Stress Softening in Rubber Vulcanizates.   Part I. Use of a Strain Amplification Factor to Describe the Elastic Behavior of Filler-Reinforced Vulcanized Rubber

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Synopsis

Measurements of Young's modulus of vulcanized rubbers containing thermal carbon black show the predicted dependence on the volume concentration given by relationships derived for a suspension of spherical particles, for example, that due to Guth, Simha, and Gold which gives $E = E_0 (1 + 2.5c + 14.1c^2)$. A simple interpretation of the results is that the strain in the rubber is increased by the presence of filler so that the ratio of the average strain to the measured overall strain is given by the factor $X = 1 + 2.5c + 14.1c^2$. This factor was used to analyze simple extension stress–strain data obtained at larger extensions. For this purpose the Mooney-Rivlin relation was used to describe the behavior of the rubber phase. Values of C_1 independent of the volume concentration and in close accord with measurements of the equilibrium volume swelling of the rubbers were obtained. Values of λ^* were also consistent with those of C_1. Analysis of stress–strain data obtained on rubbers containing smaller particle-sized carbon blacks is more complex. For these materials the relation due to Guth, viz., $E = E_0 (1 + 0.67fc + 1.62f^2c^2)$, was chosen. By the choice of suitable values of f, good agreement with the Mooney-Rivlin stress–strain relation was achieved at volume concentrations less than about 0.15.

INTRODUCTION

One of the more intriguing problems in rubber physics is the source of the increased stiffness and strength of vulcanized rubber which is produced by the addition of fine particulate fillers. In the many attempts to provide a quantitative physical basis for filler action most progress has been made in the effect of fillers on elastic behavior. Here theoretical studies have derived mainly from the formally analogous problem of the increase in viscosity caused by a suspension of solid particles.

In this approach the vulcanized rubber surrounding the filler particles is considered to be an isotropic elastic continuum having the same elastic properties as the rubber without filler. The rubber is also assumed to adhere to the filler surface, and, by considering stresses in the rubber in the neighborhood of particles, expressions can be derived relating the elastic modulus

E of the filled rubber to the modulus E_0 of the matrix.[1-3] Thus, for spherical filler particles at low concentrations, Smallwood showed that

$$E = E_0(1 + 2.5c) \qquad (1)$$

where c is the volume concentration of filler.

In deriving eq. (1) no account was taken of the interaction between neighboring filler particles, and Guth and Gold, by considering the interaction between pairs of particles, added an extra term involving the square of the concentration,[4,5] viz:

$$E = E_0(1 + 2.5c + 14.1c^2) \qquad (2)$$

These two expressions are identical to the viscosity relationships derived by Einstein and Guth, Simha, and Gold, respectively except that the viscosity η is replaced by the elastic modulus E. Several alternative expressions have been derived for the viscosity of suspensions at higher concentrations, for example, the following due to Vand[6]

$$\eta = \eta_0(1 + 2.5c + 7.17c^2 + 16.2c^3) \qquad (3)$$

and to Simha[1]

$$\eta = \eta_0(1 + 2.5c + 12.6c^2) \qquad (4)$$

As yet there is no way of discriminating between these various expressions, but for volume concentrations of less than about 0.2 they all give values of η within about 5% of each other.

Smallwood[3] showed that for low concentrations of filler ($c < 0.1$) eq. (1) fitted the observed elastic behavior of rubber containing nonreinforcing or lightly reinforcing fillers, but that serious departures occurred with more highly reinforcing fillers. Guth found that the behavior of rubber containing thermal carbon black, which consists essentially of spherical particles, conformed to eq. (2) up to volume concentrations of about 0.3.[7,8] He suggested that the departures observed with more reinforcing carbon blacks were due to their tendency to agglomerate into chainlike clusters, and for these materials he proposed the relation

$$E = E_0(1 + 0.67fc + 1.62f^2c^2) \qquad (5)$$

where f is a factor describing the asymmetric nature of the aggregated clusters as expressed by the ratio of their length to width.

In attempting to confirm the applicability of these theoretical expressions two practical problems arise. First, there is no unique value of the elastic modulus E of vulcanized rubber, as the strain increases continuously with time after application of the stress, and it is thus necessary to choose a pseudo-equilibrium value of the strain attained an arbitrarily chosen period after the application of the stress. Second, the stiffness of filler-loaded rubbers may decrease considerably as a result of stretching, and thus values of the elastic modulus obtained during the initial extension may be markedly different from those obtained after previous stretching.[9]

The softening of filler-loaded rubbers resulting from previous stretching not only leads to a difficulty in defining a meaningful equilibrium elastic modulus but also requires large changes in the shape factor f. Blanchard and Parkinson considered that such changes were improbable and suggested that the increase in stiffness produced by fillers could more realistically be described in terms of rubber–filler attachments providing restrictions in the crosslinked rubber network, and that the softening on stretching resulted from a breakdown of some of these attachments.[10] Pursuing this hypothesis, Bueche derived expressions based on the statistical theory of rubberlike elasticity for both the elastic modulus and the equilibrium swelling of the vulcanized rubber in suitable swelling agents.[11] Here the effect of the filler attachments was taken to be an increase in the number of effective network chains. He claimed that both the increase in modulus and decrease in swelling produced by fillers could be considered to be due primarily to rubber-to-filler attachments. However, the observed decrease in swelling was often much less than was consistent with the increase in modulus, and he had to invoke a detachment of rubber from the filler surface produced by the swelling agent to explain his results.

This use of the statistical theory to determine the elastic behavior of a crosslinked network of rubber chains in which some of the crosslinks are introduced by vulcanization and others by attachments of rubber chains to the surfaces of filler particles involves the implicit assumption that the attachments to the filler particles as well as the vulcanization crosslinks move affinely during deformation, an assumption which is obviously unrealistic.

It has not yet been possible to resolve the difficulties in the application of either of these two theoretical treatments nor to reconcile their conceptually different approaches. In regard to the latter, Bueche has drawn attention to the fact that the formation of extra network chains by rubber–filler attachments results in a change in the elastic properties of the rubber matrix in which the filler particles are embedded and thus his treatment cannot be developed in conjunction with the stress-analysis treatment described by eqs. (1) and (2).

The purpose of the present study is to provide experimental data of both the elastic and swelling behavior of filler-reinforced rubbers to enable their quantitative description to be more critically examined.

EXPERIMENTAL

Samples used were cut from sheets of vulcanized natural rubber about 0.1 cm. thick. The sheets were prepared by mixing 3.0 parts by weight of dicumyl peroxide with 100 parts by weight of natural rubber (RSS1) and vulcanizing for a period of 50 min. at 150°C. The main body of the investigation was carried out on material containing different concentrations of carbon black ranging from 0 to 60 phr (parts by weight per hundred of rubber). The actual concentration of black was determined from both
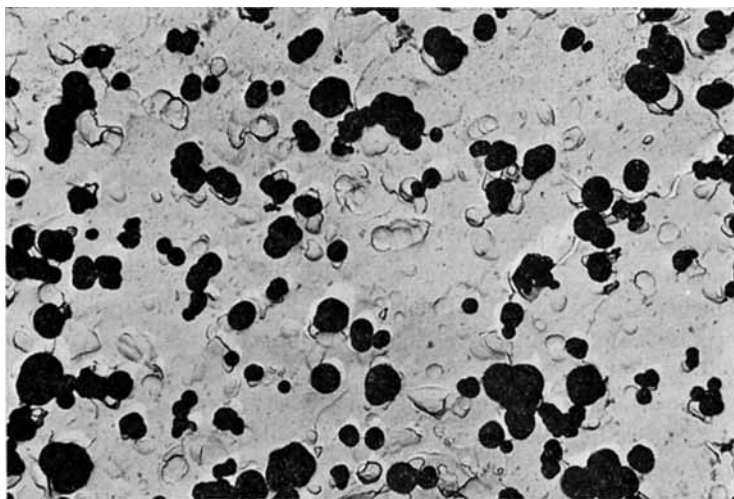
Fig. 1. Electron microscope replica of torn surface of rubber containing MT carbon black (6750×).

(1) density measurements, in which the concentration was calculated from the measured density of the rubber and the known density of the black, and *(2)* chemical analysis. The results from both determinations were within less than 1% of each other, and the results quoted are those from density determinations.

Two carbon blacks of widely differing colloidal activity were used. One of these, MT black, consists essentially of substantially spherical particles with mean diameter of about 0.4 μ. The other, HAF black, is of much finer particle size, having a mean diameter of particles of about 0.04 μ. Electron microscope replicas of torn surfaces of vulcanized rubber containing these blacks showed that the individual particles of the coarser MT black were relatively well dispersed but that the finer HAF black existed in the rubber in a much more flocculated condition with aggregates of up to about 0.3 μ (Fig. 1 and 2).

Stress–strain measurements were made in simple extension on strips of rubber 1 cm. wide × 10 cm. long cut out from vulcanized sheets by means of a die. Reference marks were made on each strip about 7 cm. apart and clamps applied to both ends. The strip was then suspended vertically by means of one clamp and incremental loads applied to the other clamp. The distance between the reference marks was measured by means of a cathetometer 3 min. after each application of load. This period was allowed to elapse to enable the sample to achieve an approximately equilibrium extension. The measurements were made at 25°C. Most measurements were made during the *initial* extension of the test samples, but some were made after repeatedly previously stretching samples to extensions in excess of the maximum they were to be subjected to in the stress–strain measurements and then allowing the samples to recover. The measurements de-
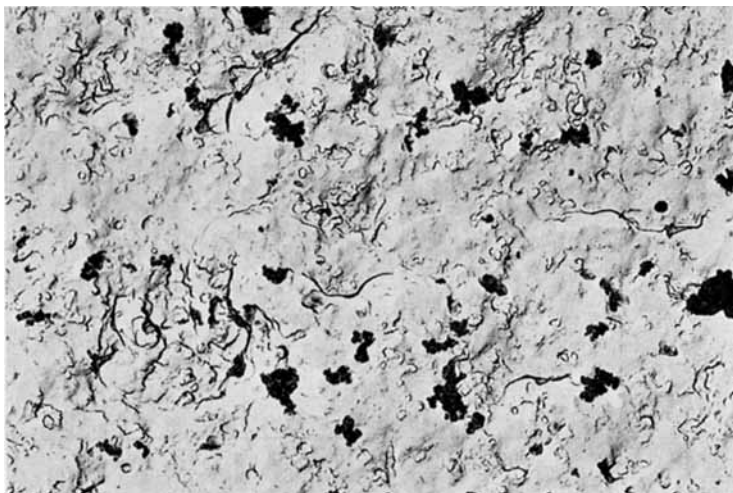
Fig. 2. Electron microscope replica of torn surface of rubber containing HAF carbon black   (6750×).

scribed in the present paper are those made during the initial extension.

Some stress–strain measurements were carried out on swollen rubbers. Liquid paraffin was chosen as the swelling liquid, as this enabled stress–strain measurements to be carried out without the need for precautions to stop the loss of swelling liquid by evaporation during the measurements. The rubber was swollen to the required degree and then allowed to stand for several days before testing to enable the rubber to become uniformly swollen by the viscous swelling liquid.

Measurements were also made of the equilibrium swelling of rubbers in n-decane. Small samples, approximately 1 cm. square, were weighed before and after immersion in n-decane for 2 days at 25°C. The samples were carefully dried with filter paper after removal from the swelling liquid before weighing. In order to determine the volume fraction of rubber (v_r) in the system rubber + swelling liquid a correction had to be made for the presence of the filler; this was simply done by subtracting the volume of the filler from measurements of both the dry and swollen volume.

RESULTS

MT Carbon Black

Stress–Strain Behavior. Stress–strain curves obtained on rubbers containing different concentrations of MT black all showed a very good linear portion from the origin up to strains of about 0.02. At higher strains the curves showed the sigmoid shape characteristic of rubberlike materials with an upward sweep of the curve at strains greater than 1 (Fig. 3). The linear portion at low extensions was used to determine Young's modulus E, the modulus at zero extension, and the values ob-
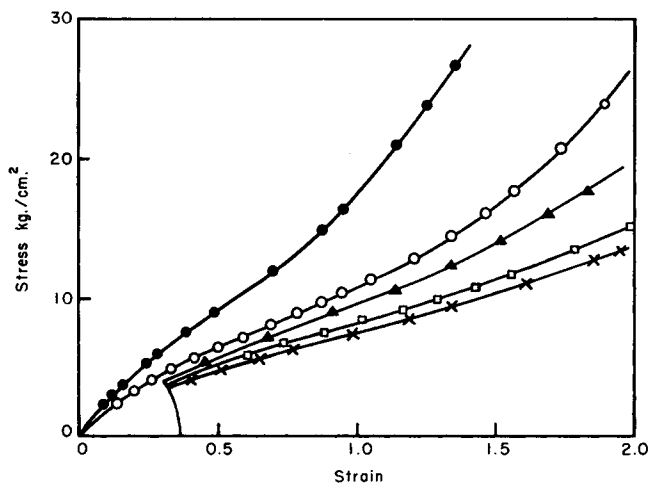
Fig. 3. Stress–strain curves rubbers containing different concentrations of MT carbon black: (●) G; (O) F; (▲) E; (□) D; (×) B.
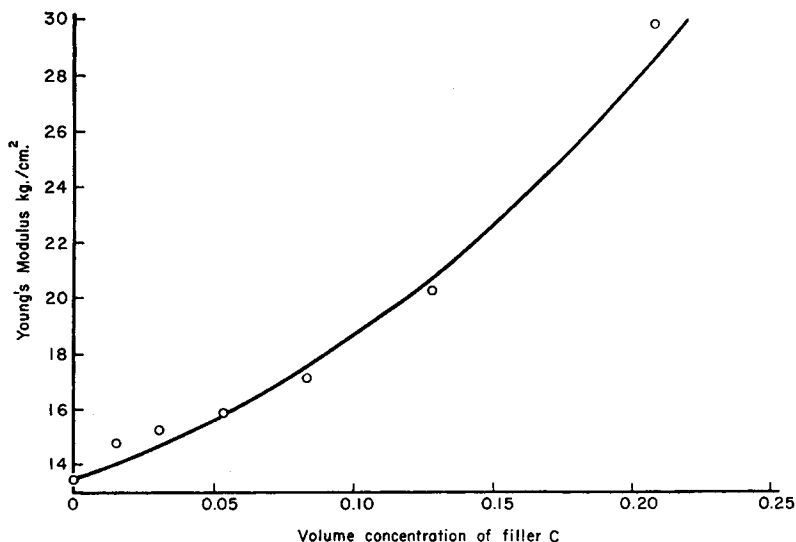

Fig. 4. Young's modulus of rubbers containing MT carbon black as a function of concentration.

tained are shown in Figure 4 plotted as a function of volume concentration of filler (c). The full line in the figure is the theoretical curve given by eq. (2), viz., $E = E_0 (1 + 2.5c + 14.1c^2)$, and there is excellent agreement between the observed and the theoretically predicted dependence of the modulus E on the volume concentration of filler.

It has previously been shown that the stress–strain behavior of natural rubber vulcanizates without fillers at larger deformations can conveniently
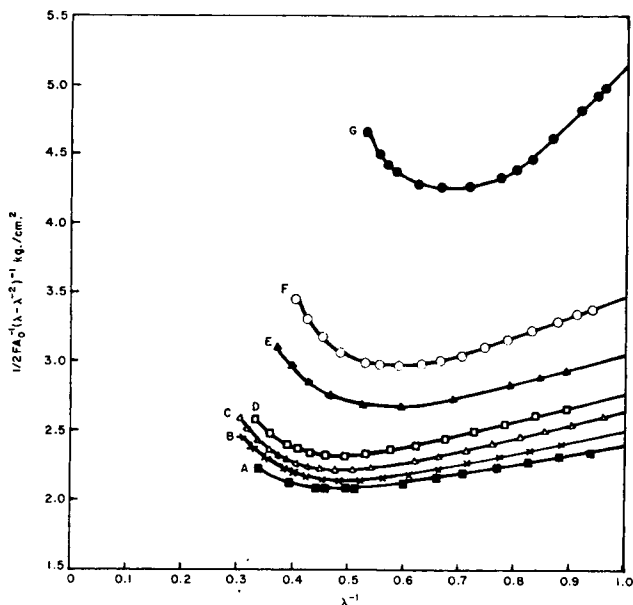
Fig. 5. Stress–strain curves plotted as $^1/_2\,FA_0{}^{-1}\,(\lambda\,-\,\lambda^{-2})^{-1}$ against λ^{-1} (MT carbon black).

be described by the Mooney–Rivlin relation[12] which in simple extension gives

$$F \,=\, 2\,A_0(\lambda\,-\,\lambda^{-2})\,(C_1\,+\,\lambda^{-1}\,C_2) \tag{6}$$

where F is the load, A_0 the cross-sectional area, λ the extension ratio, and C_1 and C_2 are parameters characteristic of the rubber vulcanizate. It has further been shown that the term involving C_1 describes behavior predicted by the statistical theory of rubberlike elasticity and that the value of C_1 is directly proportional to the number of network chains per unit volume of the rubber.

Figure 5 shows the experimental stress–strain curves given in Figure 3 replotted with $^1/_2\,FA_0{}^{-1}\,(\lambda\,-\,\lambda^{-2})^{-1}$ as ordinate and λ^{-1} as abscissa. Except for the highest concentration of filler, each of the curves show a linear relation over a range of low and moderate extensions, having an intercept on the axis $\lambda^{-1}\,=\,0$ of C_1 and a slope of C_2.

Table I gives values of Young's modulus E measured at small extensions together with values of $C_1\,+\,C_2$ and C_1 determined from the stress–strain curves given in Figure 5. The anticipated close correspondence between the measured values of E and six times the measured values of $C_1\,+\,C_2$ is shown in Figure 6. The values of C_1, apart from the rubber with the highest concentration of filler and in which there is difficulty in analyzing the stress–strain curve in terms of C_1, increase progressively with increasing concentration of filler but much less slowly than the increase in the values of E.
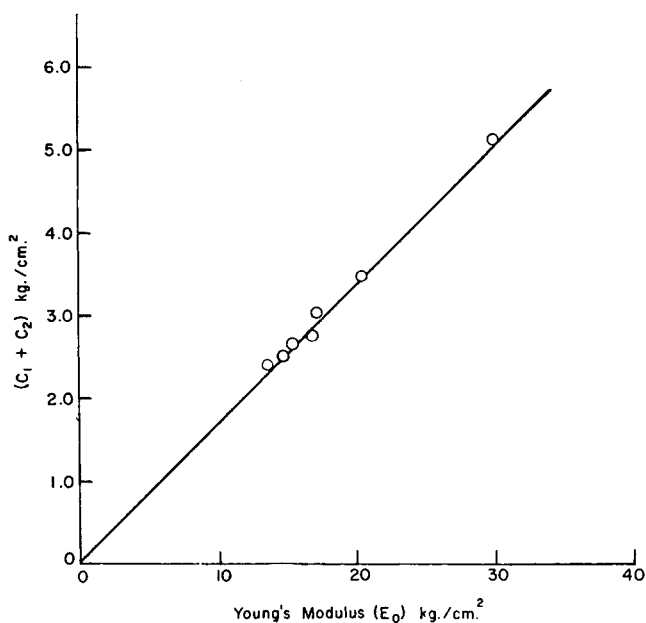
Fig. 6. Relationship between Young's modulus and $C_1 + C_2$.

Departures from linearity of the stress–strain curves in Figure 5 occur at higher extensions. Each curve passes through a minimum and shows a rapid upward rise in the value of $\frac{1}{2} FA_0^{-1}(\lambda - \lambda^{-2})^{-1}$ with increasing extension. Similar departures observed with rubbers not containing fillers have been shown to result from finite extensibility of the network chains in the crosslinked rubber.[13] The extension at which they occur has been shown to reflect the length of network chains or, alternatively, the number of network chains per unit volume, and an empirical calibration has been established for rubbers without fillers between values of λ^* (the extension at which departures from linearity are $2^1/_2\%$ of C_1) and values of C_1.

TABLE I

Vulcan-izate[a]	Volume concen-tration of black c	Young's modulus E, kg./cm.²	$C_1 + C_2$, kg./cm.²	C_1, kg./cm.²	λ^*	C_1 (from λ^*), kg./cm.²
A	0	13.50	2.39	1.69	2.20	1.70
B	0.015	14.76	2.50	1.71	2.20	1.70
C	0.0305	15.25	2.64	1.74	2.13	1.95
D	0.0535	16.65	2.76	1.80	2.13	1.95
E	0.0840	17.11	3.05	2.04	1.75	2.80
F	0.1382	20.26	3.47	2.08	1.65	3.10
G	0.2085	29.84	5.12	(1.40)	(1.30)	

[a] $M_n = 1.9 \times 10^5$.

Table I also includes values of λ^* determined from the stress–strain curves in Figure 5 and values of C_1 corresponding to the measured values of λ^* and derived from the empirical calibration between C_1 and λ^*.   To use this calibration the value of the initial molecular weight of the rubber prior to vulcanization (M_n) is required.   Solution viscosity measurements on samples taken from the unfilled base rubber (compound E) were used for this purpose and gave a value of M_n of 1.9×10^5.   The two estimates of values of C_1, i.e., that derived from the intercept of the linear portion of the stress stain curve and the ordinate $\lambda^{-1} = 0$ and that corresponding to λ^* and derived from the empirical calibration, only agree for rubber without filler and show progressively increasing divergences as concentration of filler increases.

Use of Strain-Amplification Factor.   The theoretical relations given by eqs. (1), (2), and (3) are strictly relevant only to modulus determinations made at small deformations and where the strain is proportional to the stress.   Their application at larger strains, where this proportionality no longer exists, has not hitherto been examined.

In their development the increase in modulus due to the incorporation of filler results from the consequent distortion of the stress pattern in the rubber matrix.   The matrix is prevented from deforming uniformly by adhesion of the rubber to the surfaces of the particles and thus the overall apparent strain is less than the strains occurring locally.   The ratio of the stress to strain is increased by a factor X which takes into account both this disturbance of the strain distribution and the absence of deformation in the fraction of the material composed of filler.

For several deformations and for spherical particles this factor has been shown to be

$$X = \sigma/\epsilon\, E_0 = E/E_0 = 1 + 2.5c + 14.1c^2 \qquad (7)$$

where ϵ is the strain produced by the stress σ and E_0 is the modulus of the rubber without filler.   For larger deformations where the stress and strain are no longer directly proportional it is necessary to consider whether it is the stress or the strain or a function of both the stress and the strain which is increased by the presence of filler.   There is at present no means of selecting this with confidence but *a priori* it appears more reasonable to consider that the local strains are on average X times greater than the overall strain.

The adoption of this assumption requires that the extension ratio λ in eq. (5) appropriate to the rubber matrix should be calculated from the measured overall strain ϵ by putting

$$\lambda = 1 + X\epsilon$$

This calculated value of the actual extension ratio of the rubber matrix will subsequently be referred to as Λ.

Figure 7 shows the stress–strain data of Figure 5 replotted by using this calculated value of the extension ratio.   Values of X were given by the
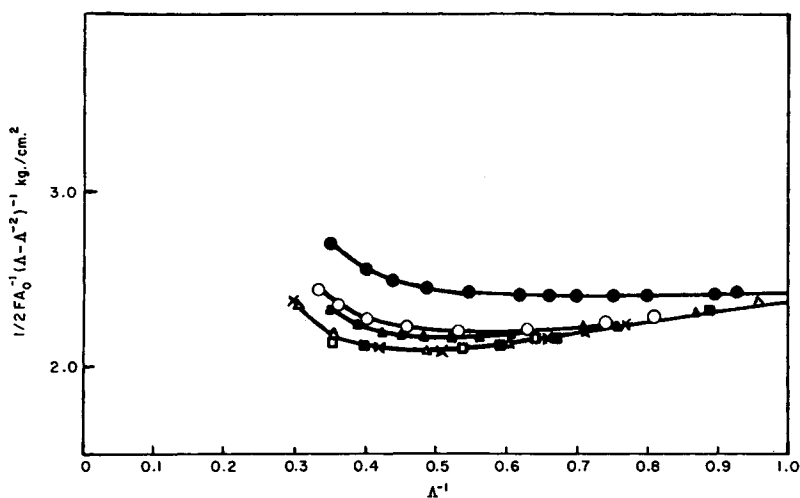
Fig. 7. Stress–strain curves in Fig. 5 replotted with the use of the strain–amplification factor. Symbols as for Fig. 5.

ratios of the values of Young's modulus measured on the filled (E) and the unfilled (E_0) rubbers.

It will be seen that the use of the strain amplification factor given by eq. (7) makes the stress–strain curves for volume concentrations of filler up to about 8% closely superpose. In each case they give values of C_1, C_2, and Λ^* which are similar to those for the rubber without filler. The results are similar to those for the rubber without filler. The results are thus consistent with the concept that the elastic properties of the rubber matrix are unmodified by filler and its effective deformation is equivalent to X times the measured overall deformation.

At higher concentrations there are significant departures but these are still relatively small and the data are, to a first approximation, in agreement with the concept of the use of strain amplification factor. Values of

TABLE II

Vulcanizate[a]	Volume concentration of black c	Factor X (E/E_0)	C_1 (corrected for X), kg./cm.^{2}	Λ^*	C_1 (from Λ^*), kg./cm.^{2}
A	0	1.00	1.69	2.20	1.7
B	0.015	1.041	1.69	2.20	1.7
C	0.0305	1.090	1.70	2.20	1.7
D	0.0535	1.173	1.70	2.20	1.7
E	0.0840	1.307	2.00	2.15	1.9
F	0.1382	1.552	1.96	2.15	1.9
G	0.2085	2.132	2.30	2.05	2.3

[a] $M_n = 1.9 \times 10^5$.

C_1, Λ^* determined from the curves in Figure 7 and of C_1 calculated from Λ^* are given in Table II.

Swelling Measurements. The equilibrium swelling of vulcanized rubber provides an alternative means of determining its elastic properties. Relationships between the volume fraction of rubber v_r in the swollen network of equilibrium and the density of network chains have been established as for example in the Flory–Huggins equation[14,15]

$$- \log (1 - v_r) - v_r - \mu v_r^2 = V_0 M_c^{-1} v_r^{1/3} \qquad (8)$$

or equivalently

$$- \log (1 - v_r) - v_r - \mu v_r^2 = (2C_1) RT . V_0 v_r^{1/3}$$

where μ is an empirical parameter which for accelerated sulfur–natural rubber vulcanizates similar to those used in this investigation has a value of 0.42 and where M_c is the number-average molecular weight of chain segments lying between adjacent crosslinks and V_0 is the molar volume of the swelling agent.

Table III gives values of the volume fraction of rubber v_r at equilibrium swelling in n-decane after correction had been made for the volume of filler present. It also gives the corresponding values of C_1 determined from an empirical calibration between v_r and C_1 established for rubber without fillers.[16] For comparison Table III also includes the two estimates of C_1 previously given in Table II and determined from stress–strain curves corrected by the strain amplification factor X.

Comparison of the three separate estimates for C_1 for each rubber vulcanizate shows that at low concentrations of filler the agreement is excellent. At higher concentrations the agreement is sufficiently close to indicate that it is possible to obtain self-consistent values of C_1, and hence of the density of crosslinking of these filled rubbers derived in these three different ways.

A progressive increase in C_1 with increasing concentration of filler is shown by each of the three estimates. This increase is due either to an increase in the density of crosslinking of the rubber matrix resulting from the presence

TABLE III

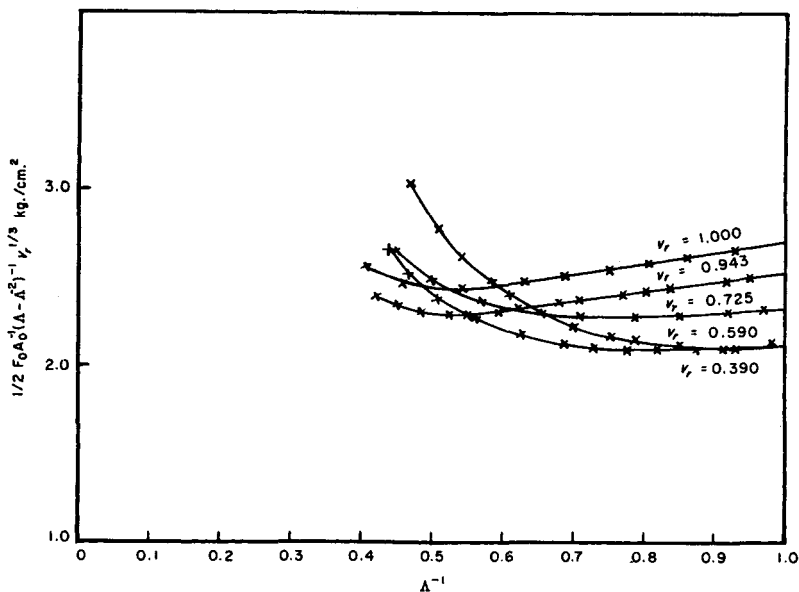| Vulcanizate[a]	Volume concentration of black c	v_r	From swelling	C_1, kg./cm.^{2} From stress–strain (corrected)	From Λ^* (corrected)
A	0	0.2955	1.70	1.69	1.7
B	0.0150	0.2935	1.68	1.69	1.7
C	0.0305	0.3015	1.79	1.70	1.7
D	0.0535	0.3005	1.77	1.70	1.7
E	0.0840	0.3070	1.90	2.00	1.9
F	0.1382	0.3150	1.98	1.95	1.9
G	0.2085	0.3330	2.34	2.30	2.3

[a] $M_n = 1.9 \times 10^5$.

Fig. 8. Stress–strain curves on swollen rubbers plotted using strain-amplification factor (MT carbon black).

of the filler or to an additional restriction on the deformation of the rubber matrix imposed by the filler.

The use of the empirically determined strain-amplification factor X makes full correction for the restriction of deformation resulting from the filler at very small deformations. The observed correspondence between the dependence of the factor X on concentration of filler and the theoretical relationship given by eq. (2) indicates that the observed progressive increase in C_1 with filler concentration is unlikely to be due to an increase in density of crosslinking due to the filler. Thus it appears that the increase in C_1 shown in analysis of stress–strain curves reflects additional restrictions due to filler which manifest themselves at higher extensions. An increase in C_1 with filler concentration is to be anticipated in the results from swelling measurements. Adhesion of rubber to the surfaces of rigid filler particles will limit the swelling of rubber in the immediate vicinity of the filler particles and thus lead to an increase in the apparent value of C_1. The contribution of this process has been discussed by Kraus,[17] but no fully satisfactory treatment has been developed. In the absence of such a treatment the significance of the close correspondence shown over the whole range of filler concentrations between the values of C_1 derived from stress–strain measurements and swelling measurements is not understood.

Stress–Strain Behavior of Swollen Rubbers. It has previously been shown that for rubbers without fillers the value of $C_1 v_r^{1/3}$ determined at different degrees of swelling from simple extension stress–strain curves is independent of degree of swelling.[18] This behavior is theoretically pre-

dicted by the statistical theory.   The value of C_2, which describes departures from the statistical theory, decreases continuously with increase in degree of swelling until with highly swollen rubber ($v_r < 0.25$) it is negligibly small.   The value of λ^* also changes on swelling and shows the theoretically anticipated dependence on degree of swelling, viz., the effective deformation of the network chains produced by both extension and swelling and given by $(\lambda - 1)^* v_r^{-2/3}$ is approximately independent of the degree of swelling.

Figure 8 shows a typical family of stress–strain curves obtained on samples of rubber vulcanizate D.   The curves are plotted as $\frac{1}{2} F A_0^{-1} (\Lambda - \Lambda^{-2}) v_r^{1/3}$ against Λ^{-1}, where the appropriate strain amplification has been introduced in the values of Λ.   They show the independence of $C_1 v_r^{1/3}$ on degree of swelling established for rubbers without fillers, but although the values of Λ^* decrease progressively with increase in the degree of swelling the dependence is only approximately in agreement with that established on gum vulcanizates (Table IV).

TABLE IV

v_r	$C_1 v_r^{1/3}$, kg./cm.^{2}	$C_2 v_r^{1/3}$, kg./cm.^{2}	Λ^*	$(\Lambda^* - 1) v_r^{-2/3}$
1.00	2.00	0.58	2.13	1.13
0.943	2.02	0.25	2.0	1.03
0.725	2.02	0.17	1.7	0.86
0.590	2.00	0.06	1.6	0.86
0.390	2.00	0.05	1.4	0.76

HAF Carbon Black

Stress–Strain Behavior.   A similar analysis of stress–strain data was carried out on vulcanized rubbers containing the smaller particle sized HAF carbon black.   Figure 9 shows values of Young's modulus E determined from the linear portions of the stress–strain curves at low extensions plotted as a function of the volume concentration of the filler.   The full line in the figure was calculated from eq. (5) with a value of the shape factor f of 6.5; this value was chosen to give the best fit to the experimental results.

Figure 10 shows the experimental stress–strain curves plotted as $\frac{1}{2} F A_0^{-1} (\lambda - \lambda^{-2})^{-1}$ against λ^{-1}.   For all but the lowest concentration of black the curves show pronounced curvature.   This makes it difficult to derive estimates for C_1 and λ^*; qualitatively the value of C_1 increases and the value of λ^* decreases with increasing concentration of filler.

Figure 11 shows the curves replotted as $\frac{1}{2} F A_0 (\Lambda - \Lambda^{-2})$ against Λ^{-1} with the use of the strain-amplification factor to derive values of Λ from the measured values of λ.   The factor X was given by

$$X = 1 + 0.67 f c + 1.62 f^2 c^2$$

the empirically determined value of f for HAF black of 6.5 being used.   The use of the strain-amplification factor gives a linear portion of these curves
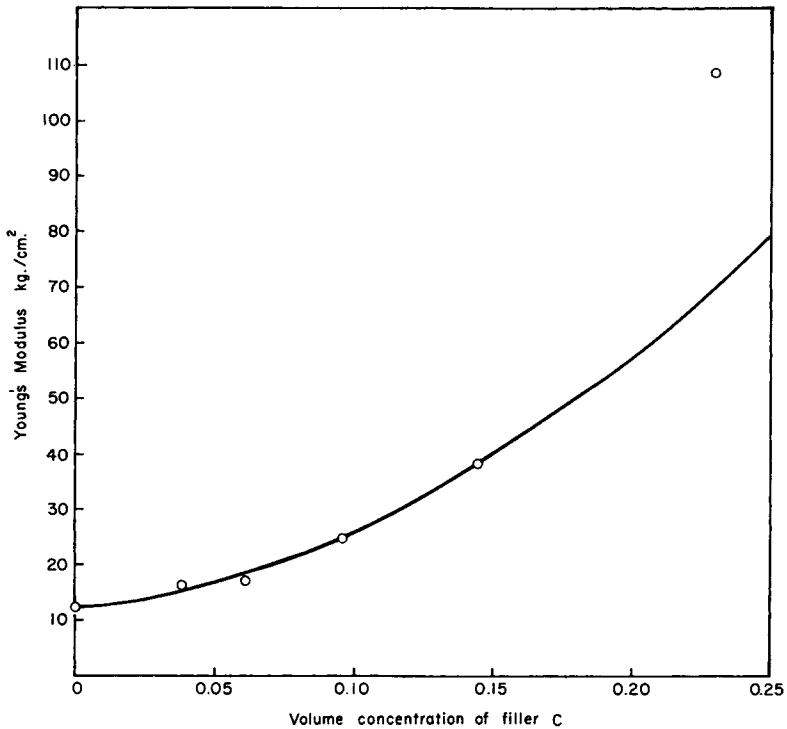
Fig. 9. Young's modulus of rubbers containing HAF carbon black as a function of concentration.

over a range of moderate and small extensions and permits values of C_1 and for the lower concentrations of filler values of Λ^* to be determined. These are given in Table V together with values of Young's modulus E and values of C_1 corresponding to the values of Λ^*; the latter were determined from the previously established relationship between λ^* and C_1.

TABLE V

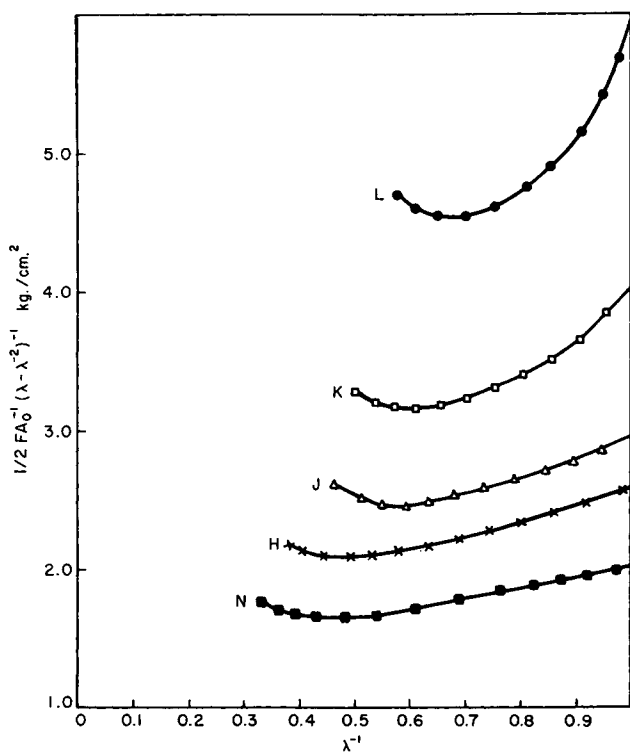| Vulcan-izate	Volume concen-tration of black c	Young's modulus E, kg./cm.^{2}	C_1 From stress–strain (corrected), kg./cm.^{2}	Λ^*	C_1 From Λ^* (corrected), kg./cm.^{2}
N	0	12.35	1.32	2.35	1.4
H	0.0383	16.06	1.42	2.30	1.5
J	0.0611	18.46	1.64	2.20	1.7
K	0.0954	24.86	1.82	2.15	1.9
L	0.144	38.51	1.96	—	—
M	0.233	108.3	—	—	—

Fig. 10. Stress–strain curves plotted as $1/2\, FA_0^{-1}(\lambda - \lambda^{-2})^{-1}$ against λ^{-1} (HAF carbon black).

In contrast to the behavior observed with MT black, the value of C_1 increases with each increase in concentration of HAF black. However the increases are relatively small.

Swelling Measurements. Table VI gives measurements of the equilibrium volume swelling v_r in n-decane after correction had been made for the volume of filler present and corresponding values of C_1 determined from the previously established calibration between C_1 and v_r.

TABLE VI

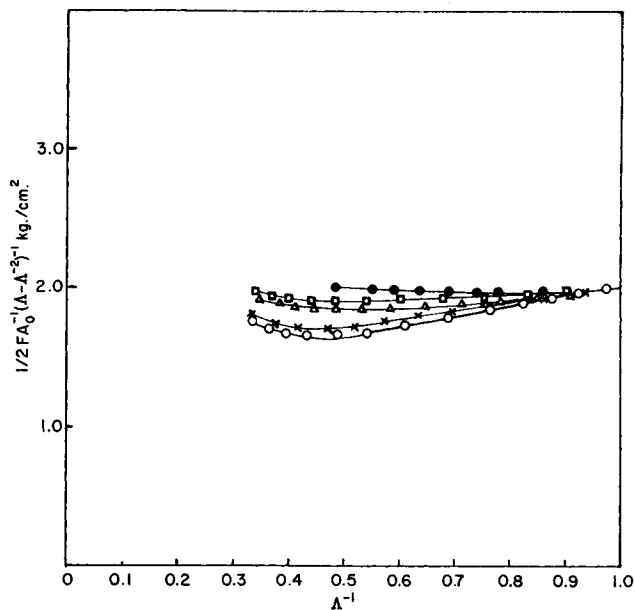| Vulcan-izate	Volume concentration of black c	v_r	From v_r	C_1, kg./cm.^{2} From stress–strain (corrected)	From Λ^* (corrected)
N	0	0.277	1.44	1.32	1.4
H	0.0383	0.289	1.60	1.42	1.5
J	0.0611	0.300	1.73	1.64	1.7
K	0.0954	0.319	2.02	1.82	1.9
L	0.144	0.337	2.36	1.96	—
M	0.233	0.368	2.85	—	—

Fig. 11. Stress–strain curves in Fig. 10 replotted with the use of the strain-amplification factor. Symbols as for Fig. 10.

Table VI also includes for comparison two other estimates of C_1 derived from stress–strain curves and from Λ^*. The three separate estimates are in fair agreement, and, to a first approximation, the results are consistent with the hypothesis that, for low and moderate concentrations of filler the effect of fillers on elastic behavior is merely to increase the actual strain present in the deformable rubber matrix—the average actual strain being X times the measured overall strain, where X is given by the ratio of Young's Moduli determined at a small extension on the filled and unfilled vulcanizates.

The observed progressive increase in C_1 with increase in concentration of filler (Table VI) indicates that it is no longer fully satisfactory to consider the rubber matrix as being completely unmodified by filler. Comparison of the values of C_1 determined from stress–strain relationships and from equilibrium volume swelling indicates that the use of the Flory-Huggins relation [eq. (8)] with the value of μ of 0.42 established for vulcanizates without filler results in somewhat larger estimates of the value of C_1 determined from volume swelling measurements.

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Résumé

Des mesures du module de Young sur des caoutchoucs vulcanisés contenant du noir de carbone thermique montrent la dépendance prévue vis à vis de la concentration volumétrique, donnée au moyen de la relation dérivée à partir d'une suspension de particules sphériques: par exemple celle de Guth, Simha et Gold qui donne $E = E_0 (1 + 2.5c + 14.1c^2)$. Une interprétation simple des résultats exprime que la tension dans le caoutchouc est augmentée par la présence de charges de sorte que la rapport de la tension moyenne à la tension globale mesurée est donée par le facteur $X = 1 + 2.5c + 14.1c^2$. Ce facteur est employé pour analyser les résultats d'une simple extension tension-élongation obtenues pour des extensions plus grandes. Dans ce but, la relation de Mooney-Rivlin est employée pour décrire le comportement de la phase caoutchouteuse. On obtient des valeurs de C_1 indépendantes de la concentration volumétrique et en accord assez proche des mesures du volume de gonflement à l'équilibre des caoutchoucs. Les valeurs de λ^* sont aussi en accord avec celles de C_1. L'analyse des résultats de tension-élongation obtenus sur des caoutchoucs contenant des petites particules de noir de carbone est incomplète. Pour ces substances la relation due à Guth c. à d. $E = E_0 (1 + 0.67fc + 1.62f^2 c^2)$ a été choisie. Par le chois de valeurs convenables, on obtient un bon accord avec la relation tension-élongation de Mooney-Rivlin pour des concentrations volumétriques inférieures à 0.15.

Zusammenfassung

Die Messung des Young-Moduls von vulkanisiertem Kautschuk mit einem Gehaltan thermischem Russ zeigt die nach der für eine Suspension sphärischer Teilchen abgeleiteten Beziehung zu erwartende Abhängigkeit von der Volumskonzentration, z.B. nach der Beziehung von Guth, Simha und Gold, welche $E = E_0 (1 + 2.5c + 14.1c^2)$ liefert. Eine einfache Interpretation der Ergebnisse liegt in der Annahme, dass die Verformung im Kautschuk durch die Anwesenheit eines Füllstoffes erhöht wird, so dass das Verhältnis zwischen mittlerer Verformung und gemessener Gesamtverformung durch den Faktor $X = 1 + 2.5c + 14.1c^2$ gegeben ist. Dieser Faktor wurde zur Analyse von Spannungs–Dehnungsdaten bei einfacher Dehnung im Bereich grosser Dehnung verwendet. Zu diesem Zweck wurde die Beziehung von Mooney-Rivlin zur Beschreigung des Verhaltens der Kautschukphase verwendet. Von der Volumskonzentration abhängige und mit der Messung der Gleichgewichtsvolumsmessung des Kautschuks in enger Übereinstimmung stehende Werte von C_1 wurden erhalten. Auch die Werte von λ^* waren mit denjenigen von C_1 in Übereinstimmung. Die Analyse der an Kautschuken mit Russen von kleinerer Teilchengrösse erhaltene Spannungs–Dehnungsdaten ist komplexer. Für diese Stofte wurde die Beziehung von Guth, nämlich: $E = E_0 (1 + 0.67fc + 1.62 f^2c^2)$ gewählt. Durch Wahl geeigneter Werte von f wurde bei Volumskonzentrationen unterhalb etwa 0.15 gute Übereinstimmung mit der Spannungs–Dehnungsbeziehung von Mooney-Rivlin erhalten.