The Dynamic Properties of Carbon Black-Loaded Natural Rubber Vulcanizates.   Part I*

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INTRODUCTION

The stress–strain curve of rubberlike materials in shear is usually linear over a fairly large range of the strain to which it is subjected. Even at relatively small strains however, nonlinearity can arise from the shape of the specimen or the mode of deformation. This is geometrical nonlinearity, which can be assumed absent if there are no harmonics in the stress response, and a low-frequency sinusoidally varying strain gives rise to a sinusoidally varying stress. However, as previous workers[1–7] have noted, when a carbon black–loaded vulcanizate is cyclically strained the recorded modulus falls as the amplitude of strain increases; this is a second type of nonlinear behavior. The effect is largely absent from the behavior of pure gum vulcanizates and those loaded with inert fillers but is present when active fillers such as carbon black and some silicas are incorporated, and it increases with increasing loading of such fillers.

One question arising from the earlier work was whether a finite amplitude of vibration existed below which there was no change in modulus, provided, of course, that the test piece had not been strained previously. This, as was pointed out by Waring,[3] would be a yield point analogous to that found in the flow properties of non-Newtonian disperse systems.

Even at a strain amplitude as low as 0.03%, Gui and co-workers[7] failed to detect such a yield point, but Fletcher and Gent[2] thought that some of their experiments clearly suggested its existence. The present work extends an earlier note about this[5] and shows that a region exists at very low strain in which the modulus remains constant with increasing strain. This may be regarded as evi-

dence of a yield point although there appears no real discontinuity in the properties. There is, therefore, an "apparent" yield point observable where modulus and phase angle measurements are extended over strain amplitudes of 0.00005 to 0.25%.

This paper also discusses the effect of temperature and the effects of concentration and type of carbon black on the dynamic modulus of carbon black-loaded natural rubber vulcanizates.

EXPERIMENTAL

The measurements were carried out at 0.1 cycles/sec. on a modified sinusoidal strain dynamic tester.[8] The instrument was used initially to study the behavior of rubber in compression–tension in the following ways.

1. A sinusoidal *stress* was applied to a cylinder of rubber 76 cm. long and of 0.635 cm. radius, and the deformation of the rubber was measured. This method was used for the smaller displacements (0.1 to 100 μ).

2. A sinusoidal *strain* was applied to the same test piece, and the stress was measured. This method was used for the larger displacements (100 μ to 1.25 cm.).

The machine was designed originally for the second method. The lower amplitudes were limited by the tolerances in the moving parts, but by using a spring between the moving anvil and the rubber test piece a large movement of the anvil was reduced to a considerably smaller movement on the rubber. In the first method, the deformation was measured directly by means of a differential transformer displacement pickup. Schematic drawings of the two arrangements used for the compression–tension measurements are shown in Figure 1.

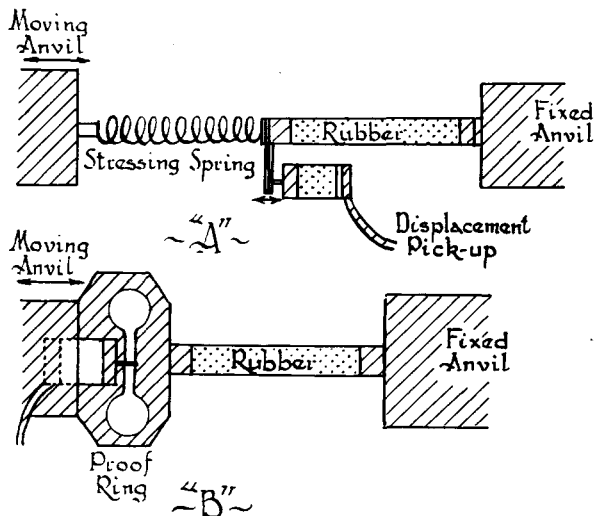After the compression–tension measurements were completed, a further set of experiments in

Fig. 1. Schematic drawings of the equipment used in the tension measurements on rubber cylinders: A, imposes a known stress, and measures the resulting deformation; B, imposes a known strain, and measures the resulting stress.
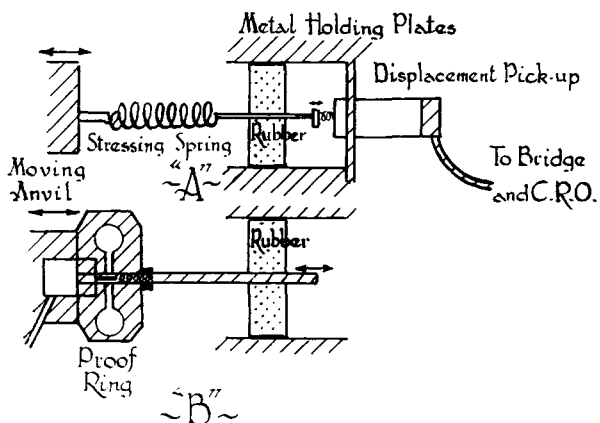

Fig. 2. Schematic drawings of the equipment used in the shear measurements on rubber cylinders: A, imposes a known stress, and measures the resulting deformation; B, imposes a known strain, and measures the resulting stress.

shear was carried out. For this, two rubber test pieces were deformed in shear.

A schematic drawing of the jig used is shown in Figure 2. The shear test pieces were cylinders of rubber 0.8 cm. in radius and 2.54 cm. long. The cylinders were bonded to the plates. The rubber cylinders were moulded in steel moulds lubricated with silicone fluid and were removed carefully from the mould to avoid straining. In fact, only very light finger pressure was required to do this.

All the dynamic tests were made first at the lowest strain obtainable and then the strain was increased incrementally to the maximum. This sequence ensured that the rubber had not been overstrained before a particular test, for the dynamic properties of filler-loaded vulcanizates are very sensitive to prior treatment.

The actual measurements made were of the phase angle δ and of the oscillatory force produced by the sinusoidal deformation. For the very low strains, as explained above, the strain response to a known sinusoidal force was measured. The ratio of stress to strain gave the figure for the modulus. Strictly, this modulus should be represented by either $|E(\omega)|$ or $|G(\omega)|$, depending on whether the deformation is compression–extension or shear. Now, $|E(\omega)| = (E'^2 + E''^2)^{1/2}$ where E' and E'' are the in-phase and out-of-phase components of the complex Young's modulus $E^* = E' + iE''$. For convenience, the modulus referred to will be $|E(\omega)|$ or $|G(\omega)|$ but will be written as E^* or G^* because tan δ is relatively small and the vector can be represented as the scalar quantity without appreciable loss of accuracy.

RESULTS

Compression-Tension

Figure 3, reproduced from a Note in this journal[6] shows the absolute Young's modulus E^* plotted against the logarithm of the dynamic strain amplitude for a range of natural rubber compounds containing increasing amounts of an MAF carbon black (compounding details are given in the appendix). The strain amplitude given both here and later refers to the total excursion of the deformation and is sometimes known as the "double
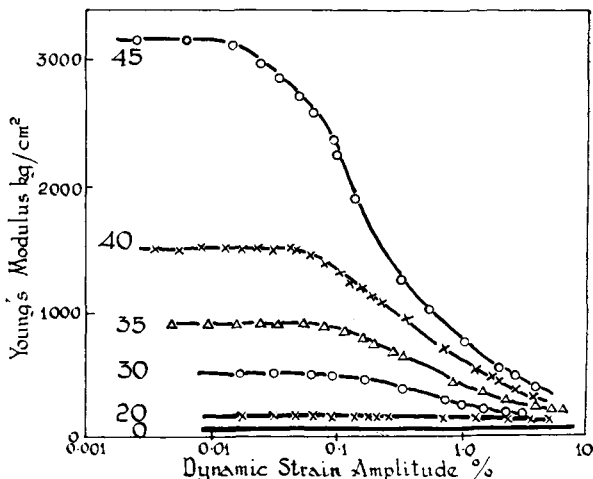

Fig. 3. Variation of Young's modulus E^* with the dynamic strain amplitude for natural rubber vulcanizates containing various proportions of MAF black.
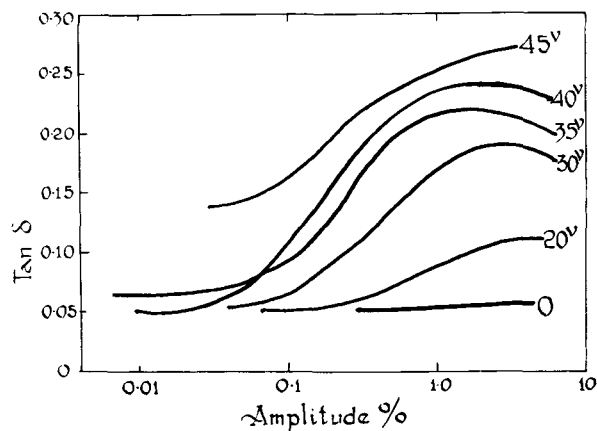
Fig. 4. Variation of tan δ with amplitude for natural rubber vulcanizates containing various proportions of MAF black.

strain." The yield point referred to in the earlier paper is apparent, E^* being constant at the very low strains, and shows clearly when the plot is linear, just as it does in the logarithmic plot. The corresponding tan δ values are plotted in Figure 4 and show that a maximum is reached at a strain corresponding to the inflexion point on the E^* amplitude curve of Figure 3.
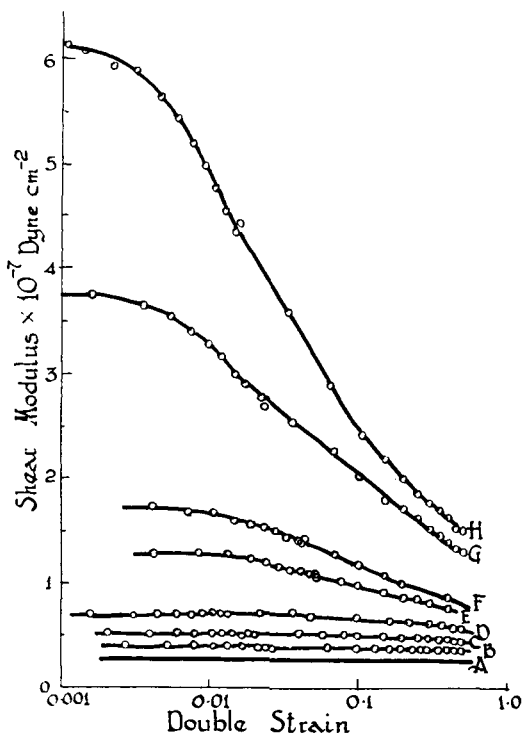

Fig. 5. Variation of G^* with strain amplitude. HAF volume concentration range, 0–29.5%. See Table I for key to curves.

Shear

The results obtained on deformation in shear show the same general picture but, because of the range of modulus in the rubbers used, have been drawn on two figures with different scales, one rubber, H, being common to both Figure 5 and Figure 6. The range of rubbers used contains increasing amounts of an HAF black (see Table II).
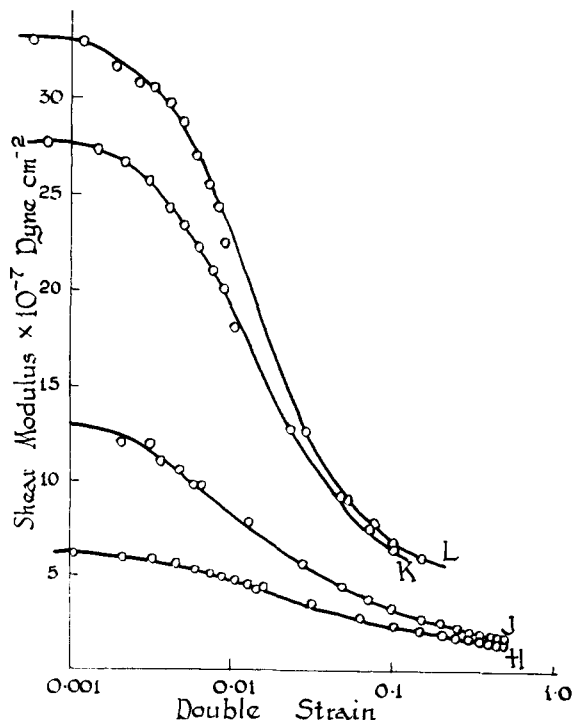

Fig. 6. Variation of dynamic shear modulus G^* with strain amplitude. HAF volume concentration range, 29.5–38.4%. See Table I for key to curves.

Method of Presentation of Results

The various empirical relationships suggested by different authors for the dependence of the dynamic modulus on strain amplitude have been discussed elsewhere[4] and, it may be noted here, a double logarithmic plot can also be used. However, it is proposed here to develop a method of presentation which emphasizes the similarities between the curves derived for different loadings of carbon black. After the analogy of these systems with the non-Newtonian behavior of liquids containing agglomerating particles,[9] for which Umstätter[10] used a log-probability plot, we may "normalize" the data between the limits at very low and very high strain. Consider the
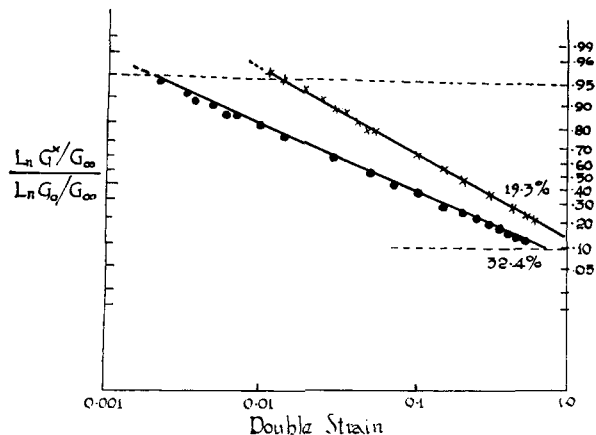
Fig. 7. Variation of the normalized modulus Z with strain amplitude for the 19.3 and 32.4% volume of HAF.

Fig. 8. Variation of Z with strain amplitude for all the HAF natural rubber vulcanizates.

shear modulus G^*; let G_0 represent its value at strains approaching zero, G_∞ its value at the high strains where there is no further change in G^* with increase of strain. Then the *normalized modulus* Z is given by [log (G^*/G_∞)/log (G_0/G_∞)]; it is shown in Figure 7, plotted on probability paper against the log of the double strain for two typical sets of results referring to rubbers with 19.3 and 32.4% volume loading of carbon black. It will be appreciated that there is some, but not very much, latitude in fixing a value for G_∞, but the variation possible is too small to influence the position of the plot on probability paper. Table I summarizes the data to be obtained both from the original plot (giving G_0 and G_∞) and the probability-paper plot (giving the mean value where $Z = 0.5$).

Table I shows clearly the enormous increase in

G_0 with increasing carbon black content. Indeed, the vulcanizate containing 38.4% by volume of black shows a modulus increasing by a factor of 125 over that of the pure gum vulcanizate.

It is convenient to consider the strain amplitude corresponding to $Z = 0.5$, and this is quoted in Table I and is derived from Figure 8. It will be noted that the strain at $Z = 0.5$ decreases regularly with increasing carbon black content. The plots in Figure 8 are substantially parallel, indicating that the width of the logarithmic strain range over which modulus changes occur remains approximately constant although its position on the axis shifts regularly. The linearity of the plots of the data on probability paper implies a relationship of the following type:

$$Z = \frac{\log G^*/G_\infty}{\log G_0/G_\infty} = 1 - \frac{2}{\sqrt{\pi}} \int_0^u \exp \{-u^2/2\} du$$

where u is a linear function of strain.

Effect of Temperature and of Heat Treatment on Modulus

Further study of the properties of the loaded rubber was made by examining the shear modulus over a large temperature range and also by noting the difference introduced by heat treatment of the compounded rubber before vulcanization. A single batch, without vulcanizing ingredients, was divided into two parts: one part was allowed to cool but the other part was heat-treated for 45 min. at 158°C. and then allowed to cool prior to the addition of sulphur and vulcanization. Both batches were allowed to stand for 24 hr. and then vulcanized in the same mould for the same period of time. These rubbers were stressed at very low

TABLE I
Results and Parameters for Deformation in Shear

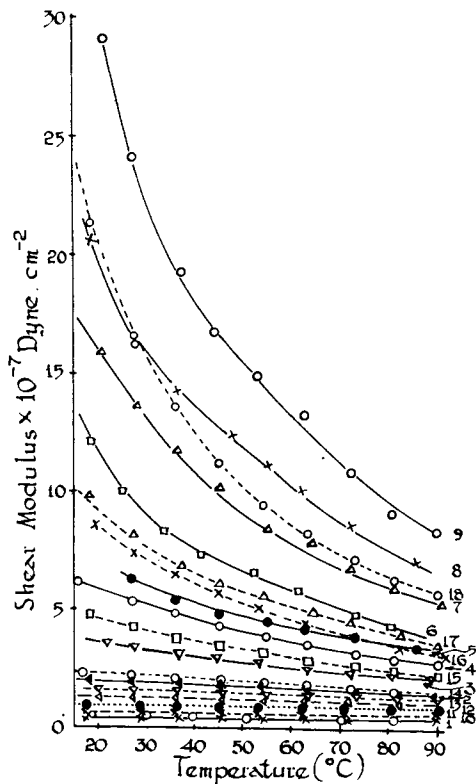| Symbol used in Figs. 5 and 6	Volume loading of black, %	G_0, Mdynes/cm.$^{-2}$	G_∞, Mdynes/cm.$^{-2}$	Values at $Z = 0.5$	
				Double stress, Mdynes/cm.$^{-2}$	Double strain
A	0	2.60	2.60	—	—
B	5.6	3.85	—	—	—
C	10.7	5.20	4.24	—	—
D	15.2	7.5	5.25	0.44	.200
E	19.3	13.0	6.25	0.83	.175
F	23.0	17.5	7.3	0.71	.125
G	26.4	37.5	10.6	1.25	.100
H	29.5	61.0	12.5	1.05	.075
J	32.4	135	16.5	1.14	.053
K	36.0	275	25.5	2.30	.056
L	38.4	328	26.0	2.30	.045

Fig. 9. Variation of G_0 with temperature, °C., for a range of HAF natural rubber vulcanizates. Full curves refer to normal vulcanizates, broken curves to the heat-treated vulcanizates. See Table II for key to curves.

amplitudes and the shear modulus was measured over a temperature range of 20 to 100°C.

The variation of shear modulus with temperature at low strains below the yield point is shown in Figure 9. The full curves refer to the normal batch and the broken curves to the heat-treated one. By comparing the results for the same concentration of black, it is apparent that the modulus
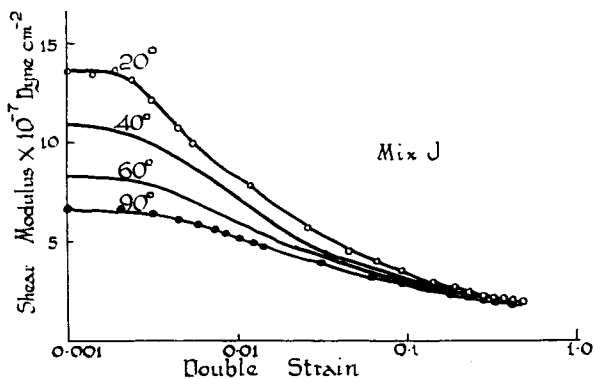
of the heat-treated rubber is lower than that of the normal vulcanizate. The effect of temperature of test is to decrease the modulus with increasing temperature, and the magnitude of the decrease is dependent on the concentration of black. The shear modulus at the larger strains becomes progressively less dependent on temperature and G_∞ is virtually independent of temperature over the range considered. This is illustrated for compound J in Figure 10. It will be recalled that the modulus of a pure gum rubber *increases* with increasing temperature as explained by the kinetic theory.

Effect of Carbon Black Type on Modulus at Low Strains

The experimental work so far reported used natural rubber compounds loaded with types of carbon black known as "medium abrasion furnace" (MAF) or "high abrasion furnace" (HAF). Carbon blacks differ both in the area of the surface and in their nature. Broadly speaking, there are two main classes known from their mode of preparation as channel blacks on one hand and furnace and thermal blacks on the other. Within these classes differing areas confer differing properties, but differences in the surface constitution exist between them. To indicate how this affects dynamic properties, a series of compounds was prepared with a range of carbon blacks of different particle size and type. The shear moduli of these compounds were measured at very low strains and the values obtained (G_0) are shown in Figure 11, plotted against the published figures for surface area which are determined by nitrogen absorption. The plot shows that all results for the furnace blacks lie on a single curve together with the lamp black. The thermal blacks, MT and FT, have the lowest values of all. The
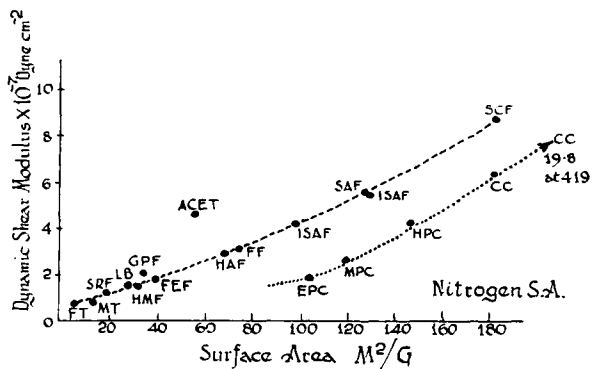

Fig. 10. Variation of dynamic shear modulus G^* with strain and temperature.

Fig. 11. Variation of dynamic shear modulus G_0 with the nitrogen surface area of the black.

channel blacks lie well below the furnace blacks on another curve. Acetylene black is distinct in behavior and many of its properties from all other blacks, as is well known.

DISCUSSION

Pigment "particles" are rigid solids, whose shape will not change. It is evident from electron microscope photographs of the dry blacks, however, that these particles may exist in chainlike formation. When dispersed in the rubber, these chains are retained to a certain extent. Deformation of the rubber–black system having occurred, the subsequent behavior of these chains or agglomerate groups will depend on the presence or absence of interparticle attractive forces. If these forces are absent, the groups will easily break up, the particles will act individually, and the system will be Hookean. On the other hand, the groups will move as single units if the particles are held together by attractive forces. However, these groups will be subjected to disruptive stresses by the deformation and, consequently, the magnitude of this disruptive stress must increase with increasing deformation. The groups will be broken down into smaller units of different dimensions and the elasticity of the material will change.

It is obvious from the normalized expression of the results that the form of the function describing the variation of modulus with strain is the same for all types and concentrations of black. The modulus has at low strains a constant value and, in so far as it does not at first change with increasing strain, a "yield point" may be said to exist although there is no true discontinuity where change in the modulus starts occurring.

Other workers[11] have referred to "hard" and "soft" zones in the loaded rubber and, in these terms, the rubber at very low strains may be regarded as possessing a maximum content of hard zones. We may assume that the proportion of hard and soft zones is determined by the type and concentration of black, the details of processing, here exemplified by the effect of heat treatment, the temperature and, of course the immediate preceding strain history.

At large strains the modulus becomes very much less strain-dependent, is insensitive to temperature, but is still very dependent on the concentration of black, as is demonstrated by column 4 of Table I. The proportion of "hard" zones is much reduced and would obviously reach a minimum at the true value for G_∞.
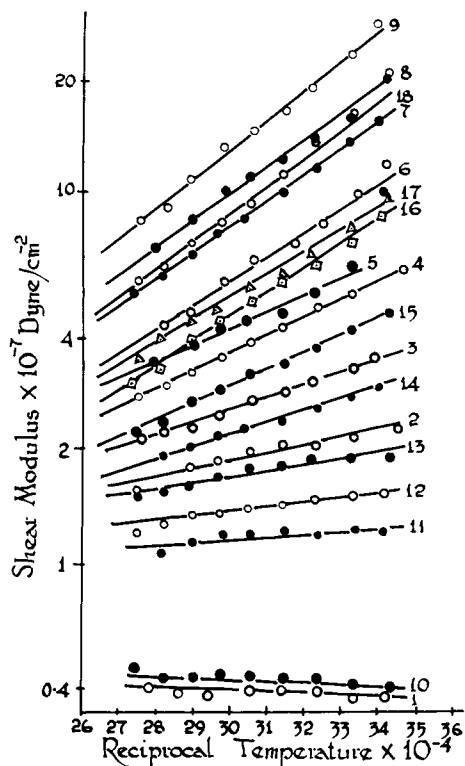

Fig. 12. Shear modulus versus reciprocal absolute temperature. Full curves refer to normal vulcanizates, broken curves to heat-treated vulcanizates. See Table II for key to curves.

If a proportion of hard and soft zones exists at very low strains we may expect the effect of temperature to reflect this proportion by influencing the equilibrium in the usual way; i.e., if K is the equilibrium constant then $d \ln K/dt = -H/RT^2$, the Van't Hoff isochore, where H is the heat of formation of the hard zone from a soft zone and R and T have the usual significance. A plot of log modulus, which we presume measures the equilibrium state, against I/T is given as Figure 12 for a range of concentration of blacks and showing also heat-treated samples. The corresponding heats calculated from the slopes of the lines in Figure 12 are given in Table II.

It will be observed that the heat is a linear function of the black concentration, as would be expected. However, the modulus of a pure gum rubber, i.e., the polymer itself, increases with increasing temperature owing to its kinetic origin, whereas the effect recorded in Figures 9 and 12 is in the opposite sense. The figures given in columns 3 and 4 of Table II represent the combined effect, and the plot of the heat against the volume concentration does not pass through zero but cuts the

TABLE II
Apparent Heat of Formation of Hard Zones and Effect of Heat Treatment

Symbols used in Figs. 9 and 12		Volume loading of black, %	Apparent heat of formation, Kcal./mole^{-1}	
			Normally processed	Heat-treated
1,	10	0	Minus	Minus
2,	11	17.3	0.9	0.5
3,	12	21.6	1.6	0.5
4,	13	25.8	2.3	0.9
5,	14	29.4	2.3	1.6
6,	15	32.7	3.0	2.3
7,	16	35.7	3.2	3.0
8,	17	38.5	3.2	3.2
9,	18	41.0	3.7	3.7

energy axis below zero at a value expected from the kinetic theory of elasticity ($H \simeq 0.8$ Kcal./ mole^{-1}).

Appendix

Compounds Used[a]
Composition in parts per 100 parts by weight of rubber

	A	B	C	D	E	F
Smoked sheet	100	100	100	100	100	100
Philblack A	0	50	85	100	110	150
Time of cure at 142°C.	40	40	40	40	50	60

[a] All contained zinc oxide, 3; stearic acid, 2; phenyl-α-naphthylamine 1; cyclohexylbenzyl sulphenamide, 0.6; and Dutrex R, 5. Parts by weight in addition to the above.

For the measurement in shear, the above basic recipe was used but with a high abrasion furnace black instead of Philblack A. For the work with different carbon blacks, the above basic recipe was used with 54 parts by weight of carbon black with a 100 parts by weight of smoked sheet.

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Synopsis

The dynamic properties of a natural vulcanized rubber containing carbon black were studied for dynamic tensions of amplitude varying greatly. It was shown that both the elastic responses and viscosity change with amplitude of oscillation and with concentration and type of carbon black. The effects of thermal treatment on the dynamic modulus were also studied. Beginning with conditions of equilibrium between the hard and soft regions of the vulcanizate for very weak stresses, the values for the formation of hard regions from soft regions were determined by means of the Van't hoff isochore.

Résumé

Les propriétés dynamiques d'un caoutchouc naturel vulcanisé contenant du carbon black ont été étudiées pour des tensions dynamiques d'amplitude variant dans de larges mesures. Il est montré qu'à la fois les réponses d'élasticité et de viscosité changent avec l'amplitude d'oscillation et avec la concentration et le type de carbon black utilisé. Les effets d'un traitement thermique sur le module dynamique ont également été étudiés. A partir des conditions d'équilibre entre les régions dures et molles dans le vulcanisat pour de très faibles tensions, les valeurs pour la formation de régions dures à partir de régions molles ont été déterminées au moyen de l'isochore de Van't hoff.

Zusammenfassung

Die dynamischen Eigenschaften eines Russ enthaltenden Naturkautschukvulkanisats wurden in einem weiten Bereich an dynamischer Spannungs-amplitude untersucht. Es wird gezeigt, das sich sowohl das elastische als auch das viskose Verhalten mit der Oszillationsamplitude und mit der Konzentration und der Art des verwendeten Russes ändert. Der Einfluss des Erhitzens und der Hitzebehandlung auf den dynamischen Modul wurden ebenfalls untersucht. Unter Verwendung der Van't Hoff Isochore wurden aus der Gleichgewichtsbedingung zwischen harten und weichen Bereichen in dem Vulkanisat bei sehr geringen Verformungen die Werte für die Bildungswärme von harten aus weichen Bereichen bestimmt.