

## Correlation of Vulcanizate Properties with Polymer-Black Interaction

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### Synopsis

The specific surface activity of carbon black, as indicated by amount of rubber bound to the black during the mixing process, has been found to be the major factor in determining the modulus of the vulcanizate at high extensions. However, modulus at low extension is independent of specific surface activity and mostly influenced by other black characteristics, such as "structure" and surface area. Further, a relationship of the Guth-Gold type based upon elastic theory was applied for predicting modulus of filled vulcanizates at high extension from that of an identically cured gum vulcanizate. The relationship is

$$M = M_0 (1 + 2.5\Phi + 14.1\Phi^2)$$

where  $\Phi$  is the reinforcement volume or volume fraction of filler plus volume fraction of bound polymer. This relationship was also used to calculate the actual elongation in a filled vulcanizate to compensate for that portion that does not elongate at all, and this actual extension ratio ( $\alpha'$ ) was utilized in the Mooney-Rivlin equation. The Mooney-Rivlin equation is the theoretical expression for the modulus of a vulcanizate as it changes with elongation and cure level (or number of effective chains per unit volume). The equation has been successfully used previously for gum vulcanizates, but not for filled vulcanizates. With the use of the corrected elongation ( $\alpha'$ ), experiment and theory are in much better agreement than previously, and a general concept of the influence of black upon vulcanizate properties can be postulated.

### INTRODUCTION

There are scores of excellent articles in the literature showing or attempting to show the correlation of some property of the vulcanizate with wearability or lifetime of the article during actual use. One of the earliest,<sup>1</sup> the work covered the period November 1940-February 1941, developed correlation coefficients between the various standard tests, and attempted to delineate the influence of one property, such as Shore hardness, upon resilience, abrasion resistance, or heat build-up. At about the same time,<sup>2-4</sup> correlations were being determined in natural rubber and neoprene between vulcanizate properties and simple physical characteristics of carbon black, such as surface area and particle size. With the development of newer and more reinforcing carbon blacks, the importance of the nature of the surface and oil absorption of the black became generally recognized

as factors in the reinforcement potential of a carbon black. The volume of work is enormous, and is well summarized and presented by Dannenberg,<sup>5</sup> Bolt and co-workers,<sup>6</sup> and Studebaker.<sup>7</sup>

By ultimate analysis of the carbon black, Studebaker<sup>8</sup> found correlations between modulus imparted to polymers and hydrogen content of the black. Another feature of reinforcing carbon black, the interaction of carbon black with polymer, was investigated by Watson,<sup>9</sup> who found that this interaction markedly affected the stress-strain properties of natural rubber vulcanizates. The work by Gessler and co-workers<sup>10</sup> on polymer-black interaction with Butyl is a classical examination of the phenomenon.

A consensus has been formed from the work on reinforcement that the more reinforcing the black, the smaller the particle size, the higher the oil absorption, and the greater the interaction with polymer. However, there are occasional exceptions noted that appear to contradict this generally accepted picture. Although modulus at 300% elongation was always decreased by heat-treating black, the Mooney viscosity might increase as a result of black heat treatment.<sup>11,12</sup> Since the reinforcement potential of a black can certainly be expected to be reflected by enhancement of "stiffness" or viscosity as well as by the amount of stress required to produce deformation in the vulcanizate, the contradictory behavior of heat-treated blacks in SBR-1500 is puzzling. Of more far-reaching concern has been the fact that the experimentally measured properties of carbon black reinforced polymers do not correspond to those expected based upon kinetic theory of elasticity or the Guth-Gold Einstein relationship for filler particles in a continuous matrix.<sup>13</sup> If the reasons for this lack of agreement between theory and practice could be discovered, then it should be that these same factors are those most important in determining the reinforcement potential of carbon blacks.

## EXPERIMENTAL

### Mixing and Torque Measurement

A Model PL-V31 Plasticorder was used in much of the mixing work. This model is equipped with temperature and shear rate controls. The torque measuring head, cam-style, was charged with 42.5 g. polymer, or 33.8 g. polymer plus 16.9 g. carbon black. Whenever necessary, preliminary runs were made to determine the temperature designed to give the actual desired batch temperature. Measurement of torque began as soon as the black was visually incorporated or, if a charging chute was used, when the chute closed tightly. Torque was measured directly on a continuous chart.

### Bound Rubber

A sample weighing approximately 0.2 g. was weighed on an analytical balance, cut into several small pieces, and placed into a preweighed, covered wire cage fabricated of 320-mesh stainless steel wire cloth. The cage con-

taining the sample was placed into a 4-oz. stoppered bottle containing 100 ml. of solvent. The sample was stored at room temperature ( $22 \pm 2^\circ\text{C}.$ ) for the required period of time (3 days for *cis*-polybutadiene and styrene-butadiene polymers.). The cage containing the bound rubber gel was then removed from the solvent, vacuum-dried at  $50^\circ\text{C}.$  to a constant weight, and then reweighed. Per cent bound rubber was calculated as percentage of rubber bound of the total amount of rubber available:

$$\text{Bound rubber (\%)} = 100 (W_d - F)/R$$

where  $W_d$  = weight of dried gel,  $F$  = weight of filler in gel (same as weight of filler in original sample),  $R$  = weight of polymer in original sample.

## DISCUSSION

To define the influence of each factor upon raw and cured polymer properties, it is obvious that as much as possible all other possible variables must be either known or remain constant. The carbon blacks varied in "structure," surface area, and polymer-black interaction, but these were easily determined. The importance of using a polymer that does not seriously change in molecular weight has been discussed in another paper.<sup>12</sup> To make valid comparisons of vulcanizate properties, it is important that a fundamental standard of comparison can be utilized. It is obviously unfair to compare the modulus of vulcanizates at different molecular weight between crosslinks  $M_c$  and number of chains per unit volume  $\nu$  when we are seeking to determine the contribution of the black to modulus. Equally unfair would be to use time of cure to optimum modulus development as the point at which to make comparisons. In order to compare vulcanizates at equivalent crosslink density, the swelling technique described by Kraus<sup>15</sup> was used, and cure times chosen for a selected reinforcement volume (volume fraction rubber in swollen gel)  $V_r$ . Although this is not without objection because of the apparent increase in crosslink density with the addition of reinforcing blacks,<sup>16-19</sup> it does represent an equitable basis of comparison, and the differences that exist in the number of chains present per unit volume because of the effect of carbon black may not be great enough to obscure the more important trends. In some fine work on reinforcement, Zapp and Guth<sup>13</sup> recognized this necessity of making comparisons at equivalent crosslink density and solved it to their satisfaction by using Butyl crosslinked to maximum state of vulcanization.

### Guth-Gold Modulus Relationship

In work on concentrated suspension, Guth and Gold<sup>20</sup> extended the well-known Einstein relationship for the viscosity of suspensions to obtain

$$\eta = \eta_0 (1 + 2.5c + 14.1c^2)$$

where  $\eta$  and  $\eta_0$  are viscosity of the suspension and of the solvent, respectively, and  $c$  is volume fraction of filler. The equation was obtained from

the hydrodynamics of viscous liquids. The suspended particles perturb the flow in the viscometer, and this perturbation increases the energy dissipated which is reflected in an increase in the viscosity of the solvent. Application of elastic theory<sup>21</sup> produced a similar relationship for Young's modulus, that is, the slope of the stress-strain curve at the origin. It is valid, however, for other points in the stress-strain curve as long as the stress-strain curves for the loaded stock differ from that of the gum stock by a multiplicative factor. The presence of polymer bonded to carbon black increases the volume above that of the carbon black alone and therefore increases the volume throughout which energy is dissipated during

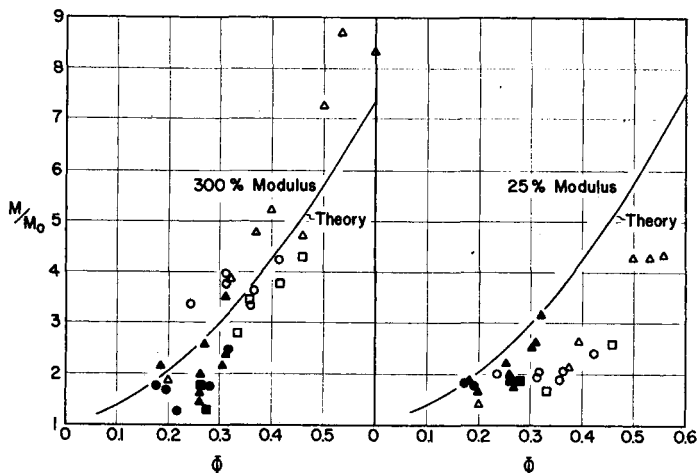


Fig. 1. Comparison of observed modulus with theoretical modulus based on reinforcement volume. ( $\square$ )  $\nu <$  gum control; ( $\circ$ )  $\nu =$  gum control; ( $\triangle$ )  $\nu >$  gum control. Solid symbols represent graphitized blacks.

tension in excess to that required by the presence of filler alone. This total volume, volume fraction filler plus volume fraction bound polymer, or reinforcement volume  $\Phi$ , becomes the factor responsible for modulus of reinforced vulcanizates rather than the volume fraction of filler  $c$  only. The relationship is similar to that of Guth-Gold

$$M = M_0 (1 + 2.5\Phi + 14.1\Phi^2) \quad (1)$$

This relationship, to be valid, requires that there is no change in molecular weight of the primary chains during processing. For the purpose a stereo-polybutadiene that has been found to undergo no important change in molecular weight during processing was used<sup>12</sup> rather than Butyl, which does show some changes.

The blacks studied and the data obtained are given in Table I. The data in Figure 1 show the agreement of 300% modulus and 25% modulus values with the curves calculated by using eq. (1). It is striking that for

300% modulus agreement of observed with calculated values is excellent on the basis of the concept of reinforcement volume, while observed values for 25% modulus are too low. This correlation implies that while modulus at 300% elongation is the result of added energy dissipation during tension caused by the presence of bound rubber, modulus at 25% elongation

TABLE I  
Properties Imparted to Cis-4 by Carbon Blacks

| Black <sup>a</sup> | Volume | Bound rubber |       | $\phi^b$ | Modulus, psi |      | Number of chains $\nu \times 10^{-4}$ , mole/cc. |
|--------------------|--------|--------------|-------|----------|--------------|------|--|
|                    |        | Wt-%         | Vol-% |          | 25%          | 300% |  |
| None               | —      | —            | —     | —        | 63           | 197  | 1.12   |
| ISAF               | 16.1   | 23.0         | 24.5  | 0.332    | 105          | 553  | 1.05   |
| ISAF (g)           | "      | 5.0          | 5.3   | 0.175    | 112          | 342  | 1.11   |
| HS-ISAF            | "      | 21.0         | 22.4  | 0.314    | 127          | 736  | 1.11   |
| HS-ISAF (g)        | "      | 7.4          | 7.9   | 0.196    | 108          | 319  | 1.11   |
| CF                 | "      | 12.5         | 13.3  | 0.240    | 125          | 661  | 1.12   |
| CF (g)             | "      | 6.3          | 6.7   | 0.186    | 117          | 424  | 1.18   |
| Thermal            | 26.9   | —            | —     | 0.202    | 89           | 367  | 1.35   |
| Thermal (g)        | "      | —            | —     | 0.202    | 101          | —    | 1.29   |
| GPF                | "      | 13.6         | 14.5  | 0.310    | 120          | 780  | 1.12   |
| FEF                | "      | 19.6         | 20.9  | 0.359    | 113          | 663  | 0.66   |
| CRF                | "      | 19.5         | 20.8  | 0.358    | 118          | 643  | 1.12   |
| HAF                | "      | 21.9         | 23.3  | 0.377    | 133          | 951  | 1.18   |
| ISAF               | "      | 26.4         | 28.1  | 0.413    | 147          | 832  | 1.14   |
| ISAF (g)           | "      | 7.6          | 8.1   | 0.263    | 134          | 391  | 1.52   |
| HS-ISAF            | "      | 33.3         | 35.4  | 0.467    | 159          | 844  | 1.04   |
| HS-ISAF (g)        | "      | 8.2          | 8.7   | 0.267    | 121          | 318  | 1.26   |
| CF                 | "      | 24.4         | 26.0  | 0.396    | 166          | 1030 | 1.35   |
| CF (g)             | "      | 7.9          | 8.4   | 0.265    | 118          | 344  | 0.90   |
| EPC                | "      | 21.1         | 22.4  | 0.370    | 130          | 704  | 1.11   |
| MPC                | "      | 26.4         | 28.1  | 0.413    | 122          | 736  | 1.05   |
| MPC (g)            | "      | 8.4          | 8.9   | 0.269    | 113          | 274  | 1.18   |
| ISAF               | 34.8   | 38.1         | 40.5  | 0.534    | 266          | 1610 | 1.52   |
| ISAF (g)           | "      | 8.5          | 9.1   | 0.311    | 164          | 460  | 1.26   |
| HS-ISAF            | "      | 41.6         | 44.3  | 0.560    | 269          | —    | 1.25   |
| HS-ISAF (g)        | "      | 7.4          | 7.9   | 0.303    | 163          | 424  | 1.35   |
| CF                 | "      | 33.9         | 36.1  | 0.501    | 266          | 1420 | 1.23   |
| CF (g)             | "      | 10.1         | 10.8  | 0.318    | 199          | 696  | 1.26   |
| Thermal            | 40.0   | —            | —     | 0.274    | 119          | 502  | 1.19   |
| Thermal (g)        | "      | —            | —     | 0.274    | 119          | 239  | 0.93   |

<sup>a</sup> (g) designates graphitized blacks.

<sup>b</sup>  $\phi$  = Volume black plus volume bound rubber/total volume.

does not depend upon polymer-black interaction. This behavior at 25% elongation is in agreement with the conclusions of Payne and Watson,<sup>22</sup> who have shown that modulus at low elongations is due chiefly to the structure of the carbon black agglomerate. We have now found indications that modulus at high elongations is due chiefly to the presence of a filler plus a factor that reflects the specific surface activity of the black.

### Mooney-Rivlin Modulus Relationship

The theory of rubber elasticity for vulcanizate in simple extension requires that

$$f/A_0 = \nu kT (\alpha - \alpha^{-2}) \quad (2)$$

where  $\nu$  is the density (number) of network chains per unit volume and  $\alpha$  is extension. The generalized theory for large elastic deformations suggested by Mooney, developed by Rivlin, and beautifully utilized by Mullins<sup>23</sup> has the form

$$f/2A_0 = (\alpha - \alpha^{-2}) (C_1 + C_2/\alpha) \quad (3)$$

where

$$C_1 = \frac{1}{2} \nu kT \quad (4)$$

$$C_2 = \frac{1}{2} RT \rho/M_c \quad (5)$$

and where  $M_c$  is number-average molecular weight between crosslinks,  $\rho$  is polymer density, and  $R$  is the gas constant ( $8.3144 \times 10^7$  erg/deg.-mole). Mullins has shown that by obtaining the full stress-strain curve of either swollen or unswollen gum vulcanizates and plotting  $f/2A_0 (\alpha - \alpha^{-2})$  versus  $1/\alpha$ , the intercept  $C_1$  is the measure of the number of chains per unit volume, and more importantly, that when done in the dry state, it is more convenient and accurate than swelling measurements. It would be especially informative to apply eq. (3) to reinforced vulcanizates, since we would obtain an independent measure of crosslink density ( $\rho/2M_c$ ) to compare with that measured by swelling and gain some insight into the phenomenon of restricted swelling found for black reinforced vulcanizates. Secondly, from the curve we could show the role of black upon modulus at low and high elongations. However, with filled vulcanizates, the data plotted according to eq. (3) give parabolic curves from which it is impossible to determine a  $C_1$  or a  $C_2$ .

Zapp and Guth<sup>13</sup> remarked upon the importance of comparing vulcanizates at equal states of extension. They show that modulus of a swollen vulcanizate equals that of the unswollen control at a higher elongation, the added elongation calculated to compensate for the extension of the chains in the swollen specimen. They used the assumption that the average linear extension of the polymer chains in the swollen vulcanizate is proportional to the cube root of the volume increase.<sup>24</sup> I have assumed that extension occurs chiefly in the unbonded portion of the polymer matrix, and that the bound polymer that reflects, at least roughly, the specific effects of reinforcing carbon blacks, should be considered as part of the solid filler phase.

The relationship given in eq. (1) that shows the influence of concentration of filler plus bound rubber on vulcanizate properties was utilized to calculate the actual elongation of the polymer matrix ( $\alpha'$ ) to compensate for the presence of a second phase that elongates not at all. This elongation

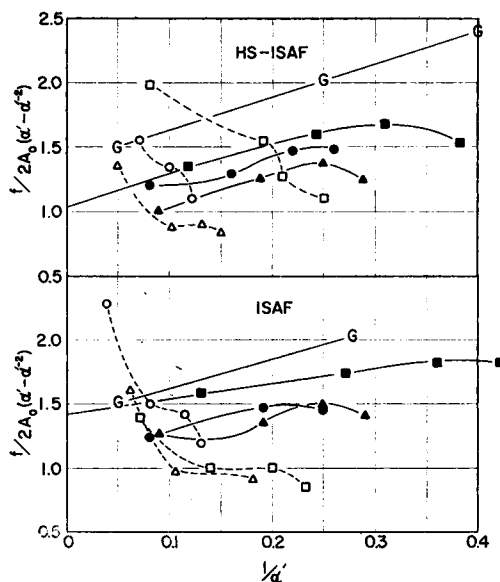


Fig. 2. Dependence of stress-strain behavior on black level and treatment. ( $\square$ ) 30 phr black; ( $\Delta$ ) 50 phr black; ( $\circ$ ) 65 phr black; ( $G$ ) gum. Solid symbols represent graphitized blacks.

now based on polymer only may enable us to apply to reinforced vulcanizates kinetic theory relationships that have so far been found valid only with gum vulcanizates. The curves have been transformed to compare with those obtained by Mullins for gum vulcanizates and are no longer parabolic in shape. The data in Figures 2 and 3 were obtained on vulcanizates at approximately equivalent crosslink density reinforced with different amounts of black. Figure 4 gives data on vulcanizates containing equal volumes of black but cured with different sulfur/accelerator levels.

The curves all possess the same three distinct features. At lower elongations (highest  $1/\alpha'$ ), the value of  $f/2A_0 (\alpha' - \alpha'^{-2})$  increases with increasing elongation and then becomes linear. The elongation at which the curves become linear is designated as  $1/\alpha'_1$ . The curves remain linear over a range of elongation and then show an abrupt increase for  $f/2A_0 (\alpha' - \alpha'^{-2})$  with further elongation. The point at which this occurs is designated as  $1/\alpha'_2$ .

The curves differ in one respect. The curves for the graphitized blacks are similar to that of a gum vulcanizate showing a positive slope for  $f/2A_0 (\alpha' - \alpha'^{-2})$  versus  $1/\alpha'$ . With standard blacks the curve possesses a definite plateau over a range of elongation, the value of  $C_2$  is zero, and the dependence of force on deformation is described by  $C_1$ .

As shown by Mullins, the curves may be used to describe what is occurring during extension. The linear portion is extrapolated to obtain  $C_1$ . The point at low elongation ( $1/\alpha'_1$ ), where the curve becomes linear, represents the elongation at which finite extension of the polymer chains

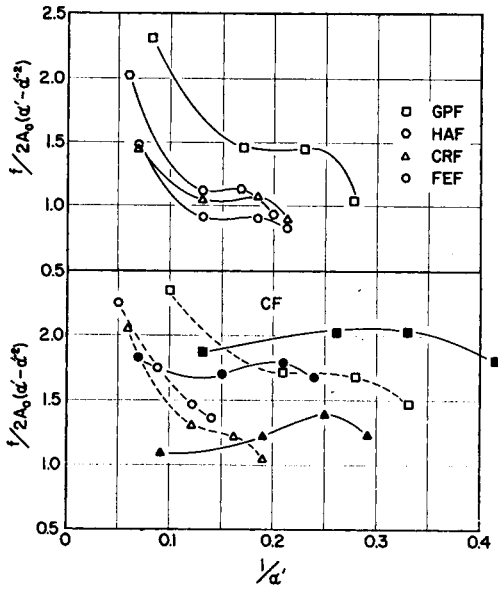


Fig. 3. Dependence of stress-strain behavior on black level and type. ( $\square$ ) 30 phr black; ( $\Delta$ ) 50 phr black; ( $\circ$ ) 65 phr black. Solid symbols represent graphitized blacks.

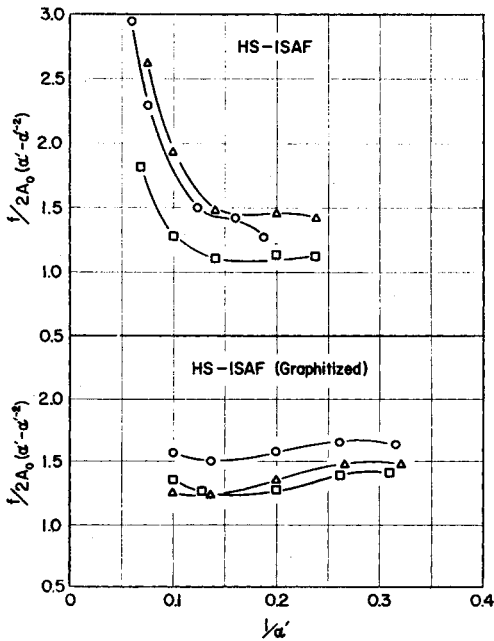


Fig. 4. Dependence of stress-strain behavior on sulfur/accelerator level. ( $\square$ ) low sulfur; ( $\Delta$ ) medium sulfur; ( $\circ$ ) high sulfur.



begins. The curve departs from linearity at a higher elongation ( $1/\alpha'_2$ ) at which the chain has become fully extended and increased force becomes necessary, sufficient to produce chain rupture. This is illustrated in Figure 4, which compares vulcanizates differing only in sulfur/accelerator level. As sulfur/accelerator was increased,  $C_1$  increased and the change from linearity seen to occur at higher  $1/\alpha'_2$ , while the  $1/\alpha'_1$  at which the curve becomes linear, is unchanged. If, as we have stated, this change to constant slope represents the elongation at which finite extensibility first comes into play, then up to this elongation ( $1/\alpha'_1$ ) modulus must be strongly influenced by some other factors. One of these other factors can be reinforcement volume as indicated by the correlations shown in Figure 1. In Figure 5 the correlation between  $\Phi$  and  $1/\alpha'_1$  is shown for several vulcanizates containing different levels of different type blacks, graphitized

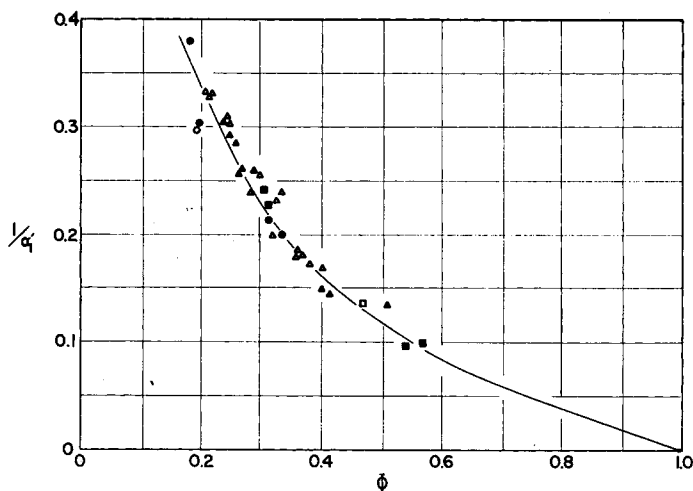


Fig. 5. Influence of reinforcement volume at low stress level.

and ungraphitized. Considering the accuracy of all the data and the visual determination of  $1/\alpha'_1$ , the agreement within the data is excellent. We can postulate, therefore, that at very low elongation the stresses are absorbed by the black as suggested also by others<sup>22,23</sup> and with increasing elongation the stresses are absorbed within the black and within the rubber bound to it by interaction with the active sites on the carbon black agglomerate. Energy continues to be dissipated at this level by the movement of chemical crosslinks within the rubber network until complete extension of the crosslinked matrix is reached. A sharp increase in stress necessary to rupture the polymer chains then occurs. With the graphitized blacks, as well as with the gum vulcanizates, there is a slight decrease in stress with continuing extension. This probably reflects the absence of any strong binding between black and polymer or greater mobility of the carbon black agglomerate within the crosslinked matrix. Either would result in some

relief of the applied stress and lessen the required incremental stress to maintain constant rate of movement of the polymer chains.

$C_1$  versus  $\nu \times 10^{-4} (V_r)$

From eq. (5) we can see that  $C_1/RT$  is equal to  $\rho/2M_c$ . It has been stated that  $C_1/RT$  determined from stress-strain properties equals the number of effective crosslinks<sup>25</sup> and will differ from the total number calculated by the technique described by Kraus<sup>15</sup> by some additive factor representing entanglements.

The molecular weights between crosslinks ( $M_c$ ) calculated by both techniques are given in Table II. There is a very obvious lack of agreement between  $M_c$  calculated by the two methods. There does appear to be some influence of reinforcement volume, but by plotting the ratio of  $2C_1(RT)^{-1}/\nu$  versus  $\Phi$ , two curves, one for graphitized black and another for standard blacks, were obtained. Recalling the postulate that the maximum point in the curve occurs at the elongation at which finite extensibility first comes

TABLE II  
Calculation of Physical Parameters of Vulcanizates

| Black   | Batch no. <sup>a</sup> | $\Phi$ | $C_1 \times 10^6$ ,<br>dyne/cm. <sup>2</sup> | Number of<br>chains $\nu \times$<br>$10^{-4}$ , mole/cc. |               | $M_c \times 10^{4b}$ |               |
|---------|------------------------|--------|--|--|---------------|----------------------|---------------|
|         |                        |        |  | From<br>$C_1$  | From<br>$V_r$ | From<br>$C_1$        | From<br>$V_r$ |
| None    | 1484                   | 0      | 1.35   | 1.15   | 1.12          | 0.800                | 0.775         |
| ISAF    | 1493                   | 0.332  | 1.00   | 0.85   | 1.05          | 1.05                 | 0.820         |
|         | 1494 (g)               | 0.175  | (1.85)                                       | 1.58   | 1.11          | 0.595                | 0.785         |
|         | 1475                   | 0.413  | 0.95   | 0.81   | 1.14          | 1.10                 | 0.760         |
|         | 1476 (g)               | 0.263  | (1.50)                                       | 1.28   | 1.52          | 0.725                | 0.585         |
|         | 1487                   | 0.534  | 1.42   | 1.21   | 1.52          | 0.765                | 0.585         |
| HS-ISAF | 1488                   | 0.311  | (1.47)                                       | 1.25   | 1.26          | 0.740                | 0.695         |
|         | 1495                   | 0.314  | 1.25   | 1.07   | 1.11          | 0.860                | 0.755         |
|         | 1496 (g)               | 0.196  | (1.67)                                       | 1.42   | 1.11          | 0.655                | 0.755         |
|         | 1477                   | 0.467  | 0.87   | 0.74   | 1.04          | 1.19                 | 0.830         |
|         | 1478 (g)               | 0.267  | (1.40)                                       | 1.19   | 1.26          | 0.775                | 0.695         |
| CF      | 1489                   | 0.560  | 1.30   | 1.11   | 1.25          | 0.825                | 0.700         |
|         | 1490 (g)               | 0.303  | (1.48)                                       | 1.27   | 1.35          | 0.735                | 0.650         |
|         | 1479                   | 0.396  | 1.23   | 1.05   | 1.35          | 0.870                | 0.650         |
|         | 1480 (g)               | 0.265  | (1.37)                                       | 1.17   | 0.90          | 0.790                | 0.945         |
|         | 1491                   | 0.501  | 1.40   | 1.19   | 1.23          | 0.775                | 0.710         |
| Thermal | 1492 (g)               | 0.318  | (1.75)                                       | 1.49   | 1.26          | 0.625                | 0.695         |
|         | 1497                   | 0.240  | 1.67   | 1.43   | 1.12          | 0.655                | 0.775         |
|         | 1498 (g)               | 0.186  | (2.05)                                       | 1.75   | 1.18          | 0.545                | 0.735         |
|         | 1469                   | 0.202  | 1.51   | 1.29   | 1.35          | 0.725                | 0.650         |
|         | 1470 (g)               | 0.202  | (1.68)                                       | 1.43   | 1.29          | 0.655                | 0.680         |
|         | 1485                   | 0.274  | 1.32   | 1.13   | 1.19          | 0.815                | 0.730         |
|         | 1486 (g)               | 0.274  | (1.22)                                       | 1.04   | 0.93          | 0.875                | 0.920         |

<sup>a</sup> (g) designates runs with graphitized blacks.

<sup>b</sup> Corrected for free ends.

into consideration, we recalculated  $C_1$  using this point rather than extrapolating the linear slope of the curve to zero  $1/\alpha'$ . These data are shown in parentheses in Table II. Considerable scatter in the data is still present, but agreement between graphitized and standard blacks is much improved. Generally, the number of chains calculated on the basis of  $C_1$  is less than the number of chains derived from swelling measurements, as would be expected if  $C_1$  represents only effective chains while swelling is influenced by the total number of chains including those caused by entanglements.

To examine this difference in results depending upon the method used for calculation, additional data were obtained with vulcanizates containing graphitized or nongraphitized black cured with different sulfur/accelerator levels (Table III). Careful examination of the data shows that the two methods give the best agreement in  $M_c$  (or number of chains) when there is no or very little bound rubber formed during mixing, that is, with the graphitized blacks. The comparison is shown in Figure 6. The values obtained with the graphitized blacks fall on or very close to the curve with a slope of 1 that indicates exact coincidence for the results obtained with the two methods.

The data obtained with a black of very low order of specific surface activity, such as thermal black, yield a curve of slope less than 1. When the specific surface activity of the black used was quite high, indicated by

TABLE III  
Number of Chains Calculated from Stress-Strain and Swelling Data

| Black <sup>a</sup> | $\Phi$  | Bound<br>rubber,<br>% | $C_1 \times$<br>$10^6$ | $V_r$   | Sulfur,<br>phr <sup>b</sup> | $M_c \times 10^3$<br>(corrected) |               | $2C_1 -$<br>$(RT)^{-1/2}$ |
|--------------------|---------|-----------------------|------------------------|---------|-----------------------------|----------------------------------|---------------|---------------------------|
|                    |         |                       |                        |         |                             | From<br>$C_1$                    | From<br>$V_r$ |                           |
| Thermal            | 0.202   | 0                     | 1.51                   | 0.387   | 1.25                        | 7.20                             | 5.90          | 0.808                     |
|                    | (0.202) | (0)                   | (1.58)                 | (0.398) | (1.50)                      | (6.92)                           | (5.48)        | (0.783)                   |
|                    | 0.202   | 0                     | 1.75                   | 0.418   | 2.00                        | 6.28                             | 4.68          | 0.730                     |
| ISAF               | 0.413   | 26.6                  | 1.10                   | 0.386   | 1.00                        | 9.63                             | 5.90          | 0.590                     |
|                    | (0.400) | (25.0)                | (1.18)                 | (0.396) | (1.25)                      | (9.01)                           | (5.56)        | (0.590)                   |
|                    | 0.397   | 24.5                  | 1.27                   | 0.416   | 1.50                        | 8.41                             | 4.80          | 0.545                     |
| ISAF (g)           | 0.202   | 0                     | 1.61                   | 0.368   | 1.25                        | 6.77                             | 6.85          | 1.01                      |
|                    | (0.250) | (6.1)                 | (1.42)                 | (0.382) | (1.50)                      | (7.60)                           | (6.10)        | (0.796)                   |
|                    | 0.232   | 3.8                   | 1.66                   | 0.402   | 2.00                        | 6.60                             | 5.34          | 0.796                     |
| HS-ISAF            | 0.362   | 20.0                  | 1.02                   | 0.350   | 1.00                        | 10.25                            | 7.80          | 0.740                     |
|                    | (0.421) | (27.4)                | (1.12)                 | (0.402) | (1.25)                      | (9.40)                           | (5.34)        | (0.540)                   |
|                    | 0.425   | 28.0                  | 1.24                   | 0.420   | 1.50                        | 8.62                             | 4.63          | 0.515                     |
| HS-ISAF (g)        | 0.202   | 0                     | 1.70                   | 0.373   | 1.25                        | 6.43                             | 6.57          | 1.02                      |
|                    | (0.239) | (4.6)                 | (1.55)                 | (0.386) | (1.50)                      | (7.03)                           | (5.90)        | (0.833)                   |
|                    | 0.227   | 3.1                   | 1.75                   | 0.402   | 2.0                         | 6.26                             | 5.34          | 0.868                     |
|                    | (0.250) | (6.2)                 | (1.45)                 | (0.359) | (1.25)                      | (7.45)                           | (7.25)        | (1.03)                    |
|                    | 0.243   | 5.1                   | 1.50                   | 0.364   | 1.50                        | 7.25                             | 7.00          | 1.02                      |
|                    | (0.246) | (5.5)                 | (1.70)                 | (0.392) | (2.00)                      | (6.45)                           | (5.70)        | (0.93)                    |

<sup>a</sup> (g) designates graphitized blacks.

<sup>b</sup> All stocks contained 1.0 phr accelerator.

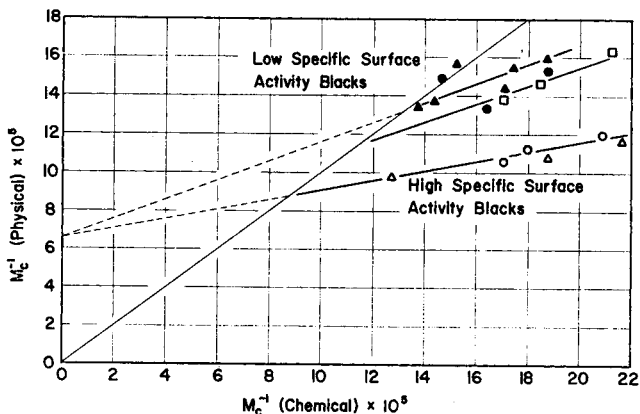


Fig. 6. Comparison of chemical and physical measurements of crosslink density. ( $\Delta$ ) ISAF; (O) ISAF-HS; ( $\square$ ) thermal blacks. Solid symbols represent graphitized blacks.

bound rubber, the slope of the curve was further decreased. These two different curves can be extrapolated back to the  $x$ -axis where they meet at a point that represents an  $M_c$  of 15,000. This value is in excellent agreement with that of Mullins<sup>23</sup> and close to that suggested by Bueche<sup>28</sup> as that at which entanglements became important in their influence on polymer properties.

### Modulus in Different Polymers

In Table IV are listed data obtained with three levels of HS-ISAF black, standard and graphitized, in SBR-1500 and stereo-polybutadiene. These data illustrate the means by which polymers are reinforced.

At each level of black, the moduli for the polymers are remarkably similar. At the highest elongations, above 200%, with standard blacks the modulus for SBR-1500 and EPT vulcanizates becomes higher than for the polybutadiene, and this is attributable to the higher cure level (greater number of chains) in these vulcanizates. In all polymers, there are only minor differences in modulus at low elongation imparted by graphitized and non-graphitized black. As elongation increases, the difference in modulus between graphitized and nongraphitized blacks becomes great, by almost a factor of three. The only important change in the black as a result of graphitization has been a marked loss in surface activity and thus a marked decrease in level of interaction between black and polymer. The similarity in modulus at low elongation for the graphitized and nongraphitized blacks suggests that at lower elongation it is mainly the volume and structure of the carbon black and polymer. As elongation is increased it is the reinforcement volume that becomes the important factor, all other factors being equal, in determining the modulus of the vulcanizate. The action of carbon black is indicated not to be specific to a polymer, but general in nature, reflecting its "structure" and specific surface activity.

TABLE IV  
Modulus of Polymers Reinforced with HS-ISAF Carbon Black

| Type             | Level,<br>phr | Poly-<br>mer <sup>a</sup> | Modulus, psi |     |      |      |      |      | Bound<br>rubber,<br>% |
|------------------|---------------|---------------------------|--------------|-----|------|------|------|------|-----------------------|
|                  |               |                           | 25%          | 50% | 100% | 200% | 300% | 400% |                       |
| Standard         | 30            | BR                        | 127          | 171 | 237  | 421  | 736  | 1136 | 21.0                  |
|                  |               | SBR                       | 117          | 161 | 227  | 470  | 950  | 1559 | 21.4                  |
| Graphi-<br>tized | 30            | BR                        | 108          | 148 | 188  | 249  | 319  | 414  | 7.5                   |
|                  |               | SBR                       | 94           | 120 | 152  | 212  | 298  | 421  | 9.6                   |
| Standard         | 50            | BR                        | 159          | 201 | 262  | 490  | 844  | 1293 | 33.3                  |
|                  |               | SBR                       | 175          | 211 | 290  | 610  | 1161 | 1754 | 33.8                  |
|                  |               | EPT                       | —            | 199 | 351  | 865  | 1636 | —    | —                     |
| Graphi-<br>tized | 50            | BR                        | 121          | 159 | 194  | 253  | 318  | 416  | 8.2                   |
|                  |               | SBR                       | 121          | 153 | 195  | 286  | 427  | 651  | 9.4                   |
|                  |               | EPT                       | —            | 164 | 205  | 285  | 420  | —    | —                     |
| Standard         | 65            | BR                        | 269          | 387 | 598  | 1001 | —    | —    | 41.6                  |
|                  |               | SBR                       | 267          | 334 | 495  | 1138 | 1928 | 2542 | 46.2                  |
| Graphi-<br>tized | 65            | BR                        | 163          | 193 | 232  | 311  | 424  | 577  | 7.4                   |
|                  |               | SBR                       | 165          | 198 | 251  | 383  | 593  | 960  | 8.9                   |

<sup>a</sup> BR = stereo-*cis*-polybutadiene rubber; SBR = styrene-butadiene rubber; EPT = ethylene-propylene terpolymer.

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### Résumé

L'activité spécifique de la surface du noir de carbone, indiquée par la quantité de caoutchouc lié au noir de carbone pendant le mélange, est le facteur prédominant dans la détermination du module du vulcanisat aux élongations élevées. Cependant, le module pour une faible élongation est indépendant de l'activité spécifique de la surface et est essentiellement influencé par les autres caractéristiques du noir de carbone, telles que la "structure" et la surface. De plus, on applique une relation du type Guth-Gold basée sur la théorie élastique pour prévoir le module des vulcanisats chargés aux élongations élevées à partir de celui d'un vulcanisat de gomme traité de façon identique. Dans la relation (établie),  $\Phi$  est le volume de renforcement ou la fraction de volume de la charge plus la fraction de volume du polymère dié. Cette relation est également employée pour calculer l'élongation réelle dans un vulcanisat chargé pour compenser la portion qui ne s'allonge pas du tout, et ce rapport d'élongation réel ( $\alpha'$ ) est employé dans l'équation de Mooney-Rivlin. L'équation de Mooney-Rivlin est l'expression théorique pour le module d'un vulcanisat lorsqu'il change avec l'élongation et le niveau de traitement (out le nombre de chaînes efficaces par unité de volume). L'équation a été utilisée antérieurement avec succès pour les vulcanisats de gomme, mais pas pour les vulcanisats chargés. En employant l'élongation corrigée ( $\alpha'$ ), l'expérience et la théorie sont en bien meilleur accord qu'antérieurement, et on peut postuler un concept général concernant l'influence du noir de carbone sur les propriétés du vulcanisat.

### Zusammenfassung

Die spezifische Oberflächenaktivität von Russ, gemessen durch die an den Russ während des Mischungsprozesses gebundenen Kautschukmenge, besass den grössten Einfluss auf den Modul des Vulkanisats bei hoher Dehnung. Der Modul bei niedriger Dehnung ist jedoch von der spezifischen Oberflächenaktivität unabhängig und wird am stärksten durch andere Russcharakteristika, wie "Struktur" und Oberflächengrösse, beeinflusst. Weiters wurde eine auf der Elastizitätstheorie beruhende Beziehung vom Guth-Gold-Typus für die Berechnung des Moduls gefüllter Vulkanisate bei hoher Dehnung aus derjenigen eines in gleicher Weise vulkanisierten ungefüllten Systems verwendet. In die Beziehung (siehe englische Zusammenfassung),  $\Phi$  ist das Verstärkungsvolumen oder der Volumbruchteil des Füllstoffes plus dem Volumbruchteil an gebundenem Polymeren. Diese Beziehung wurde auch zur Berechnung der tatsächlichen Elongation in einem gefüllten Vulkanisat verwendet, um eine Kompensation für denjenigen Teil zu erhalten, der überhaupt nicht gedehnt wird, und dieses tatsächliche Dehnungsverhältnis wurde in der Mooney-Rivlin-Gleichung verwendet. Die Mooney-Rivlin-Gleichung ist der theoretische Ausdruck für den Modul eines Vulkanisats in Abhängigkeit von Elongation und Vulkanisationshöhe (oder der Anzahl effektiver Ketten pro Volumseinheit). Die Gleichung wurde früher erfolgreich auf ungefüllte Vulkanisate angewendet, jedoch nicht auf gefüllte Vulkanisate. Mit der korrigierten Elongation ( $\alpha'$ ) ergibt sich eine viel bessere Übereinstimmung zwischen Experiment und Theorie als früher, und es kann ein allgemeines Konzept für den Einfluss von Russ auf die Vulkanisateigenschaften aufgestellt werden.

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