The Dynamic Properties of Carbon Black Loaded Natural Rubber Vulcanizates. Part II

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INTRODUCTION

When rubber is compounded with carbon black the modulus, whether measured in shear, compression, or extension, is enhanced considerably above that of the unloaded "pure gum" rubber. Part of this enhancement is lost as the strain amplitude increases, and this change has been ascribed to a structure effect.[1,2] Even at strains sufficiently large for the structure to have been eliminated, the modulus is greater than that of the pure gum and, moreover, greater by more than the amount which can be predicted as due to hydrodynamic interaction of the filler particles. This paper is concerned with the difference in modulus between that proper to the pure gum rubber and, in the nomenclature of Part I,[2] the G_∞ value of the loaded rubber. G_∞ is the shear modulus, which is independent of strain at sufficiently high strains, i.e., at strains greater than those needed to break down any structure.

The difference between the G_∞ value and the modulus of the corresponding pure gum rubber may be regarded as due to the product of two factors: (a) a hydrodynamic interaction due to the filler particles, (b) a second factor for which evidence is given suggesting that it arises from a few strong linkages known to link filler particles to the matrix. The possible contributions from these two terms are now considered.

Figure 1 is a qualitative interpretation of the shear modulus strain curves of Figures 5 and 6 of the previous paper,[2] in terms of the three factors discussed above. Quantitatively, the facts regarding the difference between $G_{\text{pure gum}}$ and G_∞ may be expressed as:

$$G_\infty = G_{\text{pure gum}} f(f,c) \cdot F(A) \qquad (1)$$

where $f(f,c)$ is the hydrodynamic effect, well known to be dependent on the shape factor, f, of the filler particles or agglomerates, and on the volume con-

centration, c, of the filler, and $F(A)$ refers to the factor (b) in the above introduction.

Experimentally, a measure of $f(f,c)$ has been obtained from model vulcanizates using glass spheres as the filler, and of $F(A)$ from equilibrium swelling measurements on rubber vulcanizates containing carbon black. The results are reported and discussed in terms of eq. (1).

HYDRODYNAMIC EFFECTS

There have been several attempts to derive formulas giving the apparent modulus due to a dispersion of particles in rubber. The earliest of these attempts was by Smallwood[3] using an analogy to Einstein's viscosity equation:[4]

$$G = G_{\text{pure gum}} (1 + 2.5c) \qquad (2)$$

where G is the modulus of the filler loaded vulcanizate. Unfortunately, this equation holds only for low concentrations of filler and amendments were derived.[5–8] That of Guth and Gold,[7] by considering the interactions between pairs of particles, added the term involving the square of the concentration of filler to Smallwood's equation and obtained:

$$G = G_{\text{pure gum}} (1 + 2.5c + 14.1c^2) \qquad (3)$$

For nonspherical particles, Guth[9] introduced a shape factor, f (ratio of diameter to width of particle), and proposed:

$$G = G_{\text{pure gum}} (1 + 0.67fc + 1.62f^2c^2 + \cdots) \qquad (4)$$

These equations were derived on the assumption that the medium wets the filler particles, but does not chemically react with the filler surface.

An empirical formula suggested by Eilers and Van Dijck[10] is given by:

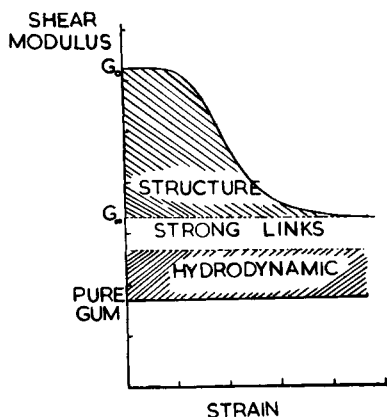$$G = G_{\text{pure gum}} \left(1 + \frac{1.25c}{1 - 1.28c}\right) \qquad (5)$$

Fig. 1. A qualitative interpretation of the shear modulus, strain amplitude curves.

Brinkman[11] obtained a similar formula as follows:

$$G = G_{\text{pure gum}} (1 - c)^{-5/2} \qquad (6)$$

This last equation gives values similar to eq. (5) up to a concentration of 0.3.

Van der Poel,[12] when studying bitumen–mineral aggregates, required a more exact equation than any of the above at the higher concentrations of filler. He derived theoretical values for the ratio of $G/G_{\text{pure gum}}$ by considering directly the rigidity of a concentration of elastic spheres in an elastic medium. If the ratio of the elasticity of the spheres to the elasticity of the rubber is 100,000 or greater, then the ratio of $G/G_{\text{pure gum}}$ for a range of concentrations was derived by van der Poel, and these values are given in Table I.

For any of the above theoretical expressions to be valid, the fillers should be completely dispersed, they must be either nearly spherical or nearly rod shaped, and there must be a complete wetting of the filler by the rubber.

One of the difficulties arising in a study of carbon black is to obtain a reliable estimate of the actual value of the shape factor for the carbon black chains in the vulcanizate. Examination of eq. (4), however, shows that only chains of lengths greater than

TABLE I
Ratios of Moduli of Loaded Rubber to Unloaded Rubber (after van der Poel)

Concn., c	$G/G_{\text{pure gum}}$	Concn., c	$G/G_{\text{pure gum}}$
0.10	1.3	0.50	8.1
0.20	1.7	0.60	21.4
0.30	2.5	0.65	42.5
0.40	4.1	0.70	78.7

five will have any appreciable effect on the $G/G_{\text{pure gum}}$ ratios. In addition, electron microscope evidence suggests that, although chain formation does survive milling, compounding, and vulcanization, the carbon black chain lengths are relatively short compared with those in the dry black. Initially it will be useful as an approximation to consider that the ultimate particle shape factor of the carbon black corresponds to that of a sphere ($f = 1$) or at most $f < 5$.

Experimental

Dynamic experiments of the type and with the apparatus previously described[2] were carried out on a range of vulcanizates of natural rubber containing glass spheres (Ballotini of 100 micron diameter). The measurements were carried out at very low dynamic strains ($<0.001\%$); and certainly at strains lower than that at which dewetting and vacuole formation occurs. Figure 2 shows the dynamic shear modulus plotted against the volume concentration for glass spheres and other fillers. It is convenient to plot the ratio $G/G_{\text{pure gum}}$ and this is done in Figure 3, which shows the smooth curve resulting from the experimental points for glass spheres from Figure 2, and compares this curve with theoretical ones derived from eqs. (2), (3), and (5), and the values given in Table I. It is apparent that none of the theoretical expressions is satisfactory at the higher concentrations of filler, although Eilers and Van Dijck's equation, and van der Poel's values are satisfactory up to a volume concentration of about 0.25 when $f = 1$.
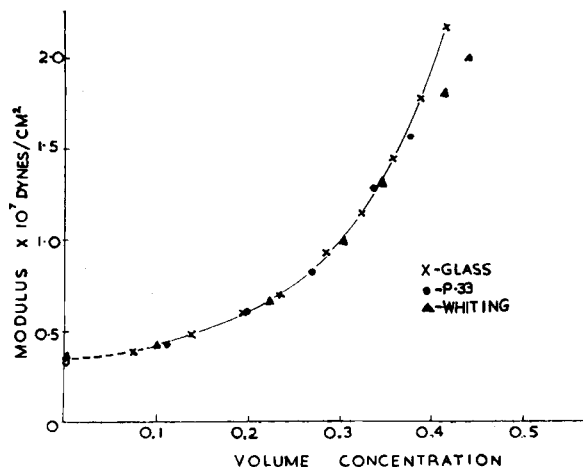

Fig. 2. Shear modulus–concentration relationship for glass spheres (crosses). Also data for a "nonstructure" black and ground whiting.
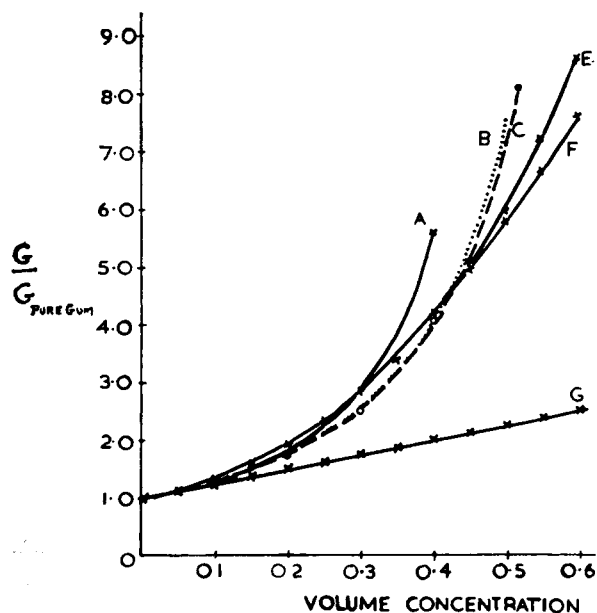
Fig. 3. Comparison with the theoretical equations of the increase in shear modulus for varying concentration of glass spheres in natural rubber: (A) Curve for glass spheres derived from Fig. 2. (B) Van der Poel values; see Table I. (C) Eilers and van Dyck values; eq. (5). (E) Eq. 3 with further terms. (F) Eq. 3. (G) Eq. 2.

A re-examination of the data discussed in van der Poel's paper reveals that he certainly obtained good agreement with his theory when he compared the experimental results of Eilers on an emulsion of bitumen particles in water. His theoretical values, however, gave lower values than the experimental for a polymethyl methacrylate–glass mixture. In addition, results on various types of aggregates in bitumen gave practical modulus values, which were slightly greater than his theoretical values over a concentration range of 0.2 to 0.5. In conclusion, one must infer from these comments and the experimental results of the glass–rubber vulcanizates, that the experimental results are slightly higher than any theory predicts at the higher concentrations. The actual experimental values for the rubber glass system are given in Table II, where

TABLE II
Estimation of $f(f,c)$ Due to Hydrodynamic Effects

Vol. concn., c	$f(f,c) = G/G_{\text{pure gum}}$	
	van der Poel	this paper
0.10	1.3	1.26
0.20	1.7	1.70
0.30	2.5	2.83
0.40	4.1	5.42

they are compared with van der Poel's theoretical values.

Figure 2 also shows the results for P33, a fine thermal black, and for ground whiting. This plot shows that, up to about 40% concentration of these materials, there is no difference in the results for glass, P33, or whiting.

Assessment of Hydrodynamic Effect

Although some of the equations give reasonable agreement with the observed data at low concentrations of filler, none do so at higher concentrations. However, we feel that only hydrodynamic effects can be present with the glass Ballotini, as apparently is also the case for whiting and P33 black, but that, instead of a function relating G to c and possibly f, the hydrodynamic effect is best allowed for empirically by using the ratio $G/G_{\text{pure gum}}$ given in Table II.

OTHER RUBBER-FILLER INTERACTION

There has been a considerable effort, apparent from the literature, to derive the many mechanisms by which rubber might be chemically combined with or strongly adsorbed on the carbon black surface.[13] Any linkage thus formed would increase the overall crosslinking, which can be determined by equilibrium swelling measurements on the carbon black loaded vulcanizates. The swelling ratio V_r, calculated from the volume of polymer only (i.e., excluding carbon black fillers, etc.) is given by:

$$V_r = \text{vol. polymer}/(\text{vol. polymer} + \text{vol. solvent}) \quad (7)$$

If the number of effective network chains per unit volume of rubber is γ, this quantity is then related to V_r by the Flory-Rehner equation:[14,15]

$$\gamma = -\frac{1}{V_s} \frac{[l_n(1 - V_r) + V_r + \mu V_r^2]}{V_r^{1/3}} \quad (8)$$

Where V_s is the molar volume of the solvent and μ is a parameter characteristic of the rubber/solvent interaction. The quantity γ is inversely proportional to the molecular weight (M_c) between "fixed points" in the network, and is taken to be a measure of the total contributions due to crosslinks, entanglements, and filler to rubber links. No attempt is made to separate these effects.

We now need to relate the effective number of network chains per unit volume to the elastic properties of the vulcanizate. This has been done from

the Mooney stored work functions and is given by Treloar[16] in the form:

$$G = -2(C_1 + C_2) \qquad (9)$$

In this equation C_1 is a modulus function associated with the degree of vulcanization and with filler-rubber bonds. $C_1 = (RT/2)\gamma$, where γ is given by eq. (8). Kraus[15] has similarly used this equation in cases in which a filler loaded rubber is involved. Mullins and Tobin[1] have shown that C_2 is approximately equal to C_1 for carbon black loaded vulcanizates[5] of natural rubber and hence we may write $G \propto C_1$. Hence, as C_1 can be estimated from equilibrium swelling measurements, these measurements will provide the *relative* magnitudes of the shear modulus.

Experimental

The values of C_1 obtained from equilibrium swelling measurements are given in Table III, column 2. Toluene was used as the solvent in these experiments and the value of $\mu = 0.391$ taken from Bristow and Watson.[17]

The third column in Table III shows the ratio of C_1 for the black loaded vulcanizate, divided by C_1 for the pure gum vulcanizate. This ratio is then as shown above, a measure of the increase in effective crosslinking when carbon black is added. This is the function $F(A)$ of eq. (1).

TABLE III
Estimation of $F(A)$ Due to Strong Rubber–Filler Linkages

Vol. carbon black, %	C_1, 10^6 dyne-cm.$^{-2}$	$\dfrac{C_1}{C_1 \text{ (pure gum)}} = F(A)$
0 (pure gum)	1.54	1.00
5.6	1.59	1.03
10.7	1.98	1.29
15.2	2.02	1.31
19.3	2.15	1.40
23.0	2.13	1.42
26.4	2.45	1.59
29.5	2.96	1.92
32.4	2.91	1.90
36.0	3.53	2.30
38.4	4.60	3.00

DISCUSSION

We have now considered the hydrodynamic effect and the other rubber–filler interaction ascribable to strong linkages between carbon black and rubber. Equation (1) may be rewritten as:

$$G_\infty/G_{\text{pure gum}} = f(f,c).F(A) \qquad (1A)$$

From Part I of this paper,[2] previously published, the values of G_∞ and $G_{\text{pure gum}}$, have been taken and are given in Table IV. Also given in Table IV is the product $f(f,c).F(A)$ obtained from the $f(f,c)$ values for inert fillers (actually glass spheres) a selection of which are given in Table II, and the $F(A)$ values given as the last column of Table III.

The validity of eq. (1A) is established by the agreement of columns 3 and 4 of Table IV for volumn loadings of 36% and less.

TABLE IV
Comparison of $G_\infty/G_{\text{pure gum}}$ and $f(f,c).F(A)$

Vol. carbon black, %	G_∞, 10^6 dyne-cm.$^{-2}$	$G_\infty/G_{\text{pure gum}}$	$f(f,c).F(A)$
0 (pure gum)	2.6	1.0	1.0
10.7	4.24	1.63	1.69
15.2	5.25	2.02	1.96
19.3	6.2	2.38	2.38
23.0	7.3	2.81	2.85
26.4	10.6	4.07	3.73
29.5	12.5	4.81	5.46
32.4	16.5	6.35	6.35
36.0	25.5	9.81	9.45
38.4	26.0	10.0	15.0

We are now in a position to put forward models that can be used to describe quantitatively the behavior of a rubber loaded with either of two types of finely divided filler, at any rate up to a loading of about 36% by volume. The quantitative data supporting these models are measurements of the dynamic shear modulus but the validity of the reasoning is not dependent on the precise form of deformation used. For fillers normally regarded as "inert," only a hydrodynamic effect exists, here designated $f(f,c)$ and predictable by van der Poel's theory[12] and less accurately by other equations discussed. Carbon black is referred to as a "reinforcing" filler in natural and other rubbers. The shear modulus is not explicable solely in terms of the hydrodynamic effect. There are two additional factors, one due to strong linkages existing between rubber and filler, here designated $F(A)$, and which is shown to be predictable from the number of such linkages measured by swelling in solvent and the effect such a number would be expected to have

from elasticity theory. Such an effect is only apparent, uncomplicated by other effects, at strains greater than that required to destroy a strain dependent structure which constitutes the third factor present with reinforcing fillers. At small dynamic strains or on an initial straining of a hitherto unstrained specimen, all three factors contribute to the measured modulus of a carbon black loaded vulcanizate.

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Synopsis

The dynamic shear modulus at very high strains, (G_∞), of carbon black filler loaded vulcanizates is regarded as due to the product of two factors: (*a*) a hydrodynamic interaction due to filler particles, and (*b*) a second factor for which evidence is given suggesting that it arises from a few strong linkages which are known to link filler particles to the matrix. Experimentally a measure of (*a*) has been obtained from model vulcanizates using glass spheres as the filler, and of (*b*) from equilibrium swelling measurements on rubber vulcanizates containing carbon black. Quantitatively, the difference between the shear modulus of the pure gum vulcanizate, $G_{\text{pure gum}}$, and G_∞ can be explained by these measurements.

Résumé

On considère le module de cisaillement dynamique à très haute élongation (G_∞) de vulcanisats chargés de noir de carbone comme le produit de deux facteurs: (*a*) une interaction hydrodynamique due aux particules de la charge; (*b*) un facteur dont l'apparition aux dépens de quelques liaisons solides existant entre la matrice et les particules de la charge est suggérée. Une mesure de (*a*) a été obtenue expérimentalement aux dépens de vulcanisats modèles où des sphères de verre jouent le role de charge. Le facteur (*b*) a été déterminé par des mesures de gonflement à l'équilibre sur des vulcanisats de caoutchouc contenant du noir de carbone. La différence entre le module de cisaillement d'un vulcanisat de caoutchouc pur, $G_{\text{pure gum}}$ et G_∞ peut être expliquée quantitativement à l'aide de ces mesures.

Zusammenfassung

Der dynamische Schermodul bei sehr hohen Verformungen (G_∞), von mit Russ gefüllten Vulkanisaten wird als das Produkt von zwei Faktoren betrachtet: (*a*) Eine hydrodynamische Wechselwirkung der Füllstoffteilchen und (*b*) ein zweiter Faktor, für welchen Hinweise gegeben werden, dass er durch einige wenige starke Bindungen verursacht wird, die bekannterweise zwischen den Füllstoffteilchen und der Matrix bestehen. Experimentell wurde ein Mass für (*a*) an Modellvulkanisaten unter Verwendung von Glaskügelchen als Füllstoff und für (*b*) aus Messungen des Quellgleichgewichts an Russ enthaltenden Kautschukteilchen erhalten. Der Unterschied zwischen dem Schermodul des reinen Kautschukvulkanisats, $G_{\text{reiner Kautschuk}}$, und G_∞ kann durch diese Messungen quantitativ erklärt werden.