

## Mixing of Carbon Black and Polymer: Interaction and Reinforcement\*

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### Synopsis

Interaction between carbon black and polymer starts during the mixing process; a primary agglomerate is formed, the composition of which is dependent upon the structure. The important carbon black properties are surface area, specific activity, structure (void, volume, anisometry), and porosity of the particles. On heat treatment of black at 3000°C., it loses its sites of high specific activity. Structure and specific activity determine incorporation time and further dispersion. During mixing, bound rubber is formed which is used as a measure of specific surface activity. In the final vulcanizate, the filler-polymer interaction is evident in reduced swelling in solvents (benzene, chloroform, cyclohexane,) etc. Below a certain critical degree of swelling, the percentage swelling is no longer dependent upon the amount of filler in the vulcanizate. Graphitized black vulcanizates exhibit in all solvents the same degree of swelling as the unfilled vulcanizate. This phenomenon is explained by the assumption of mobile adsorption of rubber chains on the carbon black surface. In untreated blacks the mobility on the surface is limited by sites of high energy of adsorption. In graphitized blacks such sites are no longer found, and swelling is unhindered by the presence of black. Reinforcement is explained by the more homogeneous distribution of tension between molecular chains due to slippage on the carbon surface.

### Introduction

Although carbon black has been used for many decades as "reinforcing" filler, rubber technologists are still uncertain about the unique property of carbon black to improve tear and abrasion resistance in rubber vulcanizates, especially in synthetic rubbers of the butadiene-styrene type. The problem of how the carbon black surface and rubber interact and whether the bond is of a chemical nature or purely physical adsorption, has not been solved unequivocally.

Stearns and Johnson<sup>1</sup> proved the presence of reactive groups on the carbon black surface and concluded that the surface groups participate in the vulcanization reaction. In this case the black particle would have become a crosslink, and we know from experience that an increase in crosslink density does not result in improved tear resistance. Therefore, these crosslinks must be of a special nature. In contrast to common crosslinks, they do not decrease hysteresis but increase it. These crosslinks break

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down during elongation and with time gradually return to their former state. Furthermore, under certain conditions, they accelerate the relaxation of tension at constant elongation. Common crosslinks do not at all or affect adversely all these properties.

### Elements of Interaction

The elements which determine the interaction are factors of capacity, intensity, and geometry, namely: (1) The total interface between polymer and solid filler which can be expressed in square meters per cubic centimeter vulcanizate or compound, and the order of which is approximately 20–50 m.<sup>2</sup>/cm.<sup>3</sup> in tire tread mixtures; (2) the intensity of interaction, as determined by the specific surface activity per square centimeter. The adsorptive energies vary considerably in different places on the black surface and their distribution probably constitutes one of the greatest variables in various types of blacks. Only in graphitized black, the surface of which is almost homogeneous, have these energies all been reduced to the same level. (3) The geometrical factors are represented by the structure which, basically, can only be the anisometry, the deviation of the particles from spherical form, and by the porosity. The latter usually plays a subordinate role, since pores of smaller size cannot be filled by macromolecules so that their inner surface cannot be included when calculating the interface with the polymer.

Greater anisometry causes looser packing of particles, and the determination of the void volume is used to measure the density of packing, i.e., the deviation from spherical form of the particles. The determination of oil absorption for measuring the void volume is widely used, whereas the determination of compressibility under high pressure is less popular. The carbon black particles form irregular structures, which partially break down during mixing. This breakdown is insignificant in the determination of oil absorption, since here only minor shearing forces are active. In the mixing of rubber compounds, however, these forces are considerably greater, so that the structure partially breaks down during processing.

It should be emphasized that none of these three factors by itself but their combination determines the behavior of the rubber vulcanizate, while in some cases a variation in one factor can be compensated for by a corresponding adjustment of the other factors. Therefore, special methods are necessary to determine the influence of any one single factor separately from the other two.

This can be demonstrated by an example. Generally, high-structure black of a certain type (e.g., ISAF) imparts a higher modulus (at 300% elongation) than the corresponding normal black. This high modulus, however, is determined by the product of anisometry and surface activity. The influence of these two factors can be separately analyzed by heat-treating these blacks at 2000–3000°C. During heat treatment the crystallographic structure of the carbon black changes and approaches that of

TABLE I  
Influence of Graphitization of Black on Vulcanizate Properties

	High-structure ISAF black		Normal ISAF black	
	Untreated	Graphitized	Untreated	Graphitized
N <sub>2</sub> surface area, m. <sup>2</sup> /g.	116	86	108	88
Oil absorption, ml./g.	1.72	1.78	1.33	1.54
Extrusion shrinkage, %	30	37	39	43
Mooney viscosity (212°F.)	83	87	73	76
Scorch time (275°F.), min.	10.5	17	18	20
Dispersion, %	99	99	99	98.2
Tensile strength, psi	3800	3400	4000	3300
Modulus (300%), psi	2100	510	1500	420
Abrasion loss, cm. <sup>3</sup> /10 <sup>6</sup> rev.	62	181	67	142
Elongation, %	450	730	630	750
Hardness	73	68	68	65
Hysteresis (log decrement)	0.204	0.297	0.238	0.318
H <sub>2</sub> O adsorption (55% R.H.), %	2.4	0	1.85	0
Bound rubber, %	25.1	0	18	0.4
Propane adsorption (P/P <sub>0</sub> = 0.001), cm. <sup>3</sup> /g.	1.03	0.25	0.93	0.31

graphite. Through recrystallization, the highly active sites on the carbon black surface lose their high activity.

The whole surface area becomes highly homogeneous and all adsorption energies are on their lowest level.

In Table I the effect of this reduction in surface activity on the vulcanizate properties is shown. A number of mechanical properties of the vulcanizate and the nonvulcanized compound for normal and high-structure ISAF before and after heat treatment at 3000°C. are included. This table shows that (1) heat treatment results in a minor decrease in surface area and increase in oil adsorption (measure for geometric structure); (2) tear resistance is decreased by 15% while modulus at 300% elongation is decreased by a factor of three or four. The latter is also true for abrasion resistance.

This decrease is caused by the removal of the highly active sites from the surface which is also expressed in the decrease in water adsorption and propane adsorption. This decrease in adsorption activity is even more obviously expressed by the lower values of bound rubber in graphitized blacks. This goes to show that modulus at 300% elongation is influenced by the surface activity rather than the structure of the carbon black. The behavior of the viscosity is anomalous, inasmuch as the graphitized carbon black compound exhibits a higher Mooney value than the compound containing untreated black.

Considering the lower adsorptive activities of graphitized blacks one would rather expect the opposite. This phenomenon can be explained by the greater breakdown found in the SBR compound containing nongraphitized black.

### Mechanism of Mixing Polymer and Black

In microscopic examinations of thin sections of vulcanizates in which black and polymer were mixed for a short time only, it is conspicuous that at all times a picture of coarse agglomerates appears which contain carbon black in almost pure rubber matrix, almost without any colloiddally dispersed carbon black (Fig. 1). Only after mixing has been continued further can one see how these agglomerates gradually disappear and make room for an increasing amount of dispersed carbon black.<sup>2</sup> In all cases, the first product is an agglomerate which is formed by penetration of rubber in the voids between the carbon black particles under the pressure which builds up during mixing in the Banbury and on the roll mill. As soon as all these voids have been filled, the carbon black is incorporated but not yet dispersed. In the ideal case, one would then find only polymer and agglomerate; in reality, however, the agglomerates are, as soon as they are formed, exposed to the shearing forces, ground up, and eventually dispersed. Consequently, both processes take place simultaneously. In Figure 2, the ideal case is illustrated. The composition of the agglomerates, therefore, is determined by the void volume per gram or per cubic centimeter carbon black. This, however, is the volume determined during the oil adsorption experi-

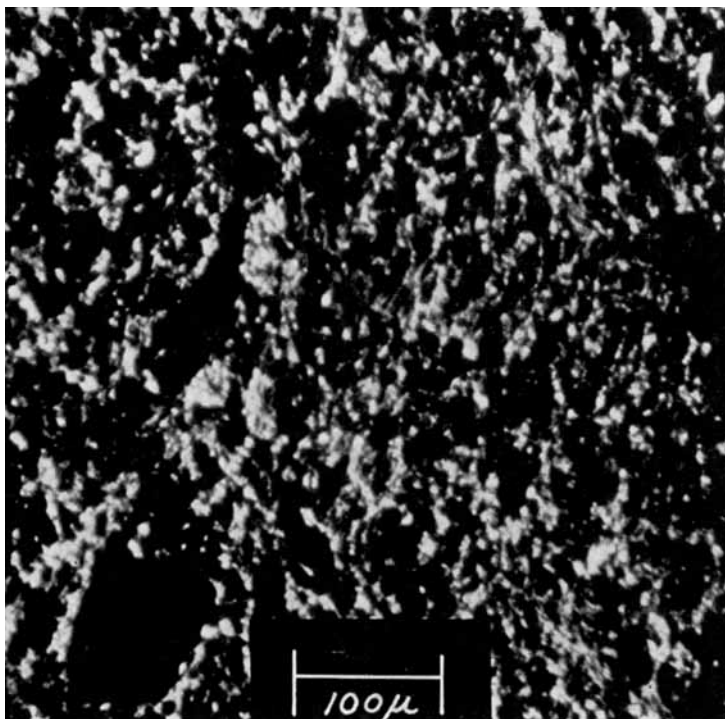


Fig. 1. Microphotograph of a vulcanizate mixed 1.5 min. (50 phr ISAF in oil-extended SBR).

ment. Therefore, this value is determinant for the carbon black concentration in the primary agglomerates. In ISAF black, the oil adsorption value is approximately  $1.30 \text{ cm.}^3/\text{g.}$  of carbon black, so that the primary agglomerates contain  $130 \text{ cm.}^3$  polymer/100 g. of carbon black, or, expressed in units of rubber technology, approximately 82 g. of carbon black/100 g. polymer.

It has been shown experimentally that masterbatches exceeding this critical value of 82 parts black per 100 parts polymer were no longer readily dispersible.<sup>2</sup> In compounds exceeding this concentration the particles come into such close contact that through adsorptive forces they form one mass and can no longer be separated during mastication by shearing forces. This critical concentration is therefore dependent upon the type of black and increases with decreasing oil absorption. In MT blacks with an oil absorption of  $0.6 \text{ cm.}^3/\text{g.}$ , for instance, it lies at approximately 180 parts per 100 parts polymer.

Blacks which are comparable in particle size and total surface area, but vary in structure (as determined by oil absorption) and therefore in void volume, require different mixing times. Since during mixing the voids between the particles are filled, a greater void volume would need a longer time to be filled. However, this is not the only determinant factor, for the

## BLACK-RUBBER VOLUME RELATIONSHIPS

### 50 PARTS OF BLACK + 100 PARTS OF RUBBER BY WEIGHT

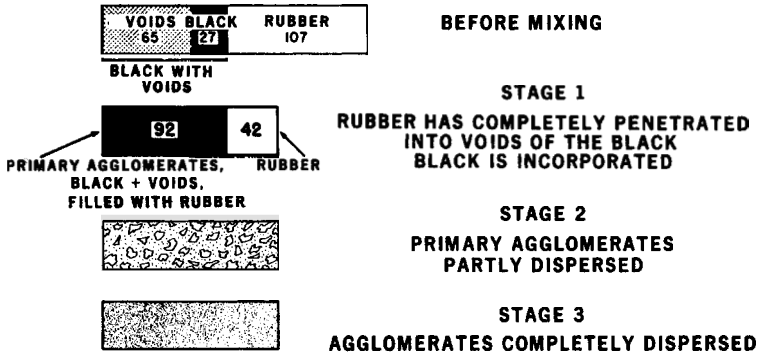
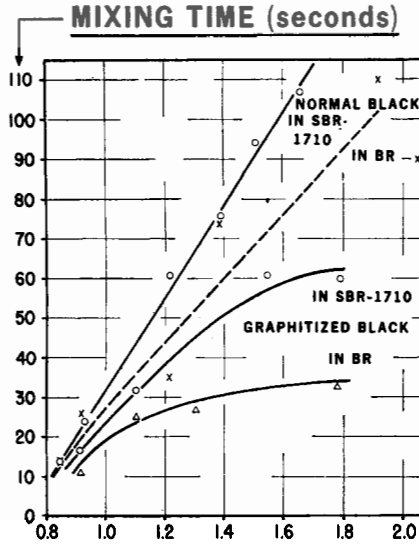


Fig. 2. Volume relationships during mixing of 50 parts ISAF black into 100 parts rubber at various stages.



activity. Through the lower adsorption penetrate between particles more readily. untreated blacks.

filling of the voids is hindered by the adsorption of the rubber molecules on the carbon black surface and is slower as the adsorption forces (surface activity) become higher. With most commercial blacks, increasing structure is coupled with increasing surface activity. Figure 3 shows how incorporation time varies with different structure and surface activity. The lower adsorption activity in graphitized blacks allows easy slippage of rub-

ber molecules on the particle surface when filling interstices during black incorporation, thus shortening the time required for this process as compared to the original blacks.

The ability for easy incorporation, however, should not be confused with dispersibility. After the black has been completely incorporated, further dispersibility is also influenced by structure and adsorption activity. In the case of higher oil absorption, the primary agglomerates contain relatively less carbon black than at low oil absorption. To achieve the final concentration of 50 parts, for example, less diluting, i.e., less mixing energy, is necessary in the case of high structure.

In brief, high-structure blacks need more incorporation energy, but once incorporated, they use less energy for dispersion than do lower-structure blacks.

Although less time is required for the incorporation of low-structure black, a better dispersion is usually obtained in the same mixing time for high-structure blacks of the same particle size.

### Bound Rubber

During mixing and dispersion an active interaction between black and polymer occurs which leads to the formation of bound rubber. Probably these bonds are of physical (adsorption on the highly active sites) as well as of chemical nature (reaction of free rubber radicals produced by shearing forces with reactive carbon black surface groups).

It has been demonstrated<sup>3</sup> that a parallel relationship exists between the formation of bound rubber and shearing forces which can be measured by the Brabender Plastograph. It was found that bound rubber is formed immediately during mixing and that it increases only slightly during storage. The torque-time curve of the Brabender Plastograph and the parallel curve of bound rubber formation are shown in Figure 4.

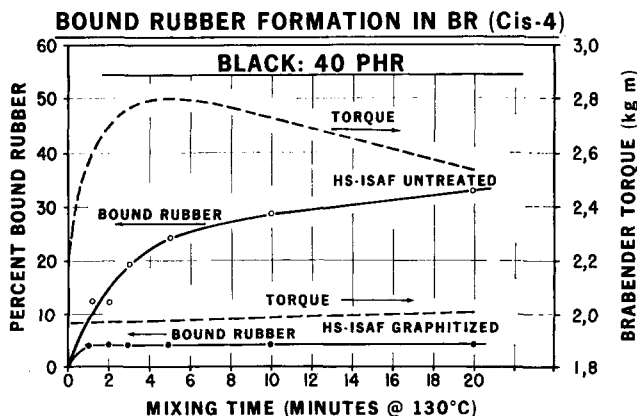


Fig. 4. Brabender curve and formation of bound rubber in polybutadiene.

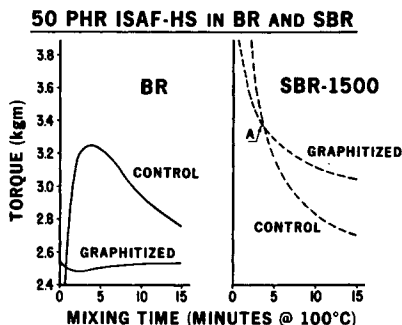


Fig. 5. Decrease in Brabender viscosity of nontreated and treated black in polybutadiene and SBR.

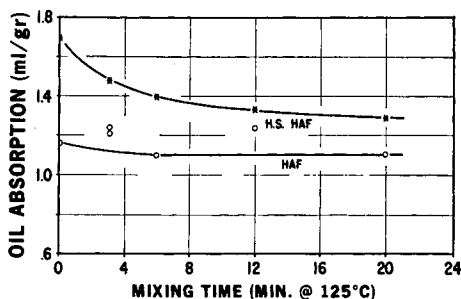


Fig. 6. Decrease in oil absorption as function of mixing time in SBR. After mixing carbon black was recovered and tested (through careful pyrolysis of the vulcanizate under nitrogen).

In many cases their relationship is obscured by the polymer breakdown. In *Cis-4* polybutadiene this breakdown below 150°C. is insignificant. However, with carbon black compounds, during mixing, maxima in torque are observed, which means that degrading forces are active. To which extent vulcanizate properties are influenced by bound rubber is uncertain. Crosslinking in the bound rubber gel appears to be very low, since swelling factors of 25-30 are obtained. Endter<sup>4</sup> showed in 1952 that this black-rubber gel is of a spongy nature, so that the real swelling ratio may be much lower and crosslink density considerably higher. As is evident in Figure 4, the formation of bound rubber is accompanied by a sharp increase in viscosity. This means that through bound rubber formation the shearing forces at constant speed of the rotors are increased, and it is these forces that affect both the further dispersion of the black and the breakdown of the polymer. Through the latter effect the vulcanizate properties are degraded after continued mixing. Figure 5 demonstrates how Mooney viscosity decreases with mixing time in an ISAF black in SBR which develops 28% bound rubber and for the same black, graphitized reaching 5% bound rubber only. In the latter case the breakdown in SBR is smaller even after having reached a point where both viscosities are identical. In polybutadiene, whose



breakdown is negligible, both black compounds behave as expected: the graphitized black with less bound rubber shows the lowest viscosity. It is probable, however, that there is also a breakdown in black structure. For high-structure ISAF it has been proved that at least during the first stage of mastication there is a breakdown in structure. In normal HAF or ISAF blacks, this breakdown is less pronounced (Fig. 6).

Another property of the compound which is affected by the structure and surface activity of the filler is the behavior during extrusion. It is generally acknowledged that blacks with a higher structure cause less extrusion shrinkage of the compound because the high structure reduces the free recovery of elastomer molecules. However, in the case of low surface activity of the black, the absorption of macromolecules is low so that the black has less influence upon the mobility of these molecules. This effect is shown in Table II.

TABLE II  
Extrusion Shrinkage of ISAF Blacks of Different Structure and Surface Activity (50 phr Black)

	Original		Graphitized	
	High	Normal	High	Normal
Oil absorption, ml./g.	1.72	1.33	1.88	1.54
Extrusion shrinkage, %	31	40 (44) <sup>a</sup>	37	44 (48) <sup>a</sup>
Propane adsorption ( $P/P_0 = 0.001$ ), cm. <sup>3</sup> /g.	1.03	0.93	0.30	0.30

<sup>a</sup> Values in parentheses refer to polybutadiene (Cis-4) containing 25% oil.

It is evident from Table II that graphitization somewhat increases the geometric structure (slightly higher oil absorption) and still shows higher extrusion shrinkage. The latter is caused by lower surface activity. This adsorptive activity may be expressed in the amount of adsorbed propane; Table II shows its decrease to approximately one third by graphitization. In addition, the shrinkage could express an indirect effect of the lesser breakdown of rubber in graphitized compounds. This effect contributes to greater extrusion shrinkage. In polybutadiene compounds, where this breakdown occurs to a smaller extent or not at all, the difference between treated and untreated black is the same as in SBR compounds. Therefore, polymer breakdown seems of little significance.

### Influence of Black on Crosslink Density and Vulcanizate Properties

The effect of fillers on crosslink density in vulcanizates is determined by modulus measurements or by swelling experiments. The latter method yields some interesting results.

One repeatedly encounters the difficulty of not knowing whether the black interferes with the vulcanization and thus causes higher crosslink density or whether it lowers the degree of swelling for physical reasons, while the crosslink density in the rubber compound remains the same.

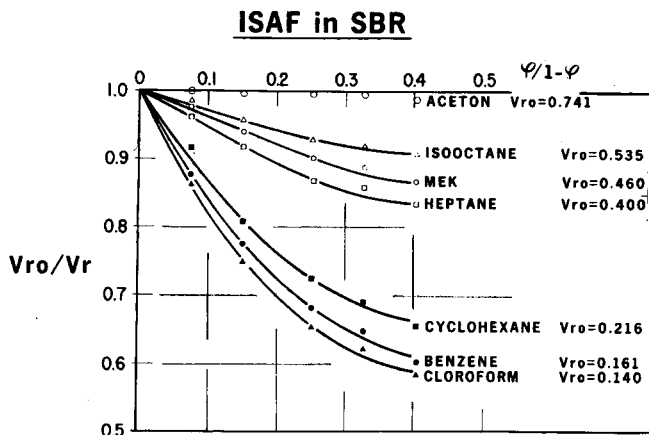


Fig. 7. Decrease in  $V_{r0}/V_r$  as a function of carbon black concentration in different solvents. With non-adhering fillers ( $\text{CaCO}_3$ , glass beads),  $V_{r0}/V_r$  increases with filler content.

Westlinning and Butenuth<sup>5</sup> assume inhomogeneous crosslinking, based upon cryoscopic measurements, the crosslink density surrounding the black particles being greater than in the rest of the matrix.

Depending upon their interaction with the elastomer in the vulcanizate, we distinguish adhering and nonadhering fillers. The former, among them carbon blacks, reduce the swelling of their vulcanizate proportional to the filler content; the latter increase swelling through the formation of voids surrounding the filler particles<sup>6,7</sup> and are not considered here.

The ratio of swelling values of pure gum and filled vulcanizates (produced according to the same recipe, under the same conditions) represents a measure of the reduced swelling caused by carbon black. It is expressed in the relationship  $V_{r0}/V_r$  of the reciprocal swelling values  $V_{r0}$  and  $V_r$ , which represent the volume fraction of rubber in the swollen pure gum vulcanizate and that in the swollen rubber matrix in the carbon black vulcanizate, respectively.

With increasing carbon black concentration in the vulcanizate, there is a proportional decrease of  $V_{r0}/V_r$ ; the proportionality constant  $m$  is dependent not only upon the type of filler but also upon the swelling medium characterized by  $V_{r0}$ . The stronger the medium, that is, the smaller  $V_{r0}$ , the greater is the constant  $m$  of a certain black. This is expressed in Figure 7.

On plotting the constant  $m$  versus  $V_{r0}$  for solvents of different swelling power, a straight line is obtained as demonstrated in Figure 8. As is obvious from Figure 8, a  $V_r$  value for  $m = 0$  is found which, for almost all blacks in SBR, is approximately 0.62. This value for  $V_{r0}$  corresponds with the degree of swelling of approximately 60% in pure gum vulcanizates. Therefore, the carbon black no longer inhibits swelling in solvents of this or less swelling power, so that the swelling is the same for all carbon black con-

centrations and the unfilled vulcanizate. This is the case with swelling in acetone ( $V_{r_0} = 0.75$ ), for instance. It is remarkable that this critical  $V_{r_0}$  value is roughly the same in all blacks and changes only slightly to higher values with increasing crosslink density.

This phenomenon may be explained by the fact that the molecular chains cling to the black surface, still allowing an extension corresponding to approximately 60% isometric swelling. It is different from the behavior of nonadhering fillers which show an increase in swelling with increasing filler content since vacuoles (filled with solvent) are formed around the filler particles. Thus a delicate balance must exist in the case of unrestricted swelling between adhesion and nonadhesion.

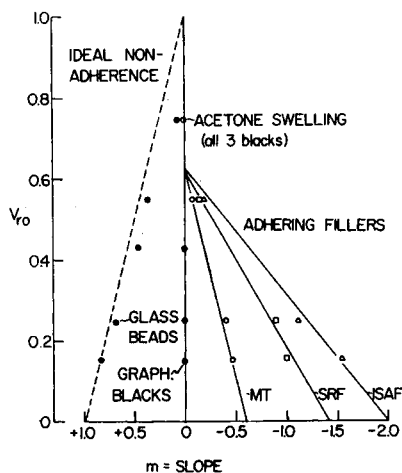


Fig. 8. Tangent  $m$  as function of reciprocal swelling,  $V_{r_0}$ . For  $m = 0$ ,  $V_r$  has a value which in most blacks, is approximately 0.62.

There is a category of blacks exhibiting a different behavior in having no influence upon vulcanizate swelling in all solvents; even the strongest. These are the so-called graphitized blacks, the surface of which has become homogeneous by heat-treatment between 2000 and 3000°C. They represent a special case, insofar as the molecular chains are not detached from the surface but maintain their adherence, although they do not in any way inhibit swelling. The restriction of swelling of adsorbed rubber is caused by its inability to move laterally along the surface. If there is no restriction, a mobile adsorption must exist which allows great mobility of adsorbed macromolecules along the surface but which would require much greater energy for the complete removal of the molecule from the surface.

In normal, nongraphitized blacks this two-dimensional mobility is limited by highly active sites, the presence of which is shown by measurements of adsorption energies<sup>8</sup> (Fig. 9). Therefore, we find that they do not influence swelling up to a certain value but restrict swelling beyond this critical value.

### $Q_s$ AS A FUNCTION OF COVERAGE

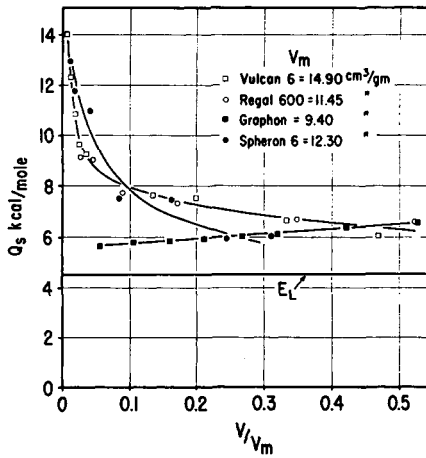
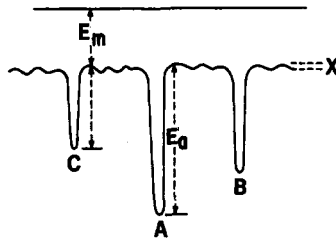


Fig. 9. Differential adsorption energies  $Q_s$  of propane on various blacks at different stages of coverages. High adsorption energies at small  $V/V_m$  indicate sites of high activity. In graphitized blacks, these have disappeared.

### POTENTIAL ENERGY PROFILE

#### I UNTREATED BLACK



#### II GRAPHITIZED BLACK



Fig. 10. Schematic illustration of potential profiles for surfaces of untreated and treated carbon black. A, B, and C represent sites of high activity (after Ross and Olivier<sup>9</sup>).

In Figure 10, the potential profiles of both types of carbon black are shown schematically. In untreated blacks, potential wells of considerable depth are present.

This concept of interaction between carbon black and rubber through limited or unlimited two-dimensional mobility of adsorbed macromolecules allows an insight into the mechanism of reinforcement.

### Mechanism of Reinforcement

The term "reinforcement" has been defined in many ways; here we mean, in first instance, the improved tensile strength achieved by adding carbon black to noncrystallizing elastomers such as butadiene-styrene copolymer. This tensile strength is increased from 20 kg./cm.<sup>2</sup> in the pure gum vulcanizate to 250 kg./cm.<sup>2</sup> through addition of 50 parts reinforcing carbon black. In the beginning of this paper we already mentioned that this unique property of black cannot be explained by the assumption that a number of inflexible chemical bonds are created, since such bonds principally are no different from crosslinks and these normal crosslinks do not lead to any improvement in tensile strength.

Therefore, the forces between black and elastomer must be of a special nature.

The actually measured tensile strength of solids, as generally known, reaches only a fraction of the theoretical value which is obtained by adding all bonding forces that are active in the direction of elongation. For elastomers, this fraction has been approximated as 0.1-0.05.<sup>10</sup> This low strength can be explained by unequal loading of the molecular chains in the vulcanizate during elongation.

During elongation of a noncrystallizing, unfilled vulcanizate the most highly elongated chains will reach their maximum elongation first and break. In this way they no longer carry a part of the tension and thus lose their importance in regard to tensile strength. At continued elongation, the next most highly elongated chains are the ones that break next, and this process is repeated until eventually only a few chains contribute to the final tensile strength. Therefore, the unequal distribution of loading is the cause of low tensile strength.

This heterogeneous distribution can only be offset or at least improved by a slippage process. If the most highly elongated molecular chains do not break down and retain their part in the elongation, the resultant more homogeneous stress distribution will lead to a considerably stronger material. This importance of homogeneous distribution was emphasized as early as 1944 by Alexandrov and Lazurkin.<sup>11</sup> A mechanism of this kind is actually made possible through mobile adsorption. Rubber chains adsorbed on the carbon black surface can still remain in two-dimensional motion on the surface without being separated from it. At sufficiently high elongation, they slip along the surface, since the amount of energy per chain segment required for this process is lower than that required for complete separation from the surface.

Since adsorptive energies are additive, they can reach considerable values if a large number of successive segments are adsorbed. One must imagine that, while chains slip along the surface during elongation, an increasing number of distributed segments line up in sequence on the surface and thus build up the tension that balances the elastic forces at a given elongation, whereby the greatest contribution comes from the points of high adsorptive activity.

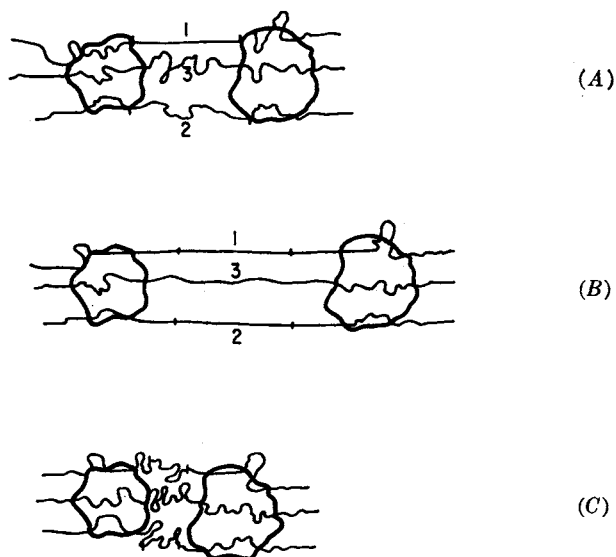


Fig. 11. Schematic illustration of slippage of molecular chains on carbon black surface: (A) Slightly elongated; chain 1 completely extended; chain 3 almost without tension. (B) More highly elongated; chain 1 slipped along surface without breaking; little slippage of chain 2 was necessary until chain 3 was elongated also; chains bear total tension together. (C) After retraction, all chains are of the same length; At repeated elongation, lower stresses than during the first experiment are obtained; Marks on chain 1 and chain 2 indicate original contact points with carbon black particles.

This process is comparable to crystallization which occurs in natural rubber, and, to a smaller degree, in neoprene, butyl, and some stereoregulated polymers as well. All pure gum vulcanizates of crystallizing elastomers exhibit much greater tensile strength than the ones of noncrystallizing elastomers and are only slightly, if at all, reinforced through addition of carbon black.

Seen in the light of the above presentation, it is plausible that carbon black particles and polymer crystallites are active in a similar way, namely as distributors of the stresses during extension.

In Figures 11A and B this process between two black particles is demonstrated schematically. At a low elongation of the test piece, chain 1 is completely elongated, and, if slippage were not possible, it would soon break down under continued elongation; chain 2 would follow the same pattern. However, the chains can slip along the surface with the most probable motion of the segments in the direction of elongation and thus they can reach position B where all three chains sketched bear part of the total load.

A similar theory was presented in somewhat different form by Houwink<sup>12,13</sup> in 1954.

After retraction of the sample, the original situation is not resumed immediately, as illustrated in Figure 9. All chains between two particles have been brought to the same length; and when the test piece is now stretched

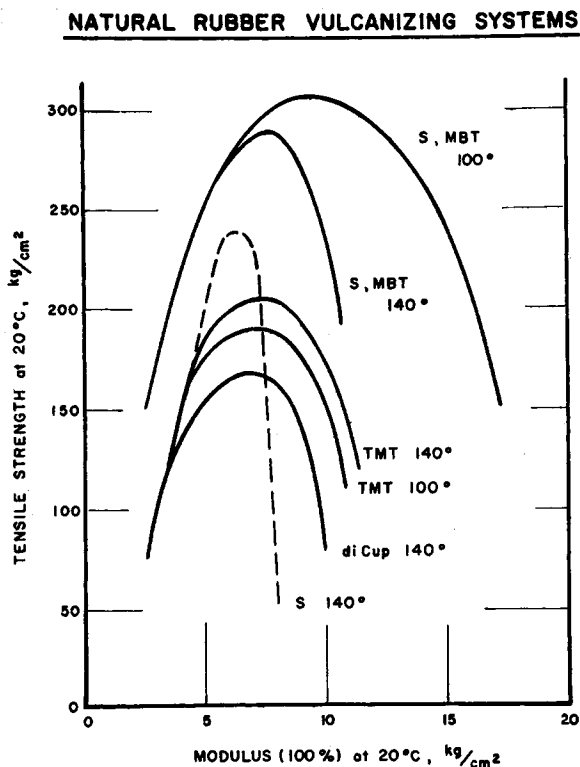


Fig. 12. Tensile strength of pure gum vulcanizates with different crosslinking agents as a function of crosslink density.

for the second time, less energy is required since it is no longer necessary to furnish the frictional energy which was required at the initial elongation in order to make the molecular chains slide along the surface. Thus, a lower modulus is found during repeated elongation.

This phenomenon, known as Mullins effect, is explained by this picture, although actual chain breakage may occur which accounts for the more permanent loss of modulus. After retraction, the sample slowly resumes its original condition. The whole concept is based on the equalization of stress effected by slippage of elastomer chains. Such viscoelastic processes are dependent upon time and temperature. Therefore, it is to be expected that at faster elongation reinforcement is first increased<sup>14</sup> but eventually decreased when the slippage process can no longer match the faster buildup of elastic tension. At low rate of deformation ( $10^{-2}$  cm./sec.), 50 phr of HAF black improves the tear strength of a pure gum SBR vulcanizate about a hundredfold. At higher rate of deformation (1–10 cm./sec.) this difference disappears.<sup>15</sup>

Stress-relaxation measurements show that the rate of relaxation increases with increasing filler content. The activation energy of these relaxation processes yields information on the slippage process. Exact measurements,

however, are not yet available. The postulate cited here is linked with the following experimental facts:

Carbon black vulcanizates exhibit a permanent set after elongation, whereas pure gum vulcanizates show no or a considerably smaller permanent set. This permanent set increases with increasing filler content. The same is true for the hysteresis, which, according to this theory, is due to the losses of friction between gum and carbon black surface. At higher temperatures, the tension of a carbon black vulcanizate at constant elongation decreases in contrast to that of a pure gum vulcanizate for which the elastic tension increases with temperature as required by the kinetic theory of elasticity.

A further support is found in the effect of various types of chemical bonds as crosslinks in pure gum vulcanizates of natural rubber. These are divided into nonstable sulfur bonds of the polysulfide type, di- and monosulfide bonds of medium stability, and stable carbon-to-carbon bonds produced with peroxide. As has been shown by Bateman,<sup>16</sup> tensile strength is highest in vulcanizates with nonstable sulfur bridges and it is lowest in stable peroxide vulcanizates, as illustrated in Figure 12. Labile crosslinks which lead to high tensile strength are also found in polar elastomers such as carboxyl rubbers which are crosslinks by means of metal salts.<sup>17,18</sup> The properties of methylvinylpyridine rubbers crosslinked with metal oxides were studied by Brucksch<sup>19</sup> and by Kopylov et al.<sup>20</sup> They show high tensiles which, however, decrease rapidly at higher temperatures.

Permanent set and stress relaxation decrease with increasing stability of crosslinks, whereas aging improves.

So the same picture presents itself again. The nonstable crosslinks—through breakdown and reformation—make an equalization in tension possible, thus leading to greater strength. The peroxide vulcanizates are the weakest because no reformation of their crosslinks after breakdown is possible.

An important theoretical contribution was made by Wake,<sup>21</sup> who calculated adsorption entropy of *n*-butane and 1-butene on channel blacks based on adsorption measurements by Polley et al.<sup>22</sup> In these calculations a lower entropy value is attributed to the locally adsorbed gas molecules than to the molecules adsorbed but retaining two-dimensional mobility since the latter still have freedom of two-dimensional translation.

Therefore, the difference in entropy between free and adsorbed gas molecules is smaller for mobile adsorption than in the case of local adsorption. Assuming simplified conditions, this difference can be calculated. Wake calculated an entropy value of 13.8 entropy units for mobile adsorption *n*-butane, whereas a value of 12.7 entropy units was found for the experimentally determined adsorption isotherm of *n*-butane on channel black. For butene on channel black, a value of 16 entropy units was found; values of 12 entropy units and 38 entropy units were calculated for mobile adsorption and for local adsorption, respectively, in this case. The experimental values are in better agreement with mobile than with local adsorption. Further adsorption temperature measurements showed that



in the case of ionic crystal powders ( $\text{BaSO}_4$ ,  $\text{CaCO}_3$ ) this mobility does not exist but that adsorption, at least of polarizable molecules such as cyclohexane, is strongly bound on local sites.

These phenomena indicate that in rubber-carbon black compounds and vulcanizates the rubber molecules are adsorbed on the surface and still possess a two-dimensional mobility on this surface. The most strongly elongated chains can slip along the surface and equalize the high stress. This relative movement of molecular chains is equivalent to a movement of carbon black particles related to the rubber matrix. It offers an explanation for the unique properties of carbon black in rubber.

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### Résumé

L'interaction entre le noir de carbone et le polymère débute lors du processus de mélange; un agglomérat primaire est formé dont la composition dépend de la structure. Les propriétés importantes du noir de carbone sont sa surface, son activité spéci-

fique, sa structure (volume vide anisométrie) et la porosité des particules. Par traitement thermique du noir à 3000°C il perd ses sites d'activité spécifique élevée. La structure et l'activité spécifique déterminent le temps d'incorporation et la dispersion future. Au cours du mélange, le caoutchouc lié est formé et est utilisé comme une mesure de l'activité de surface spécifique. Dans le vulcanisat final, l'interaction polymère-charge est évidente telle qu'elle résulte du gonflement réduit dans les solvants (benzène, chloroforme, cyclohexane) etc. En-dessous d'un certain degré critique de gonflement, le pourcentage de gonflement n'est plus dépendant de la quantité de charge au sein du vulcanisat. Les vulcanisats graphitisés montrent pour tous les solvants le même degré de gonflement que le vulcanisat non-charge. Ce phénomène est expliqué en admettant l'adsorption mobile des chaînes de caoutchouc sur la surface du noir de carbone. Dans le noir non traité, la mobilité à la surface est limitée aux sites de haute énergie d'adsorption. Dans les noirs graphitisés, de tels sites ne sont plus trouvés et le gonflement n'est plus empêché par la présence du noir. Le renforcement est expliqué par la distribution la plus homogène de tension entre les chaînes moléculaires due au glissement à la surface du carbone.

### Zusammenfassung

Die Wechselwirkung zwischen Russ und Polymerem beginnt während des Mischungsprozesses, ein primäres Agglomerat wird gebildet, dessen Zusammensetzung von der Struktur abhängig ist. Die wichtigen Russeigenschaften sind spezifische Oberfläche, "spezifische Aktivität," Struktur (Hohlraum-Volumen, Anisometrie) und Porosität der Partikel. Durch Hitzebehandlung von Russ bei 3000°C verliert er seine Bezirke mit hoher spezifischer Aktivität. Struktur und spezifische Aktivität bestimmen die Aufnahmedauer und die weitere Dispergierung. Während des Mischens wird "gebundener Kautschuk" gebildet, der als Mass für die spezifische Oberflächenaktivität benutzt wird. Im Endvulkanisat äussert sich die Füllstoff-Polymer-Wechselwirkung in einer herabgesetzten Quellung in Lösungsmitteln (Benzol, Chloroform, Cyclohexan) etc. Unterhalb eines gewissen kritischen Quellungsgrades hängt die prozentuelle Quellung nicht mehr von der Menge des Füllstoffes im Vulkanisat ab. Graphitierte Russ-Vulkanisate zeigen in allen Lösungsmitteln den gleichen Quellungsgrad wie das ungefüllte Vulkanisat. Diese Erscheinung wird durch die Annahme einer beweglichen Adsorption von Kautschukketten an der Russoberfläche erklärt. Bei unbehandelten Russen wird die Beweglichkeit an der Oberfläche durch Bezirke mit hoher Adsorptionsenergie eingeschränkt. Bei graphitisierten Russen sind keine solchen Bezirke mehr vorhanden und die Quellung wird durch die Gegenwart von Russ nicht behindert. Die Verstärkung wird durch eine homogenere Spannungsverteilung zwischen den Molekülketten infolge Gleitens an der Kohleoberfläche erklärt.

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