABLE I
G'_0, G'_∞, $(G'_0 - G'_\infty)$, Strain Work, and Width Values

Mix desig-nation	Tempera-ture of heat treatment, °C.	$G'_0 \times$ 10^{-7}, dyne/cm.²	$G'_\infty \times$ 10^{-7}, dyne/cm.²	$(G'_0 - G'_\infty)$ $\times 10^{-7}$, dyne/cm.⁻²	Width, dyne/cm.²	Strain work $\times 10^{-4}$ at $Z = 0.5$
A	—	5.8	1.1	4.7	2.54	3.5
B	—	6.0	1.35	4.67	2.56	3.5
C	—	5.9	1.30	4.60	2.56	3.5
D	—	4.9	1.05	3.85	2.56	3.8
E	850	7.85	1.40	6.45	2.56	4.0
F	1050	9.87	1.35	8.52	2.82	2.4
G	1500	12.30	1.40	10.90	2.88	2.4
H	2700	12.60	1.28	11.32	3.09	1.9

work noted in another study of the effect of the degree of dispersion of the black[5] on the dynamic properties when the strain work at $Z = 0.5$ was shown to decrease when the microdispersion of the black was poorer.

The linearity of the plot on probability paper of the normalized modulus against the logarithm of the strain work implies a relationship of the following type:

$$Z = (G' - G'_\infty)/(G'_0 - G'_\infty)$$

$$= 1 - (1/\sqrt{2\pi}) \int_{-\infty}^{x} \exp\left\{-(x - \mu)^2/2\sigma^2\right\} dx$$

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

$$\sigma = (x_{0.10} - x_{0.90})/2.56$$

where $(x_{0.10} - x_{0.90})$, referred to below as the "width" of the distribution, is the difference between the values of the logarithms of the strain work values corresponding to $Z = 0.10$ and $Z = 0.90$, respectively. From Table I, it can be seen that the width increases significantly for the blacks subjected to high heat treatment. The increase in width can be associated with a worsening dispersion of the carbon black.[5]

Circular Arc Plots

The G'' results in Figure 2 show that G'' reaches a maximum at approximately the strain at the inflection point on the corresponding G'–amplitude curve in Figure 1. Figure 5 shows plots of G'' versus G', where the points for a particular vulcanizate are seen to lie on the arc of a circle in a manner reminiscent of the Cole-Cole plot for complex electrical permittivities.[3,4]

The smallest arcs belong to the normal high structure blacks (compounds C and D). The normal and low structure blacks possess intermediate arcs, whereas the arcs of the heat-treated blacks are larger than any of the
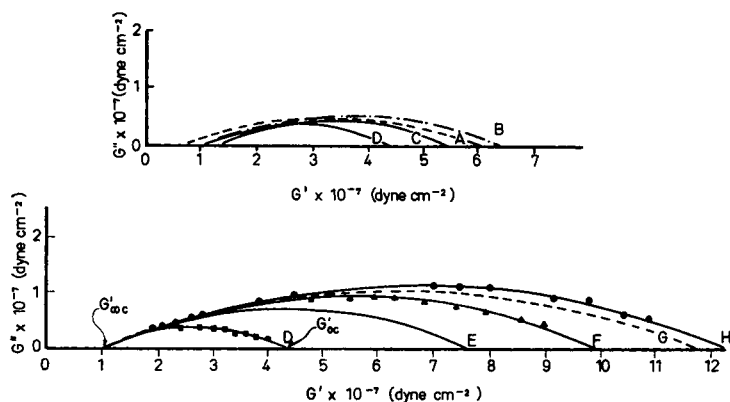
Fig. 5. Cole-Cole type plots of G'' vs. G'.

untreated blacks and also increase in size with the increase in the temperature of the heat treatment. The intercept of the arcs on the G' axis provide values of G'_{0c} and $G'_{\infty c}$ at low and high strains respectively, and these values are given in Table II together with the values of the maximum of G'', G_{max}'', indicated by the arcs.

TABLE II
Derived Data from Cole-Cole Type Plots of G'' Against G'

Mix designation	$G'_{0c} \times 10^{-7}$, dyne/cm.^{2}	$G'_{\infty c} \times 10^{-7}$, dyne/cm.^{2}	$G''_{max} \times 10^{-6}$, dyne/cm.$^{-2}$
A	6.0	0.80	4.8
B	6.3	1.15	4.9
C	5.3	1.20	4.7
D	4.3	1.10	3.7
E	7.5	1.10	6.4
F	9.9	1.10	8.8
G	11.5	1.10	10.0
H	12.1	1.10	10.7

The G'_{0c} and $G'_{\infty c}$ values quoted in Table II are similar to the values of G'_0 and G'_∞ quoted in Table I which were derived by the normalization procedure, although the G'_0 values are generally slightly higher than the G'_{0c} values obtained from the Cole-Cole type plots. Presumably, the difference exists because a finite G'' must exist for the pure gum phase of the vulcanizate alone, so the "true" G'_0 value must correspond to some finite value of G'', and not to the extrapolated value when G'' is zero. Of greater importance is the connection between G''_{max} and the $(G'_0 - G'_\infty)$ values (see Fig. 6). It can be seen that:

$$G''_{max} = 0.10 \, (G'_0 - G'_\infty)$$

This linear relationship and the Cole-Cole plot emphasize the close relationship between the out-of-phase and in-phase shear modulus values. A similar relationship with the coefficient of $(G'_0 - G'_\infty)$ as 0.17 was ob-
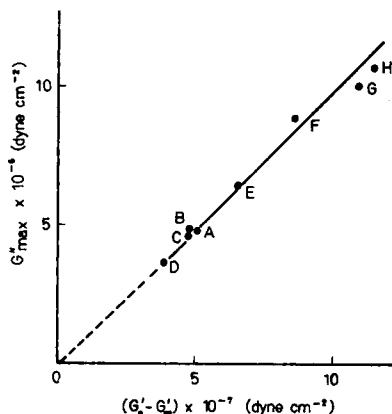
Fig. 6. G''_{max} vs. $(G'_0 - G'_\infty) \times 10^{-7}$ dynes/cm.^{2}.

served previously[4] for a wide range of blacks and fillers. The reason for the discrepancy between these two coefficients is not known, and further critical experimentation on this point is obviously required. However, within a consistent series of vulcanizates, the linear relationship between G''_{max} and $(G'_0 - G'_\infty)$ is apparent.

It is of further interest to note that for the compounds D to H, in which the structure remains constant, although the surface characteristics are altered, all the arcs in Figure 5 extrapolate to 1.1×10^7 dyne/cm.^{2}; this is to be expected if $G'_{\infty c}$ and G'_∞ are solely functions of the hydrodynamic effect due to the concentration and shape factor of the carbon black particle and the modulus of the pure gum rubber phase.

Tensile Measurements

Figure 7 shows the tensile stress plotted against the percentage extension on the rubber. Compounds B, C, and D, the normal and high structure blacks, possess similar stress–strain characteristics, and are the stiffest (at high extensions) of the rubbers studied. The low structure black, compound A, is softer than the normal and high structure blacks. Compounds D–H show a progressive softening with the increase in the temperature of the heat treatment of the carbon black; indeed, we have here a situation in which the rubbers which were the stiffest according to the low amplitude dynamic tests become, in fact, the softest at the high tensile extensions. This behavior parallels that observed by Payne[5] by altering the degree of dispersion, i.e., the poorer the dispersion the higher the dynamic modulus at low strains, but the lower the tensile modulus at high extensions.

DISCUSSION

Anderson and Emmett[6] studied the surface complexes on four commercial carbon blacks by heating them during evacuation at temperatures reaching 1200°C. and analyzing the evolved gases. They found that
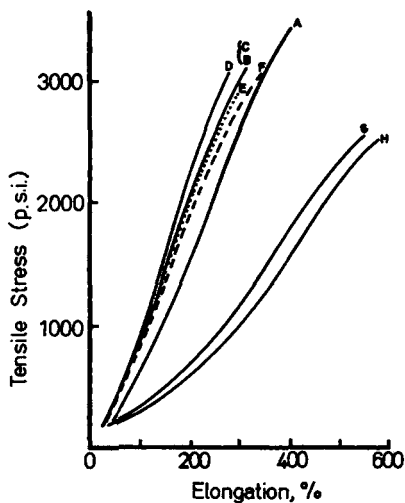
Fig. 7. Tensile stress–elongation curve. See introduction for details of vulcanizates.

most of the carbon dioxide was evolved in the 300–600°C. range, the carbon monoxide in the 600–900°C. range, and the hydrogen in the 900–1200°C. range.

Schaeffer, Smith, and Polley[7] reported data of various kinds on four grades of carbon black after heating to a range of temperatures from 1000 to 3300°C. They show that graphitization begins to appear about 1000°C., which is the temperature of maximum evolution of hydrogen. These authors also noted that after 2 hr. heating at 2700°C., the particles of P33 black, originally spherical, assume hexagonal and octagonal shapes. These authors also recorded a continuous change in the crystallite size with the temperature of heat treatment, and showed a rapid change in crystallite size about 1800°C.[7,8]

Schaeffer, Smith, and Polley[9] have recorded the striking effect of heat treatment of black on the tensile modulus. With the fully reinforcing carbons this reduction in modulus is complete at 1500°C., and heating to higher temperatures produces no further decrease. Nearly all the loss in modulus occurs at temperatures below those where graphitization, indicated by crystallite growth, has advanced significantly. The interesting conclusion is drawn, supported by ultimate analyses, that the decrease in stiffness is associated principally with removal of surface hydrogen.

Parkinson[10] reported that there is a profound change in electrical resistivity on the removal of the chemisorbed oxygen and hydrogen from the surface of the black. The resistivity decreases drastically with the temperature of heat treatment up to about 1000°C., reaches a minimum at about 1500°C., and then rises slightly to a constant value at temperatures up to about 3000°C.

It is usual to associate an increase in electrical conductivity with increased high-strain tensile modulus.[10] However, heat treatment of the black provides an instance of an increase in conductivity of the rubber

accompanying a decrease—and a very large decrease—in tensile modulus, although there is a marked increase in the dynamic modulus at low strains. This is understood if the first observation refers to the fact that a more reinforcing black, usually one of higher structure, provides both increased conductivity and increased tensile modulus. In the case of the heat-treated blacks, the dynamic properties clearly suggest decreased microdispersion, which would increase the conductivity of the rubber as well as the low amplitude dynamic modulus, but this poorer dispersion would also be accompanied by reduced high strain tensile properties.

All the dynamic measurements discussed in this paper suggest that the effect of heat treatment is to bring about a poorer microdispersion of the black. The removal of the volatile matter and the incipient graphitization of the black increases the aggregation tendencies of the black and certainly appears to prevent the association between the rubber and the black surface being as effective in bringing about a dispersion during mixing, as with the normal black surface.

The high structure blacks, compounds C and D, possess the lowest dynamic modulus and associated hysteretic properties, thus suggesting that a better microdispersion has been obtained than with the normal structure black, compound B. Little difference was observed between the behavior of the normal and the low structure blacks.

The effect of heat treatment of the black is to remove the volatiles, thus changing the chemical nature of the surface, and producing partial graphitization as shown by the change in crystallite length.[8,10] The effect of the changed nature of the black is to impair the ability of the rubber to disperse the black, which aggregates together, thus increasing the conductivity,[10] increasing the dynamic modulus at low strains, increasing the hysteresis because of the larger amount of aggregated structure present, but reducing the tensile strength of the vulcanizate. All these effects are increased with the temperature of the heat-treatment process.

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Résumé

On a étudié les propriétés dynamiques d'une série de caoutchoucs naturels vulcanisés et chargés de noir de carbone, afin de déterminer leur rapport d'amplitude. Les noirs de HAF que nous avons étudiés possédaient une structure faible, normale ou élevée, et une série de noir de structure élevée a été chauffée jusqu 2,700°C. Le traitement thermique du "noir" a augmenté le module de cisaillement dynamique a basse amplitude et l'hystérésis, mais a réduit le module de tension à élongation élevée. On a étudié ces effets en tenant compte de la dispension du "noir."

Zusammenfassung

Die dynamischen Eigenschaften einer Reihe von russgefüllten Naturkautschukvulkanisaten wurden in Bezug auf ihre Amplitudenabhängigkeit untersucht. Die untersuchten HAF-Russe besassen geringe, normale oder hochentwickelte Struktur und eine Reihe der Hochstrukturrusse wurde einer Hitzebehandlung bis zu 2700°C unterworfen. Der Einfluss der Hitzebehandlung auf den Russ bestand in einer Erhöhung des dynamischen Schubmoduls und der Hysterese bei geringer Amplitude, jedoch in einer Herabsetzung des Schubmoduls bei hoher Verformung. Dirse Effekte wurden in ihrer Abhängigkeit von der Russdispersion untersucht.