

Bound Rubber in Elastomers: Analysis of Elastomer-Filler Interaction and Its Effect on Viscosity and Modulus of Composite Systems

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Synopsis

Bound rubber measurement may be very misleading as a measure of elastomer-carbon black interaction because sometimes only part of the apparently bound rubber is truly adsorbed on the carbon black surface. A theory is proposed which utilizes bound rubber measurements, but separates truly adsorbed rubber from other insoluble gel and enables calculation of the adsorbed elastomer layer thickness, a numerical value of interaction. Measurements of interaction were obtained for many different rubbers, including polybutadienes, styrene-butadienes, EPDMs, and butyl, with several different furnace blacks. An equation for viscosity of a rubber-carbon black composite is proposed, based on the degree of interaction obtained from the theory and the possible varying degree of orientation of the composite as the rate of shear is changed. This has been applied experimentally both to soluble elastomers and to an elastomer containing a non-rigid gel. The modulus of a vulcanized composite is shown to be related to the effective volume fraction of filler, which is equivalent to the volume fraction of filler plus adsorbed rubber, at temperatures above the glass transition temperature, regardless of the type of rigid filler. Below the glass transition temperature, the modulus depends only on the filler volume concentration.

INTRODUCTION

This paper is concerned with the problem of determining a quantitative measure of elastomer-carbon black interaction and how such interaction influences the viscosity of the composite and the modulus of the filled vulcanizate. Bound rubber measurements have long been used to characterize interactions between an elastomer and filler. However, in some instances, bound rubber may be very misleading as a measure of interaction because only part of the apparently bound rubber is truly adsorbed on the carbon black surface. The following analysis shows how bound rubber data can be used to obtain an adsorbed elastomer layer thickness and relates this to viscosity and vulcanizate modulus.

DETERMINING INTERACTION FROM BOUND RUBBER DATA

If a solvent in which a particular elastomer is normally completely soluble is contacted with a composite mixture of that elastomer with carbon black, part of the elastomer usually remains insoluble. This insoluble

elastomer or bound rubber has been regarded to be an adsorbed fraction of the elastomer which is either physically or chemically bonded to the surface of the carbon black. There is convincing evidence that, in many instances, the carbon black particles act as free-radical acceptors,^{1,2} chemically reacting to radicals formed by mastication of the elastomer in a mill or other dry-mixing process used to disperse the black in the gum elastomer. Chemical additives³ which help to initiate radical formation can sometimes cause a dramatic increase in bound rubber. One such promoter is Elastopar (trademark of Monsanto Chemical Company, St. Louis, Missouri), a mixture consisting of 33 $\frac{1}{3}$ % N,4-dinitroso-N-methylaniline and inert filler. It is very effective in increasing the interaction of carbon black with butyl rubber. On the other hand, addition of radical acceptors such as DPPH (1,1-diphenyl-2-picrylhydrazyl) can cause a marked decrease in bound rubber.⁴ In adsorption phenomena of this type, both the surface activity and surface area of the black are important variables.⁵ If surface activity is maintained constant while surface area in a composite is increased, one might reasonably expect the volume fraction of bound rubber to increase in direct proportion to available surface area. This concept is equivalent to the idea that the adsorbed elastomer may be regarded as a layer covering the surface of the black with a uniform (or average) thickness ΔR_0 . This shell structure concept has been discussed by many people.⁶ The value of ΔR_0 could be taken as a measure of interaction between the elastomer and carbon black, assuming complete dispersion of the black. For a given fixed surface activity of carbon black, the equilibrium value of ΔR_0 should depend only on the properties of the elastomer and not on the specific area of the carbon black or concentration of carbon black in the composite (so long as unbound elastomer remains present). At present, the underlying properties of elastomers which cause ΔR_0 to vary from one elastomer to another are not completely known. However, it is common knowledge that saturated elastomers exhibit less interaction than unsaturated elastomers of the same molecular weight.

In the following analysis of bound rubber, a more general case is treated in which the pure elastomer is only partially soluble in solvent (i.e., the pure elastomer contains some gel). This situation arises with EPDM elastomers, which are often insoluble due to ethylene crystallinity and with highly branched, high molecular weight SBR or emulsion butadiene rubber. In these cases, the insoluble elastomer remaining with the carbon black after leaching is not only the truly adsorbed rubber but also the gel portion of the pure gum. If [BR] is the fraction of apparently bound rubber (i.e., cm³ insoluble polymer/cm³ polymer in the composite), [AR] is the fraction of polymer made insoluble (or adsorbed) by the carbon black particles, and G is the fraction of gel in the gum, then

$$[\text{BR}] = [\text{AR}] + G. \quad (1)$$

The volume of rubber made insoluble, V_{AR} , is simply

$$V_{\text{AR}} = \Delta R_0 S' \quad (2)$$

in which S' is the total surface area due to carbon black exposed to the soluble portion of the gum. Then

$$[\text{AR}] = \frac{V_{\text{AR}}}{V_{\text{polymer}}} = \frac{\Delta R_0 S'}{V_{\text{polymer}}} \quad (3)$$

If S is the total surface area of carbon black in the composite, we can define $f = S'/S$ as the fraction of total surface area which is exposed to soluble gum, and write

$$[\text{AR}] = \Delta R_0 f \left(\frac{S}{V_{\text{polymer}}} \right) \quad (4)$$

$$\left(\frac{S}{V_{\text{polymer}}} \right) = \left(\frac{V_{\text{C.B.}}}{V_{\text{polymer}}} \right) \left(\frac{S}{V} \right)_{\text{C.B.}} \quad (5)$$

If ϕ is the volume fraction of carbon black in the composite, ρ is the density (1.84 g/cm³) of carbon black particles, and A is the specific surface area of carbon black (cm²/g), then

$$\frac{V_{\text{C.B.}}}{V_{\text{polymer}}} = \frac{\phi}{1 - \phi} \quad (6)$$

and

$$\left(\frac{S}{V} \right)_{\text{C.B.}} = \rho A. \quad (7)$$

Thus, substituting eqs. (5), (6), and (7) into eq. (4),

$$[\text{AR}] = \Delta R_0 f \left(\frac{\phi \rho A}{1 - \phi} \right) \quad (8)$$

and eq. (1) becomes

$$[\text{BR}] = \Delta R_0 f \left(\frac{\phi \rho A}{1 - \phi} \right) + G. \quad (9)$$

It is reasonable to assume that, when the carbon black concentration and fraction of gel in the gum are not too high, the fraction f is independent of the carbon black specific surface area and concentration. Thus, if the bound rubber is determined for a series of composites of a particular polymer in which $\phi \rho A / (1 - \phi)$ is varied (by varying ϕ or A), then the data, when plotted as $[\text{BR}]$ versus $\phi \rho A / (1 - \phi)$, should yield a straight line whose slope is $\Delta R_0 f$ and intercept is G . To determine ΔR_0 , and thus the carbon black interaction from the slope of the straight line, the value of f for the series of composites must be known. At present, the direct determination of f is not possible. However, it is possible to determine the permissible range of f values. The upper limit of f is unity (i.e., all of the carbon black surface is exposed to the soluble portion of the gum). The probable lower limit of f occurs when the carbon black concentration is the same in both the soluble portion and gel portions of the gum. For

this case, $f = 1 - G$. In a given composite, the actual value of f in this range will most likely depend on the relative viscosities of the gel and soluble portions of the gum. If the gel is hard, highly crosslinked polymer, the carbon black will prefer the softer soluble portion. If, on the other hand, the gel is soft and merely reflects branching or ethylene crystallinity (e.g., EPDMs), the carbon black will probably distribute evenly throughout the polymer and $f = 1 - G$. It would, if possible, always be best to measure the bound rubber in a solvent that completely dissolves the pure gum. Then there would be no possibility of ambiguity in the results because the value of f must equal 1.0 and the slope of the straight line (passing through the origin) would equal ΔR_0 .

EXPERIMENTAL

The elastomers studied were all commercially available materials and are listed in Table I. None were oil extended. All the materials were assumed to be 100% polymer for the purposes of calculating bound rubber.

Only furnace-type carbon blacks (Columbian Carbon Co.) were used in these experiments, and their dimensions are listed in Table II. The carbon black surface areas were taken from the manufacturer's brochure. They were determined by nitrogen adsorption. The surface average diameters have been calculated assuming that the particles are spherical. Thus, the surface average diameter $D = 6/\rho A$.

The FEF and APF carbon blacks were mixed only with the *cis*-polybutadiene and emulsion SBR samples, while the SAF, ISAF, and HAF carbon blacks were mixed with all of the elastomers. The carbon blacks were dry-mixed with each elastomer in two stages, first by Brabender Plastograph

TABLE I
Elastomers Studied

Type	Trade name	Manufacturer
<i>cis</i> -Polybutadiene	Cisdene 100	American Synthetic Rubber Co.
Polybutadiene(40 <i>cis</i> /50 <i>trans</i> /10 vinyl)	Diene 45	Firestone Tire & Rubber Co.
Emulsion SBR (23% styrene)	Synpol 1500	Texas-U.S. Chemical Co.
Alfin SBR (15% styrene)		National Distillers & Chem.
Emulsion butadiene	(non-oil extended) Synpol 8407	Texas-U.S. Chemical Co.
Solution SBR	Stereon 700	Firestone Tire & Rubber Co.
Butyl rubber	Butyl 218	Enjay Company
Ethylidene norbornene (ENB) EPDM	Royalene 501	Uniroyal, Inc.
1,4-hexadiene (1,4-hex) EPDM	Nordel ECD729	du Pont Company
Dicyclopentadiene (DCPD) EPDM	Royalene 304	Uniroyal, Inc.
Ethylene-propylene rubber	Royalene 1623	Uniroyal, Inc.

TABLE II
Carbon Black Dimensions

Type	Surface area, m ² /g	Surface average diameter, Å
SAF	155	210
ISAF	131	249
HAF	100	326
FEF	80	408
APF	48	680

at 120°C and 30 rpm for 10 min, and then by mill mixing on a 3 × 8 in. lab mill at 82°C for 10 min. The following carbon black loadings were used: 22–25 phr, 34–37.5 phr, 50–52.5 phr, and 75 phr. These correspond to volume fractions of approximately 0.10, 0.14–0.16, 0.19–0.20, and 0.27, respectively. The concentration of 75 phr was used only in mixing the emulsion SBR and butyl rubber compounds. Samples of pure elastomer were also subjected to these mixing conditions in order to obtain a gel value corresponding to $\phi = 0$. This is important because of the possibility of a change in the unbound gel content due to mastication. In order to study the effect of N,4-dinitroso-N-methylaniline on the interaction of carbon black with butyl rubber, an additional set of butyl rubber compounds were mixed with 0.33 phr N,4-dinitroso-N-methylaniline (1.0 phr Elastopar).

Bound rubber was determined after keeping the composite samples at room temperature for at least 24 hr. Samples to be leached weighed less than 0.5 g, and they were cut into strips less than 1 mm wide and about 5 mm long. Toluene (75 ml) was used as the solvent, and the leaching was at room temperature for 24 hr. For the DCPD-EPDM composites, additional bound rubber measurements were made at 70°C using xylene as the solvent. The concentration of dissolved polymer was determined by evaporation of 25-ml samples of solution and weighing the dry polymer. The weight of bound rubber was determined by subtracting the weight of dissolved polymer from the weight of polymer in the composite.

RESULTS

Adsorbed Elastomer Layer Thickness

Elastomers Containing Gel

Most of the pure elastomers studied did not contain a portion insoluble in toluene at room temperature. Only the emulsion butadiene rubber and two of the EPDM rubbers (1,4-hexadiene and dicyclopentadiene) contained substantial gel. Figure 1 is an example of a plot of [BR] versus $\phi\rho A / (1 - \phi)$ for the emulsion butadiene data. The straight line is a least-

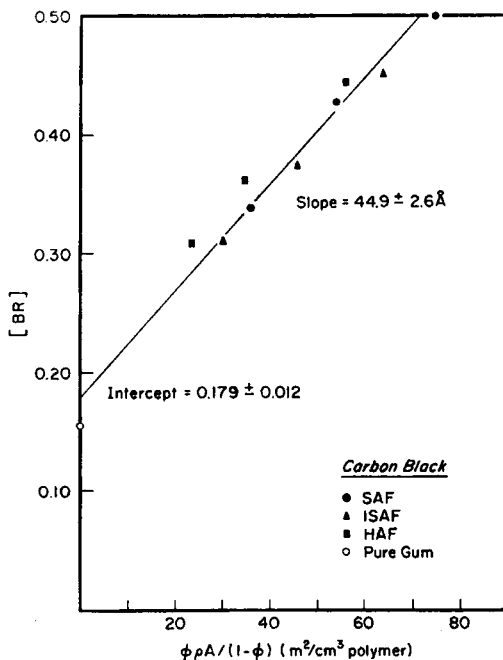


Fig. 1. Bound rubber correlation for emulsion butadiene rubber.

squares fit with a slope of 44.9 \AA and an intercept equal to 0.179. The correlation coefficient for this line is 0.987, indicating that a straight line fits the data very well. Thus, the assumption that the fraction f is independent of carbon black surface area and loading appears justified. If none of the carbon black penetrated the unbound gel, f would equal 1.0 and the value of ΔR_0 would equal the slope of the line (45 \AA). However, if the black did enter the unbound gel, with a concentration equal to the concentration in the soluble portion, then f would equal $1 - G = 0.821$ and ΔR_0 would be $44.9/0.821 = 54.6 \text{ \AA}$. This latter assumption is believed to be more realistic because the gel is probably just high molecular weight, branched material which is rheologically similar to the soluble gum at the temperature of mixing (120°C).

Because of the inherent uncertainty in determining ΔR_0 when the elastomer contains a large amount of gel, leaching conditions that result in lower gel are preferable. Figure 2 shows two sets of bound rubber data for the DCPD-EPDM. One set is the data obtained using toluene at room temperature, and the other is from using xylene at 70°C . The slope of the straight line is greater for the xylene, and the gel content is decreased. This indicates that carbon black has penetrated the gel (in toluene at room temperature) phase. The slope and intercept for the toluene data are $\Delta R_0 f = 16.1 \text{ \AA}$ and $G = 0.284$. The slope and intercept for xylene data are $\Delta R_0 f = 27.0 \text{ \AA}$ and $G = 0.035$, respectively. Using the assumption that

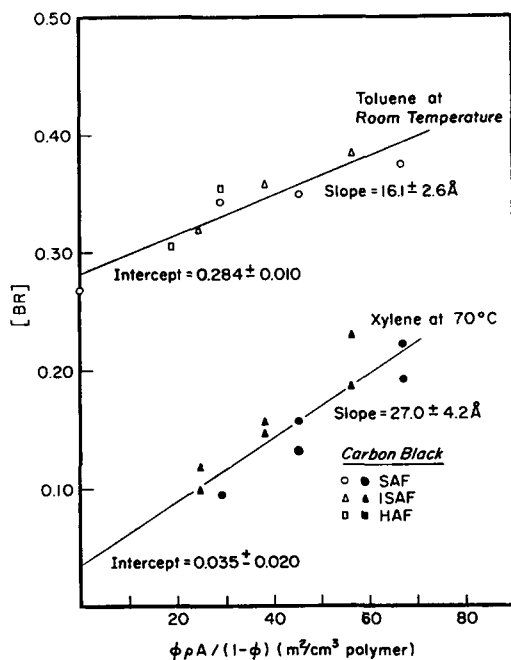


Fig. 2. Bound rubber correlations for DCPD-EPDM, showing effect of leaching temperature.

$f = 1 - G$ for both cases, ΔR_0 equals 22.5 Å and 28.0 Å calculated from the toluene and xylene data, respectively. These results are in much closer agreement than the values of ΔR_0 obtained by setting $f = 1$. Thus, we conclude that carbon black tends to distribute uniformly throughout elastomers that contain a "soft" gel phase.

Soluble Elastomers

Most of the elastomers studied contained no gel. For these materials, a least-squares slope was calculated by forcing the intercept to be zero. For example, Figure 3 shows the bound rubber correlation for pure butyl rubber, which is completely soluble in toluene. The slope in this case is equivalent to ΔR_0 , and its value is 28.3 Å. Table III is a compilation of the adsorbed elastomer layer thickness for all of the elastomers studied. The value of G for each elastomer is also given. Values of $G = 0$ were determined by measuring the gel in the unfilled masticated gum and finding complete solubility in toluene. For the cases where G is not zero, the value of G is the least-squares intercept. The values of ΔR_0 are all calculated from a least-squares slope with $f = 1 - G$. The effect of adding 0.33 phr N,4-dinitroso-N-methylaniline to the butyl rubber, simultaneously with the addition of carbon black, can also be observed in Figure 3. The slope of this least-squares line (also forced through the origin because the unfilled ma-

TABLE III
 Adsorbed Elastomer Layer Thickness^a

Elastomer	Per cent gel (100G), %	Layer thickness (ΔR_0), Å
<i>cis</i> -Polybutadiene	0	74.7 ± 3.2
Polybutadiene(40 <i>cis</i> /50 <i>trans</i> /10 vinyl)	0	67.7 ± 2.1
Emulsion SBR/23% styrene)	0	54.1 ± 1.5
Alfin SBR	0	52.0 ± 1.4
Emulsion butadiene	17.9 ± 1.2	54.6 ± 3.2
Solution SBR	0	40.9 ± 2.0
Butyl rubber	0	28.3 ± 1.6
Butyl rubber + N,4-DNMA ^b	0	53.0 ± 1.5
ENB-EPDM	0	34.6 ± 1.8
1,4-Hexadiene-EPDM	12.4 ± 3.0	34.7 ± 8.1
DCPD-EPDM	28.4 ± 1.0	22.5 ± 3.6
DCPD-EPDM ^c	3.5 ± 2.0	28.0 ± 4.4
Ethylene-propylene rubber	0	27.4 ± 1.3

^a Furnace blacks, Brabender mixed (120°C, 10 min, 30 rpm), milled at 82°C for 10 min. Toluene at room temperature used as solvent. Values ± standard deviations given in columns.

^b N,4-Dinitroso-N-methylaniline.

^c Xylene at 70°C used as the solvent.

terial is completely soluble) is 53.0 Å. Thus, this promoter can practically double the interaction of butyl rubber with carbon black.

In order to ascertain the mechanism by which this promoter so dramatically increased butyl rubber-carbon black interaction, GPC curves of molecular weight distributions of the butyl rubber were obtained and are shown in Figure 4. Curve A represents the molecular weight distribution of the pure butyl rubber after milling for 10 min at 82°C. This curve is identical to the curve for the pure unmilled elastomer (curve not shown in Fig. 4). Curve B is the resultant molecular weight distribution after adding 0.33 phr N,4-dinitroso-N-methylaniline to pure butyl rubber and masticating the gum under the same conditions that were previously used to mix carbon black with the rubber. Curve B shows a substantial fraction of high molecular weight material which is not present in the original elastomer. This material might be the result of molecular weight enhancement caused by a free-radical reaction with the N,4-dinitroso-N-methylaniline. When pure butyl rubber is masticated, some free radicals might also be formed; but if they do form, they must recombine to form the original molecular structure.

The dashed curves of Figure 4 are the molecular weight distributions of the unbound rubber (soluble in toluene at room temperature) in typical carbon black composites containing 75 phr SAF black. Curve C is for the polymer to which no N,4-dinitroso-N-methylaniline has been added, and curve D is for the elastomer containing the promoter. Both curves C and D represent lower average molecular weight material than the original pure gum, and curve D shows none of the high molecular weight elastomer found when the promoter was added to rubber containing no carbon black

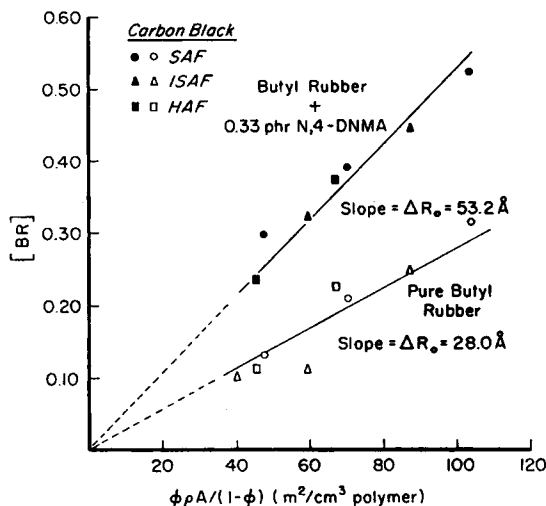


Fig. 3. Bound rubber correlation for butyl rubber, showing effect of adding N,4-DNMA.

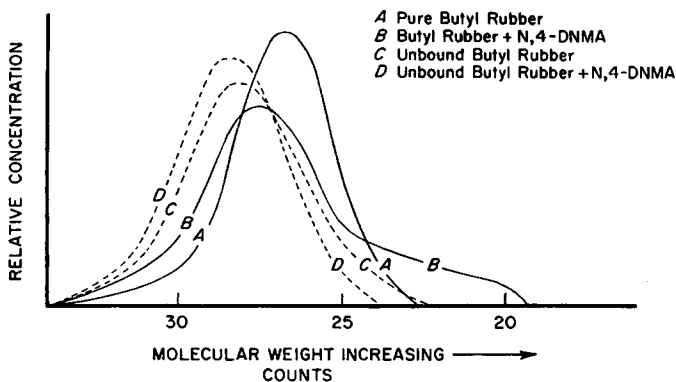


Fig. 4. Molecular weight distributions of butyl rubber, showing effect of adding N,4-DNMA.

(curve B). This indicates that when carbon black is present, the increased concentration of free radicals (mechanochemically formed by the promoter) must preferentially react with the surface of the carbon black rather than recombining to form high molecular weight elastomer.

Effect on Viscosity

There is, at present, no generally accepted theory for accurate prediction of viscosity in systems of rigid particles suspended in viscoelastic fluids. Starting with the work of Einstein⁷ on dilute suspensions of spheres, most theoretical investigations have been based on the assumptions that the fluid is Newtonian and that there is no adsorption of fluid on the surface of the particles. Guth, Simha, and Gold⁸ and Vand⁹ extended Einstein's

theory to include moderately concentrated suspensions by taking into account hydrodynamic interactions between the spheres. Recently, Lee¹⁰ extended the work of Vand to include three-body collisions of spheres. All of these theories result in a power series of the form

$$\frac{\eta}{\eta_0} = 1 + 2.5\phi + k_2\phi^2 + k_3\phi^3 + \dots \quad (10)$$

where η is the suspension viscosity and η_0 is the viscosity of the Newtonian fluid. In Einstein's theory, k_2 , k_3 , and higher-order terms are zero. Guth and Simha calculated a value of $k_2 = 14.1$, and Vand calculated a value of $k_2 = 7.349$, but they did not calculate any higher-order terms. Lee calculated the coefficients k_2 and k_3 .

Landel and co-workers,¹¹ experimenting with suspensions of particles of arbitrary shape and size distribution randomly dispersed in Newtonian liquids, obtained the following empirical equation:

$$\frac{\eta}{\eta_0} = \left(1 - \frac{\phi}{\phi_m}\right)^{-2.5} \quad (11)$$

where ϕ_m is the maximum volumetric loading of particles (or packing factor). For a system consisting of monodisperse spheres, $\phi_m = 0.74$. Using the binomial expansion, this equation may be changed into the series form of eq. (10).

It is unlikely that the above equations are directly applicable to the viscosity of elastomer-carbon black composites because (1) elastomers are non-Newtonian and (2) there is bound rubber adsorbed on the surface of the black. There is also evidence that, at moderate concentrations of carbon black ($\phi > 0.10$), a three-dimensional network of bound rubber-carbon black is formed which effectively acts as a second continuous phase within the continuous unbound elastomer. The fact that a piece of the composite material will swell¹² in a solvent while maintaining its shape and while the soluble elastomer dissolves is an indication of the existence of such a network structure. Brennan, Jermyn, and Boonstra¹³ recognized the problem of adsorption and tried to account for it by assuming that the volume fraction to be used in the Guth equation is not the volume fraction of carbon black alone, but the combined effective volume fraction, ϕ_e , of carbon black and bound rubber. Their calculation of the Mooney viscosity using ϕ_e in place of ϕ in the Guth equation resulted in values higher than experimentally observed, but the agreement was much better than the original Guth equation. If ϕ_{BR} is the volume fraction of bound rubber for an elastomer in which $G = 0$, then

$$\phi_{BR} = (1 - \phi)[BR]. \quad (12)$$

This equation, together with eq. (9) and the effective volume concept, $\phi_e = \phi + \phi_{BR}$, yields the following relationship:

$$\phi_e = [1 + \rho A \Delta R_0] \phi \quad (13)$$

or, since the surface average diameter $D = 6/\rho A$,

$$\frac{\phi_e}{\phi} = 1 + \frac{6\Delta R_0}{D}. \quad (14)$$

An effective volume concentration may be sufficient to account for the bound rubber in the composite, but the problem of non-Newtonian behavior, or the dependency of relative viscosity (η/η_0) on shear rate, still must be dealt with if a theory is to have a chance at success. If the change in viscosity of a composite with shear rate ($\dot{\gamma}$) is simply due to the non-Newtonian characteristics of the gum alone, then the relative viscosity, in which the viscosity of the composite and pure gum are both determined at the same shear rate, would be independent of shear rate. In actuality, this relative viscosity [$\eta(\dot{\gamma})/\eta_0(\dot{\gamma})$] of an elastomer-carbon black composite tends to decrease as the rate of shear increases.¹⁴ This fact may be explained by regarding the composite material as a system which is capable of orientation when subjected to a shear field. Under shear stress, the system can no longer be considered as consisting of randomly dispersed discrete spherical particles. Rather, an initially random three-dimensional network, consisting of carbon black and bound rubber, might become more and more nonrandom or oriented as the shear rate is increased.

If orientation is to be considered as a major factor affecting the rheology, some insight may be gained by examining the most highly oriented composite system, a system consisting not of discrete spheres but of laminated material consisting of flat layers of rigid matter alternating with layers of viscous Newtonian liquid. In order to determine the increase in the viscosity of this composite system over that of the liquid, one can analyze what happens when a single layer of rigid material is placed in Newtonian liquid between parallel plates, as in Figure 5. If the viscosity of the fluid is η_0 , the area of the upper plate is S , and the distance between plates is y , and shearing force F is applied to the upper plate, then, in the absence of the rigid layer, the upper plate would move at velocity V given by

$$\frac{F}{S} = \eta_0 \frac{V}{y}. \quad (15)$$

When a rigid layer of thickness h is present, the upper plate would move at velocity V' in response to force F . Since the fluid viscosity is unchanged,

$$\frac{V'}{y-h} = \frac{V}{y} \quad (16)$$

or, if ϕ_e is the volume fraction of rigid material,

$$V' = \left(\frac{y-h}{y} \right) V = (1 - \phi_e) V. \quad (17)$$

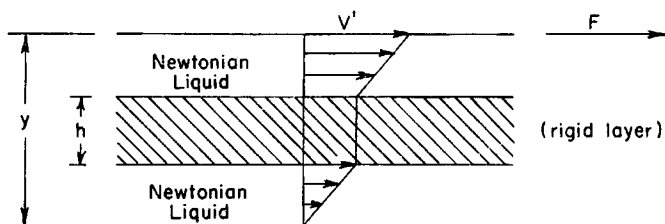


Fig. 5. Laminated composite system.

The apparent viscosity of the two-phase system is given by

$$\frac{F}{S} = \eta \frac{V'}{y} = \eta(1 - \phi_e) \frac{V}{y}. \quad (18)$$

Since the left side of eqs. (15) and (18) are equal,

$$\frac{\eta}{\eta_0} = (1 - \phi_e)^{-1}. \quad (19)$$

Note that this equation has the same form as eq. (11). The similarity between these two equations is more evident when, in eq. (11), ϕ_e is used instead of ϕ and ϕ_{em} is used instead of ϕ_m . The term ϕ_{em} is the packing factor, or maximum volumetric loading of carbon black plus bound rubber. In any composite the upper limit of ϕ_{em} is unity. For example, in the case of monodisperse spherical filler particles in which bound rubber layers can overlap or penetrate each other,

$$\phi_{em} = 0.74 \left(\frac{\phi_e}{\phi} \right) \leq 1.0. \quad (20)$$

Substitution of eq. (14) into eq. (20) yields

$$\phi_{em} = 0.74 \left[1 + \frac{6\Delta R_0}{D} \right] \leq 1.0. \quad (21)$$

The maximum possible value ($\phi_{em} = 1.0$) is achieved when $\Delta R_0/D \geq 0.058$. This condition, $\phi_{em} = 1.0$, was fulfilled by all of the composites used in this study; i.e., by adding enough carbon black to these elastomers, it is theoretically possible to achieve 100% bound rubber and to eliminate interstices between effective particles. Therefore, eq. (11) can be written

$$\frac{\eta}{\eta_0} = (1 - \phi_e)^{-2.5}. \quad (22)$$

The only difference between eq. (19) and eq. (22) is that the exponent is -1.0 for the completely laminated material and -2.5 for the random suspension of discrete particles. This suggests that, for intermediate degrees of orientation or nonrandomness, the following equation might apply:

$$\frac{\eta}{\eta_0} = \frac{ML}{ML_0} = (1 - \phi_e)^{-N} \quad (23)$$

in which the value of N depends on the degree of orientation of the system.

The parameter N is likely to depend on the type of elastomer, on the ratio ϕ_e/ϕ , and on the shear rate. For a given elastomer-carbon black system, the ratio ϕ_e/ϕ increases as the carbon black diameter decreases, according to eq. (14). It would be expected that, at a given shear rate, higher values of ϕ_e/ϕ result in greater orientation due to the presence of more deformable bound rubber in the network, as opposed to rigid carbon black.

Equation (23) can be applied in correlating Mooney viscosity data. Mooney viscosities were determined for the *cis*-polybutadiene and emulsion SBR systems at 100°C, and for the DCPD-EPDM system at 120°C because of its higher gum viscosity. The Mooney was run at speeds of 0.049, 0.195, 2.0, and 13.2 rpm for all of these samples. Torque measurements were taken after running for 4 min for speeds below and including 2.0 rpm. At 13.2 rpm, the torque was taken at 1 min after starting rotation. If eq. (23) is valid, a graph of the log (ML/ML_0) versus log ($1 - \phi_e$) should be linear, with slope equal to $-N$ and passing through the origin. Each value of ϕ_e should be calculated from eq. (14) using values of ΔR_0 from Table III. Note that the Mooney torque of the composite (ML) and of the pure gum (ML_0) must be measured at the same shear rate.

Plots of the *cis*-polybutadiene-SAF carbon black data on these coordinates, at the different shear rates, are shown in Figure 6a. As the shear rate is increased from 0.049 rpm to 13.2 rpm, N decreases from 2.72 to 1.04. Figure 6b is a similar plot for the DCPD-EPDM-SAF carbon black data. Here, as the shear rate increases from 0.049 rpm to 13.2 rpm, N decreases from 2.32 to 1.00, indicating a greater degree of orientation at low shear rates than *cis*-polybutadiene. The DCPD-EPDM data are an example of a system containing a large amount of gel (28.4%) at room temperature. However, as previously mentioned, this gel is not rigid, and its amount tends to greatly decrease as the solvent temperature is increased. At the temperature of the viscosity measurement, the gel is rheologically more similar to the toluene-soluble gum than it is to a rigid filler. Hence, the viscosity correlation appears valid for gel-containing elastomers as long as the gel is not rigid. If ϕ_e were simply taken to be the volume fraction of filler plus apparent bound rubber, the plot of log (ML/ML_0) versus log ($1 - \phi_e$) would not be linear.

For the emulsion SBR, Figure 7 shows how, at the same shear rate (2.0 rpm), the value of N depends on the size of the carbon black particles (or ϕ_e/ϕ). For the large APF ($D = 680 \text{ \AA}$) particles, $\phi_e/\phi = 1.59$ and $N = 2.03$, while for SAF ($D = 210 \text{ \AA}$) particles, $\phi_e/\phi = 2.89$ and $N = 1.08$.

At present, the degree of orientation parameter N must be experimentally determined by at least one data point. Once the bound rubber and Mooney viscosity of that point are determined, the Mooney viscosity (at the same shear rate) at any other concentration of that particular carbon black may be estimated from eq. (23).

Effect on Modulus of Vulcanizate

The presence of bound rubber in a carbon black-rubber compound is reflected in the physical properties of vulcanizates: modulus, hysteresis, large deformation, and failure characteristics.^{8,15}

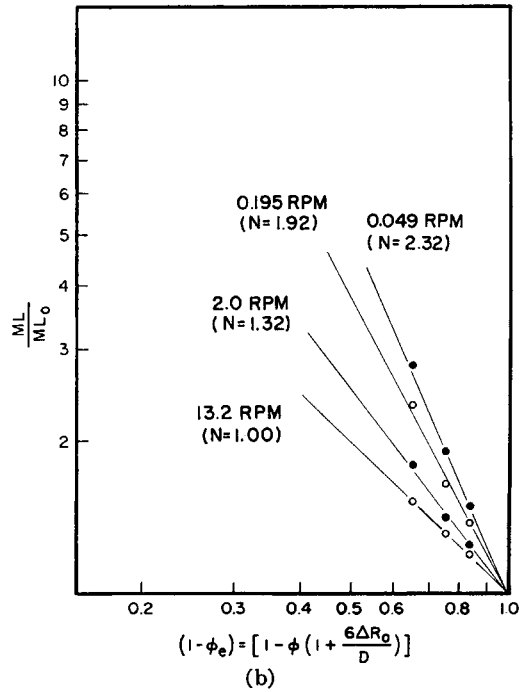
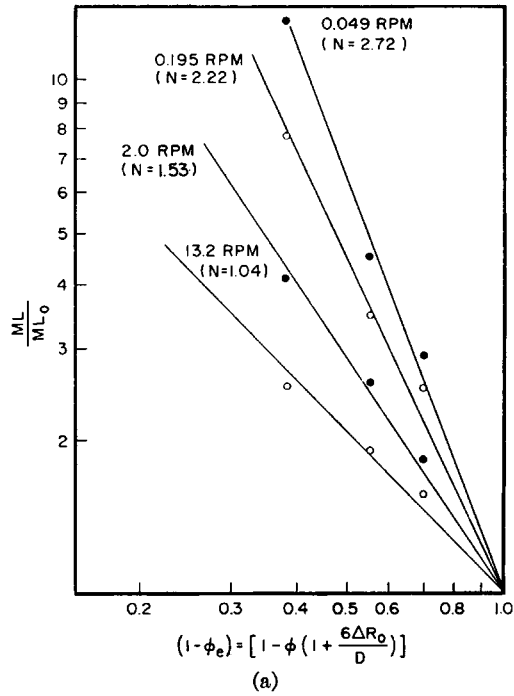


Fig. 6. Effect of shear rate on degree of orientation and viscosity: (a) *cis*-polybutadiene-SAF carbon black composite; (b) DCPD-EPDM-SAF carbon black composite.

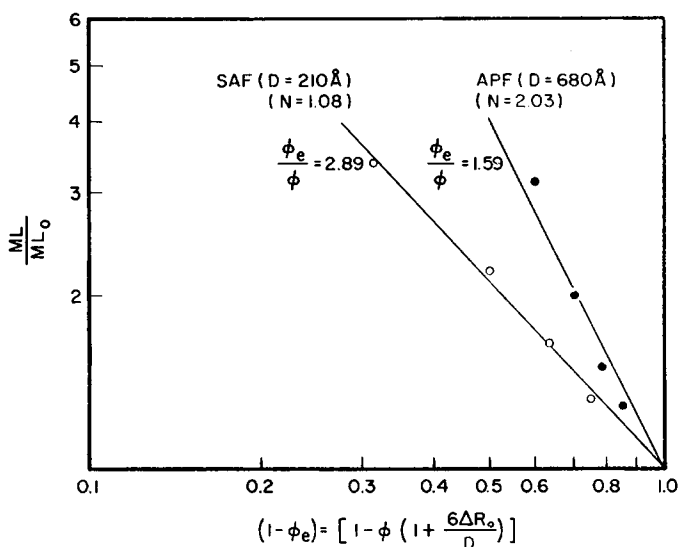


Fig. 7. Effect of carbon black particle size on degree of orientation and viscosity of SBR 1500 composites at 2 rpm.

In this work, SBR 1500 was used to study modulus. Various fillers were used, including various-size furnace carbon blacks (SAF, ISAF, HAF, FEF, and SRF) (Phillips Petroleum), graphitized HAF carbon black, and calcium carbonate particles, which are nonactive fillers. The curative was tetramethylthiuram disulfide (Tuex) only, no free sulfur. The concentration of Tuex was 3.5 phr. The curing temperature and time were 307°F and 45 min, respectively. The filler mixing was accomplished using only a mill at a temperature of 82°C for 15 min. The concentration of the filler particles was varied from 20 to 60 phr for the active carbon blacks, and from 30 to 200 phr for the nonactive CaCO_3 particles.

A Vibron machine of Toyo Measuring Inst., Japan, was used to measure the real part of the dynamic modulus, E' , of the composites; temperature was varied from -75°C to 100°C , and the measuring frequency was 3.5 cps. The strain is less than 0.1% in the Vibron. An example of the variation of E' with temperature and composition is shown in Figure 8 for the HAF-filled SBR 1500.

The relative modulus (ratio of modulus of the compound to the modulus of the cured gum) was used to analyze the modulus variation due to filler concentration. Figure 9 shows the variation of relative real modulus (E'/E_0') versus volume fraction of various fillers at 50°C . The relative curves are not strongly dependent on temperature in the range from 15°C to 75°C . At the same volumetric loading of filler, the modulus increases when the active surface area is increased. This phenomenon has been well recognized qualitatively.^{6,15,16} It can be explained quantitatively using the effective volume concept stated by eq. (13). Figure 10 shows the curves of E'/E_0' versus effective volume fraction ϕ_e , which was calculated

using the value of 54 \AA for ΔR_0 of SBR 1500 taken from Table III. This result indicates that the modulus variation due to filler concentration could be described by a single curve, regardless of the filler surface activity, if the effective volume fraction is used. When the data are carefully examined,

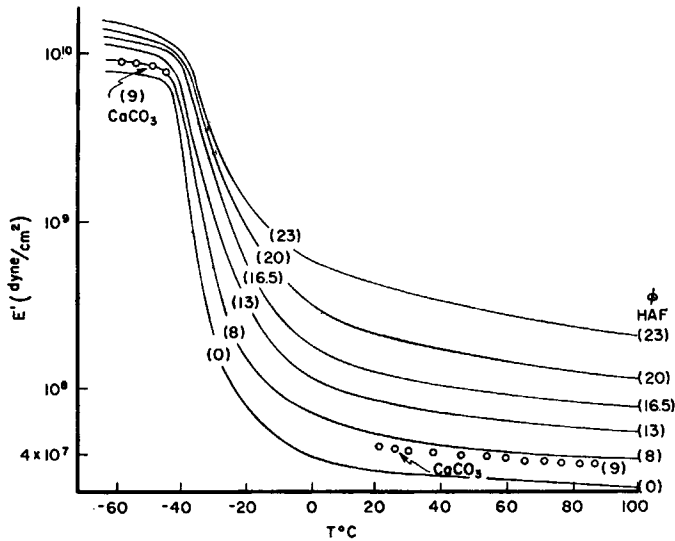


Fig. 8. Variation of real modulus with filler concentration and temperature. SBR 1500—Carbon Black and SBR 1500— CaCO_3 .

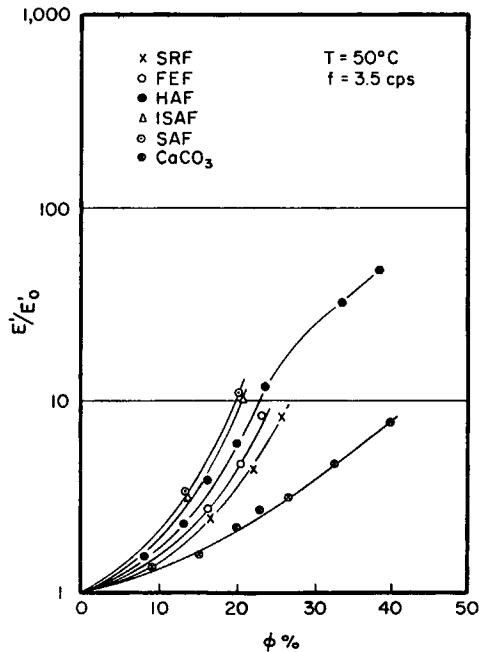


Fig. 9. Variation of relative real modulus with volume fraction of various fillers at 50°C SBR 1500—carbon black and CaCO_3 .

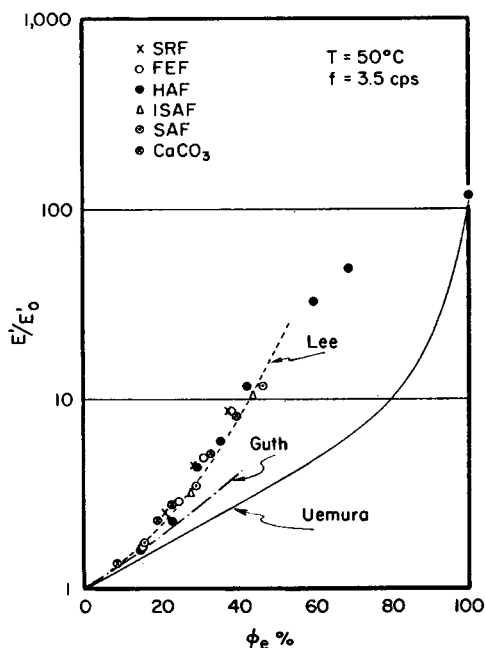


Fig. 10. Variation of relative real modulus with effective volume fraction of fillers. SBR 1500-carbon black and CaCO_3 .

it appears that the thickness layer decreases with increase in the specific surface area of the active carbon blacks. This fact may be due to the degree of dispersion of carbon black particles. The smaller particles are generally more difficult to disperse than large particles, in a dry mixing process. The thickness layer of bound rubber may also be calculated by fitting the modulus data to the CaCO_3 curve. These results are shown in Table IV.

The values for ΔR_0 of the active blacks are in excellent agreement with the value of 54.1 \AA obtained by bound rubber measurement (Table III). In the case of graphitized HAF, the value of $\Delta R_0 = 27 \text{ \AA}$ is 50% of the ac-

TABLE IV
Values of ΔR_0 from Modulus Data

Filler	Surface area, m^2/g	$\Delta R_0, \text{ \AA}$
CaCO_3	—	0
SRF ^a	27	58
FEF ^a	46	58
HAF ^a	80	54
ISAF ^a	117	50
SAF ^a	135	50
Graphitized HAF ^b	100	27

^a Philipps Petroleum Co.

^b Columbian Carbon Co.

tive HAF. Since the surface activity of graphitized carbon black is lower than that of active blacks, it is difficult to measure bound rubber for normal loadings of graphitized black because a three-dimensional network is not easily established and carbon black becomes dispersed in the solvent. This problem is circumvented by adding the graphitized carbon black to a composite containing active carbon black which serves to form the network structure. Thus, three SBR-1500 composites were mixed under the conditions specified in the experimental section. The recipes and per cent bound rubber (in toluene at room temperature) are given in Table V.

From the differences in per cent bound rubber (subtracting the per cent bound rubber in sample #1 from samples #2 and #3), the surface activity of the graphitized HAF carbon black is found to be 51% of the active HAF. This is in agreement with the data in Table IV.

The results in Table IV indicate that as far as SBR-carbon black vulcanizates are concerned, a certain amount of immobile or rigid elastomer exists, even above room temperature. Examination of the spin-spin relaxation time by the NMR method applied to bound rubber itself also supports this concept.¹⁷ Waldrop and Kraus¹⁸ however, reported that the spin-lattice relaxation time does not show any evidence of the existence of an immobile elastomer layer around the carbon black. The value of ΔR_0 in the cured systems is coincidentally very nearly equal to the one measured before curing. Presumably, this may be caused by a rapid curing agent (e.g., Tuex) which tends to quench the unbound elastomer and prevents the formation of additional bound rubber.

Below the glass transition temperature of the gum, the modulus of filled vulcanizates depends only on the filler content regardless of the activity of filler. Figure 11 shows the curves of E'/E_0' versus volume fraction of filler itself, ϕ , at -60°C for HAF and CaCO_3 . This is understandable because, below the glass transition temperature, the mobility of the bound rubber could be the same as the gum. In this temperature region, the material is a simple composite similar to a plastic and rigid filler system. This fact can be explained theoretically.¹⁹⁻²¹

Theoretical derivations for composite moduli are still naive. However, theoretical expressions for variation of viscosity with filler concentration

TABLE V
Recipes and Bound Rubber for SBR-1500 Composites

Composite	#1	#2	#3
			50 phr HAF plus 25 phr graph. HAF
	50 phr HAF*	75 phr HAF	
Bound rubber, %	24.9	40.8	32.7
Bound rubber difference (from #1), $\Delta\%$		15.9	8.1

* Columbian Carbon Co.

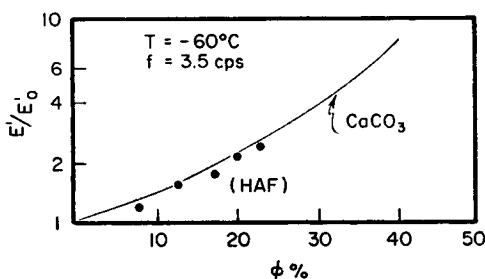


Fig. 11. Variation of relative real modulus with filler volume fraction below the glass transition temperature. SBR 1500-HAF and CaCO_3 .

often are applied to the modulus variation. Thus, the recent work of Lee on the viscosity of concentrated suspensions, which results in the following expression for viscosity,

$$\frac{\eta}{\eta_0} = \frac{1}{(1 - \phi)^{(2.5 + 1.92\phi + 7.73\phi^2)}} \quad (24)$$

might also apply to modulus. When this expression is plotted on the E'/E_0' versus ϕ_e coordinates of Figure 10, it coincides with all of the data points. In Figure 10, the theoretical curves calculated from the Uemura and Guth equations are also presented. The value of E'/E_0' at $\phi_e = 1$ was obtained from leached and compressed material.

CONCLUSIONS

Bound rubber measurements can be used to determine the interaction of elastomers with carbon black, but care must be taken to separate the truly bound elastomer from unbound "gel" in the gum. When the unbound "gel" is "soft", e.g., EPDM rubbers, the carbon black, when dry-mixed, tends to distribute uniformly in both the gel and soluble portions of the gum.

The viscosity of a rubber-carbon black composite appears to be a function of the effective volume fraction of filler (filler plus bound rubber, the degree of orientation of the composite (a parameter depending on both the shear rate and particle size of the filler), and the viscosity of the pure gum.

The presence of bound rubber affects the modulus of a cured composite. Above the glass transition temperature, the modulus depends on the effective volume fraction of filler (filler plus bound rubber). Below the glass transition temperature, the relative modulus depends only on the filler volume fraction.

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