Role of particulate fillers in elastomer reinforcement: a review

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In a treatise of this size it is impossible to discuss reinforcement in all its ramifications. The author has attempted to put the emphasis on an understanding of the observed phenomena wherever possible and has gone into detail only when necessary. Naturally the judgement of the importance of details is a subjective matter and not everybody may agree with the author's treatment. An attempt is made to present a unified picture in which differences between concepts and theories are given secondary importance and the agreements between them are emphasized. Much of the subject will deal with carbon black, the most universally used reinforcing filler, but other fillers such as the silicas with their coupling agents are also discussed and compared with carbon black. Similarities and differences between fillers are related to the resulting differences in the properties of the final elastomer–filler composite. Some attention is also given to the growing importance of the fibrous filler. Several review articles and books have dealt with reinforcement. See references 1 to 5.

REINFORCEMENT: THE GENERAL PHENOMENON

Reinforcement is a phenomenon that has many forms and applications and generally requires composites of at least two elements. The classical form is reinforced concrete; others are fibre glass-reinforced polyester resins, phenol formaldehyde resins reinforced with cotton or other fibres and short fibre reinforced plastics. A somewhat different type of reinforcement is presented by the improvement in properties of metals such as aluminium or copper by the dispersion of finely divided oxides (Al_2O_3) in the metal. For high temperature applications of metals and resins, carbon or boron fibres (whiskers) are used.

In many of these composites the mechanism is easy to see. The high longitudinal strength of the embedded fibres or strands is imparted to the composite, the vehicle serving to hold the long strands in place. However, in the case of alumina in metal a different explanation must be sought. The effect is similar to that of glass powder added to certain glues (gum arabic), which has long been a practice to improve its holding properties and decrease brittleness. Brittleness means easy fracture under very small deformation; brittle materials require low energy for fracture. This is caused by the short range of intermolecular forces and the resulting easy propagation of small cracks or flaws in the material or at its surface under the high local stresses at relatively slight deformations. These cracks develop and grow in a direction perpendicular to the direction of the main stress. To reduce brittleness it is necessary to prevent the propagation of small cracks to larger ones. This is done by purposely introducing a large number of irregularities in the crystal lattice (the oxide particles). Here small cracks can form which relieve local stress peaks so that there is no large stress accumulation at any point. The local stresses at the tip of the crack increase with the length of the crack so that crack propagation leads to catastrophic failure. Griffith's classic equation[6] states that the strength of a material is inversely proportional to the square root of the length of the cracks. When there is plastic or viscous flow possible at the tip of the crack (which may be less than 1 μm long), this flow dissipates the energy build-up and the critical energy value required for propagation is not reached so that the crack is stabilized. Clearly, this viscous flow at the tip of the crack requires time and this makes fracture time- and temperature-dependent. Many materials will appear brittle when bent or stressed very rapidly (glass), or at low temperature, whereas under very slow loading they can withstand enormous pressures. In elastomeric and plastic substances considerable plastic flow is often possible; as a consequence brittle fracture only occurs at very high rates of stress (or at low temperature). Failure under normal rates of deformation is due to non-uniform stress distribution so that local stresses surpass the critical crack propagation levels. Further tearing is a relatively slow process because of the high amount of stress-dissipating plastic flow which can occur. This points to the underlying general principle of strength and reinforcement of materials – namely, equal distribution of stress over the load-bearing bonds. One can calculate a theoretical strength for a glass or a vulcanized rubber based on addition of the number of atomic bonds going through a cross-section and assuming affine deformation of the test piece. The strength calculated in this way comes out to be 100 to 1000 times higher than that which is experimentally found. The reason is, in simple terms, that we do not pull all these bonds at the same time or with equal force. Unless applied gradually over an infinitely long time, the stresses are non-uniform. At some points they surpass the internal bond strength, breaking bonds and forming cracks which lead to a greater concentration of stress while other bonds may not carry any load at all. In final analysis the imposed stress is only carried by a relatively small number of bonds; when they break, others may come into play, which, so far have not carried much of the stress. When the stresses increase systematically, as on a tensile testing machine, more and

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more of the high load-carrying bonds are broken until none are left to take a greater part of the ever-increasing stress and the sample breaks. Therefore any means that lead to a more uniform distribution of the imposed stress over the many available load-carrying bonds will result in reinforcement. The means to do this may vary with the material, from the introduction of a large number of small cracks so that no large ones need to form for the harder materials, to providing points of molecular slippage on particulate fillers for elastomeric polymers. The same reinforcement principle holds for all: more uniform distribution of micro or molecular stresses. Improvement of impact strength of plastics by admixture of suitable rubbers is not considered reinforcement. In rubber there can only be reinforcement of vulcanizates, i.e. after formation of a permanent network. Plastics which rely on strong secondary intermolecular forces for their strength are not reinforced by particulate fillers. Reinforcement of elastomers is characterized by the increase in modulus (stiffness) and improvement of fracture properties such as tensile strength, tear and abrasion resistance. Energy at rupture (the integrated area under the stress–strain curve) is often taken as a numerical measure for reinforcement, but this criterion has a few exceptions (graphitized black).

Sometimes a less correct but more easily accessible entity is calculated, the tensile strength on actual cross-section, which is tensile strength × extension ratio (at 100% elongation the extension ratio is 2).

TYPES OF FILLERS

History

The use of fillers in rubber goes back to the times when the South American Indians used latex for the fabrication of shoes and clothing; they are known to have used gunpowder (carbon + sulphur + saltpetre) to impart the fiery magic of gunpowder to the article; probably the carbon powder provided some protection against light while sulphur may have caused partial vulcanization. In the early days of rubberized clothing the rubber layer became tacky after some time by oxidation. The tackiness could be alleviated by dusting with talcum powder. When rubber mastication and mixing were invented, the next logical step was to incorporate the talcum powder in the rubber in an attempt to prevent tackiness. At the same time it was discovered that relatively large amounts of powders such as clay, whiting, lithopone, zinc oxide, etc., could be incorporated in natural rubber without detracting too much from its strength after vulcanization while stiffness and hysteresis increased. In 1904 the reinforcing effect of carbon black was discovered by Mote in England and around 1911–12 this beneficial effect became common knowledge and general practice in tyre tread compounding. The large development of carbon black came after the introduction of synthetic rubbers, particularly of SBR (GR–S) during World War II because its strength as a pure gum vulcanizate is so low as to make it useless; SBR needed carbon black to bring out its potential for practical usefulness. At the same time it was found that synthetic rubbers combined with new types of carbon black (oil furnace types) made tyre treads of greater abrasion resistance than the traditional channel black with natural rubber. Before carbon black attained such a predominant position, inorganic fillers like soft and hard clays, whiting, lithopone, zinc oxide and various types of silica were (and still are) used to obtain certain properties of stiffness, colour or price. In the last two decades, silica manufacturers have made a concentrated effort with limited success to match the reinforcing properties of carbon black in rubber. The attraction of a reinforcing filler which could yield brightly coloured rubber products is evident. Organic materials such as powdered melamine formaldehyde[7] and urea–formaldehyde resins, lignin[8] and starch[9], have been tried but have not become commercially important. Some of these could be added to latex which has advantages for special applications. Their main advantage is the combination of light colour (which allows use of brightly coloured pigments) with low density, i.e. below 1.5 as compared to 2 to 5 for the inorganics. Aqueous dispersions of carbon black are also mixed with rubber latex; after removal of the aqueous vehicle, the resulting dry crumb is known as black masterbatch. In 1949, 22% of all styrene rubbers in the US were in the form of carbon black masterbatch. This figure dropped to a low of 10% in the 1950s, rose to over 20% during the 1960s and dipped below 20% again after 1970. The latest figure for 1976 is just under 15%. The production (consumption) of carbon black in 1977 was 1.52 million long tons in the US and 3.73 million long tons worldwide. The production of all white fillers together is a little less than one-half of the carbon black total.

RUBBER–FILLER COMPOSITE

The mixing process and its mechanism will not be discussed here since it has been treated in previous articles and does not enter into the present arguments[10–12].

Once a filler dispersion in rubber is obtained and the response to deformation of the composite is to be analysed, one can consider three types of interaction which influence its viscoelastic behaviour:

(1) interaction between rubber molecules, attraction, relative movement and elastic recovery;

(2) interaction between filler particles and rubber;

(3) interaction between filler particles themselves.

Interaction between polymer molecules

The interaction between macromolecules is mainly determined by the (chemical) nature of the molecule, its regularity, mobility of its segments, degree of steric hindrance and the presence of stable or transient crosslinks and entanglements and loose ends in the vulcanizate. The presence of fillers alters the relative segmental mobility of the polymer only slightly. The latter is expressed by the glass transition temperature of filled elastomers in comparison with the unfilled polymer. With the most active fillers in sufficient quantity this point is raised (actually widened to a range) by only a few degrees. This is shown in *Figure 1*, where the maximum in mechanical loss angle is taken as a criterion (Smit[13]); Kraus and Gruver[14] showed the same effect by dilatometry. The effect that is found can be ascribed to the lesser mobility of the adsorbed elastomer molecules and adjacent layers compared to segments remote from the filler surface. However, the effect is complicated by new entanglements due to adsorption, which are different for tight vs. loose networks.

Filler–elastomer interaction

The most important interaction is that between filler and base polymer; the properties of the composite are mainly dependent on this interaction.

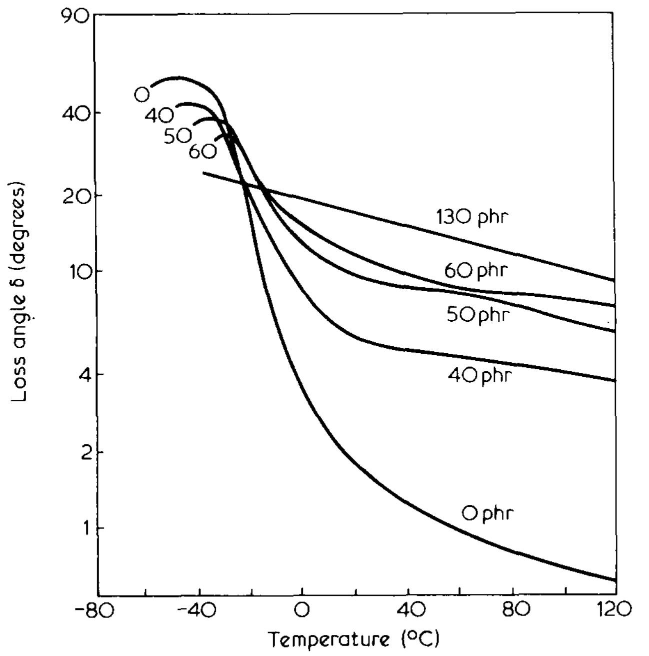


Figure 1 Maximum in loss angle of natural rubber vulcanizates moves only slightly to higher temperatures by the incorporation of up to 60 phr of ISAF black. [Reproduced by kind permission of Rubber Division, American Chem. Soc. from Smit, P. P. A. *Rubber Chem. Technol.* 1968, **41**, 1201 ©]

Hydrodynamic effect. In 1906 Einstein[15] calculated that due to hydrodynamic effects the viscosity, η_0, of a liquid will increase by the addition of uniform spheres by a factor:

$$\eta = \eta_0(1 + 2.5c) \qquad (1)$$

where c is the volume fraction of the spheres.

Conditions for the validity of this equation are: wettability of the particle surface, uniform spherical particles, no interaction between particles. The last two requirements are never met in real dispersions of fillers in an elastomeric vehicle. Guth and Gold[16] added a quadratic term to cover higher concentrations to account for the interaction between the spheres

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

For coarser fillers (above 0.5 μm diameter) this equation agrees fairly well with experimental values up to intermediate concentrations (30%) but for fine particle size carbon blacks the actual increase in viscosity is much more than this equation predicts. It does not take particle size into consideration. For 50 phr HAF black (N330) the value of the volume fraction c is just about 0.20. The numerical value of equation (2) for $c = 0.20$ is

$$\eta = 2.07\,\eta_0$$

so the viscosity of the dispersion should be roughly twice that of the vehicle.

With reinforcing blacks in rubber the ratio may be closer to 4 to 5 when viscosities are measured with the Mooney viscometer.

Guth[17] introduced a shape factor f, the ratio of the longest dimension of the particle to the shortest and derived the equation:

$$\eta = \eta_0(1 + 0.67fc + 1.62f^2c^2) \qquad (3)$$

This equation has also been proven to be valid in a number of cases but for reinforcing blacks f values close to 6 have to be assumed. The aggregates of carbon black seen under the electron microscope in general do not show such a large anisometry. Explanations for the large effect of reinforcing blacks have been brought forward by Brennan[18] who argued that the rubber adsorbed on the carbon–aggregate surface (bound rubber), should be counted as part of the filler particle. Since this not only increases the total filler volume but at the same time decreases the amount of vehicle the effect is large, so large that in a number of cases the calculation leads to higher viscosities than are actually found. Hess[19] considers only part of the bound rubber, the 'bonded rubber', as part of the carbon black filler. The Guth–Gold equation has survived much of its criticism although lower coefficients than 14.1 for the c^2 term have been suggested and, remarkably, it can also be applied to the 'modulus' (load per cm^2, at a fixed elongation) of rubber vulcanizates particularly 'Young's modulus', the slope of the stress–strain curve at the origin[20]. Medalia[21] in studies on dynamic modulus corrected the filler volume for rubber, occluded in and between aggregates.

Bound rubber. The interaction between filler and elastomer is shown by the phenomenon of 'bound rubber'. If reinforcing carbon black or any other reinforcing filler is incorporated in an elastomer on a roll mill or in an internal mixer, part of the rubber becomes insoluble in ordinarily good rubber solvents and forms an insoluble gel with the filler. In a mix of 50 phr of ISAF (N220) black in SBR about 35% of the rubber originally present adheres to the black and becomes insoluble. The soluble or extractable rubber is of a lower average molecular weight than the original rubber[22,23]. The gel contains all the filler (carbon black for instance), its particles or aggregates, held together by strands of macromolecules attached to the filler surface and running from aggregate to aggregate forming one extremely loose network with the carbon black aggregates acting as multiple crosslinks. The degree of swelling of the rubber in this gel (in toluene or xylenes, for instance) is extremely high – of the order of 2000–3000%. V_r, the fraction of rubber in the swollen matrix is the reciprocal of the swelling and in this case is about 0.03–0.05, compared with about 0.25 for a well-crosslinked unfilled vulcanizate; in other words the crosslink density of the carbon gel is only a small fraction of that of a vulcanizate and most probably does not contribute significantly to the chemical crosslinks in the final black vulcanizate. However, a high percentage of bound rubber is indicative of high interaction activity and therefore is associated with a high degree of reinforcement by the filler. The formation of bound rubber can be reduced to almost nil by surface treatment of the filler, in the case of carbon black by heating to 1500°–2500°C.

In some cases the polymer–filler interaction is too strong for practical use, such as is the case of fumed silica in certain silicone rubbers. A slow reaction between filler–hydroxyl and elastomer reactive silanol groups[24] results (after storage for a few weeks or months) in a seemingly partly crosslinked compound, which is unfit for use, as such. Be remilling, the compound can be 'refreshed' or knit together again and the milling time required to 'knit' is of great importance for the practical use of the compound. A long 'knit time' means waste of time and energy. The manufacture of both fillers and elastomers is directed towards minimizing the knit time.

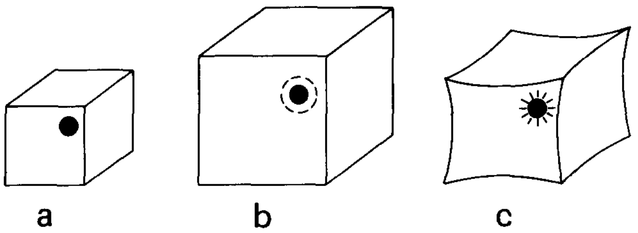


Figure 2 Swelling of filled vulcanizates: (a) original vulcanizate element with filler particle, (b) vulcanizate element swollen to 300% with non-adhering filler particle surrounded by pocket of solvent, (c) swollen vulcanizate element with adhering filler particle, restricting swelling

Effect on swelling. The solid surface of the filler can have three types of interaction with the elastomer, adherence at fixed points, non-adherence, and adherence with 2-dimensional mobility over the surface of the filler. These may come combined in various ways as will be discussed later. The difference in type of interaction becomes clear when swelling a vulcanizate in solvents of increasing swelling power and comparing the degree of swelling with that of the unfilled vulcanizate, assuming that the chemical crosslink density of the polymer has not been changed by the presence of the filler.

Figure 2 shows an element of a crosslinked polymer filled with a non-adhering and with an adhering filler particle. The degree of swelling is usually expressed in terms of its reciprocal, the fraction

$$V_r = \frac{\text{Volume of rubber}}{\text{Volume of the swollen rubber-solvent gel}}$$

It is very much dependent on the swelling power of the solvent (high swelling power means low V_r) and the crosslink density[25]. Higher crosslink density means more restraint on the network and thus results in lower swelling, that is higher V_r (in the same solvent).

In a filled vulcanizate the important unit is

$$V_{rf} = \frac{\text{Volume of rubber in vulcanizate (i.e. total volume minus filler volume)}}{\text{Volume of swollen rubber gel (i.e. total swollen volume minus filler volume)}}$$

and it is of interest to determine the ratio $R = V_{r0}/V_{rf}$ (V_{r0} is V_r of the unfilled vulcanizate), with increasing filler loading.

If the filler swelled just as much as the surrounding rubber–matrix, then that ratio would stay equal to unity as the percentage of filler in the compound increases. However, most fillers do not swell and if the matrix is restricted by the filler through attachments on the filler surface the ratio V_{r0}/V_{rf} will decrease as the filler loading increases. Remarkably, this ratio increases with increasing filler fraction if the filler is of the non-adhering type as was pointed out by Kraus[26]. The reason is that in this case a pocket filled with solvent forms around each filler particle. Since this solvent in the pocket is not taken into account the ratio V_{r0}/V_{rf} increases with the filler volume fraction δ. This is the case with fillers such as whiting, barytes, clays, etc.

In *Figure 3*, V_{r0}/V_{rf} is plotted vs. the filler loading expressed as volume ratio of filler to rubber in the compound $\phi(1 - \phi)$ for adhering and non-adhering fillers.

The relationship is approximately linear at least for concentrations which are not too high and the slope m varies with the particle size of the filler, the swelling power of the solvent, and the reinforcement potential of the filler (Boonstra and Taylor[27]). It gives clues to the reinforcement mechanism as will be discussed later.

Heat treatment of reinforcing blacks to 2500°–3000°C (graphitization) leads to a filler which shows a most interesting swelling behaviour in vulcanized rubber.

In this case the value of $R = V_{r0}/V_{rf}$ stays unity over a large range of loadings, so it is neither an adhering filler which would be indicated by a declining value of R with increasing filler loading nor non-adhering, in which case R would increase with loading. This phenomenon, which is also found with some types of silica in silicone rubber[28] can be explained by assuming mobile adsorption which will be discussed in section 5 on mechanism of reinforcement.

Voet and Cook[31] found that silica in SBR can behave as an adhering filler when the vulcanization system follows a radical mechanism (peroxide or TMTD as accelerator). For a cure with Zn–DMDC + S (ionic mechanism) the swelling indicates the silica is a non-adhering filler. The same authors followed the degree of adherence by means of the volume increase of the vulcanizate when stretched. Small vacuoles form at each particle, depending in size and number on the level of adherence. Together these amount to a measurable increase in volume. Voet and coworkers found a much lower increase when a silane coupling agent was used.

Filler–filler interactions

This third interaction, the filler–filler interaction, has been rather neglected in past research until recently. In the case of carbon black this neglect is due to the old concept (based on images of channel and thermal blacks) that the basic unit of the black is a nearly spherical particle and its size the determinant for surface area and its behaviour in rubber. Since the introduction of the oil furnace blacks in the early forties (now the major type manufactured) a different picture has emerged. It is now generally accepted that the primary particles which may be approximately spherical are fused together to much larger aggregates. These aggregates may contain from a few to several hundred or a thousand primary particles and are the units that actually determine the behaviour in rubber and other vehicles. At high and intermediate concentrations these aggregates form a continuous network of secondary bonds which accounts for some

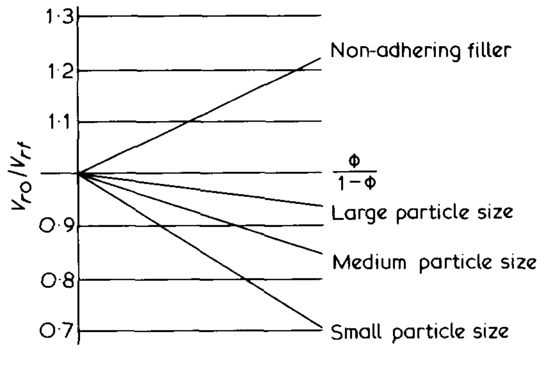


Figure 3 Relative swelling R(= V_{r0}/V_{rf}) of filled vulcanizates as a function of filler loading for various fillers.

of the deformational characteristics of the black vulcanizate, particularly at small deformations. In the old concept it was fairly clear that the black primary particles were practically completely incompressible and their deformation could be neglected; however, this is not the case with the aggregates. This is evident when dry black is put under compression. A high-structure black exhibits a large amount of elastic recovery. It is usually conceived that the carbon black network which exists in a vulcanizate containing about 50 phr of high structure black is broken at rather small deformation (about 5% in unidirectional elongation) and loses most of its elasticity. However, it is also assumed that the network reforms after sufficient rest time and so it must also play a part in the hysteresis losses of the vulcanizate under cyclic deformation at larger deformations; the fragments of the network continue to be deformed or broken and reformed. Under severe attritic conditions the aggregates themselves may break (see the section below on structure). The bonds holding aggregates together are much stronger than the secondary interaggregate bonds and break only under high stress concentrations. Little research has been done to determine which part of the hysteretic losses of a vulcanizate are due to filler–filler interaction.

Dynamic elasticity and hysteresis. Work by Payne[29] on cyclic deformation of vulcanized rubber samples in compression or shear at various amplitudes and frequencies has thrown some light on the particle–particle interaction. Under these cycling conditions a 'dynamic' in-phase elastic modulus G' and a loss modulus G'', 90° out of phase with deformation can be determined. The complex modulus, the modulus measured at any moment, is:

$$G^* = (G'^2 + G''^2)^{1/2}$$

Payne showed that the elastic dynamic modulus at very small amplitudes is high, drops very rapidly as the amplitudes increase, to level off at the highest amplitudes. It is demonstrated by *Figures 4a* and *4b* where dynamic shear modulus is plotted vs. amplitude of oscillation. The effect is reversible provided enough time is allowed for recovery.

A vulcanizate with 23 vol % loading of N330 type black in butyl rubber shows a dynamic modulus of 9.7 MPa at amplitudes of less than 0.1% but as the amplitude increases beyond 1% a rapid decrease occurs, at 10% to the value of 2.6 MPa, nearly a factor of 4 lower. At still higher amplitudes the decline continues further to 1.4 and still has not levelled off. The pure gum vulcanizate shows a constant modulus of 0.2 over the whole range. In the region of low amplitudes the high modulus is constant over about a decade of amplitude. The effect is more pronounced at higher black loading; as concentrations decrease it becomes less noticeable and practically disappears below 10 vol % loading. This higher modulus at low strains is caused by the elastic deformation of the network formed by the carbon aggregates. Support for this concept is the observation that additional work on the carbon black (by attrition), or on the compound by more and more intensive milling, reduces the high modulus at low amplitude and so flattens the whole curve. This is particularly demonstrable for butyl rubber as

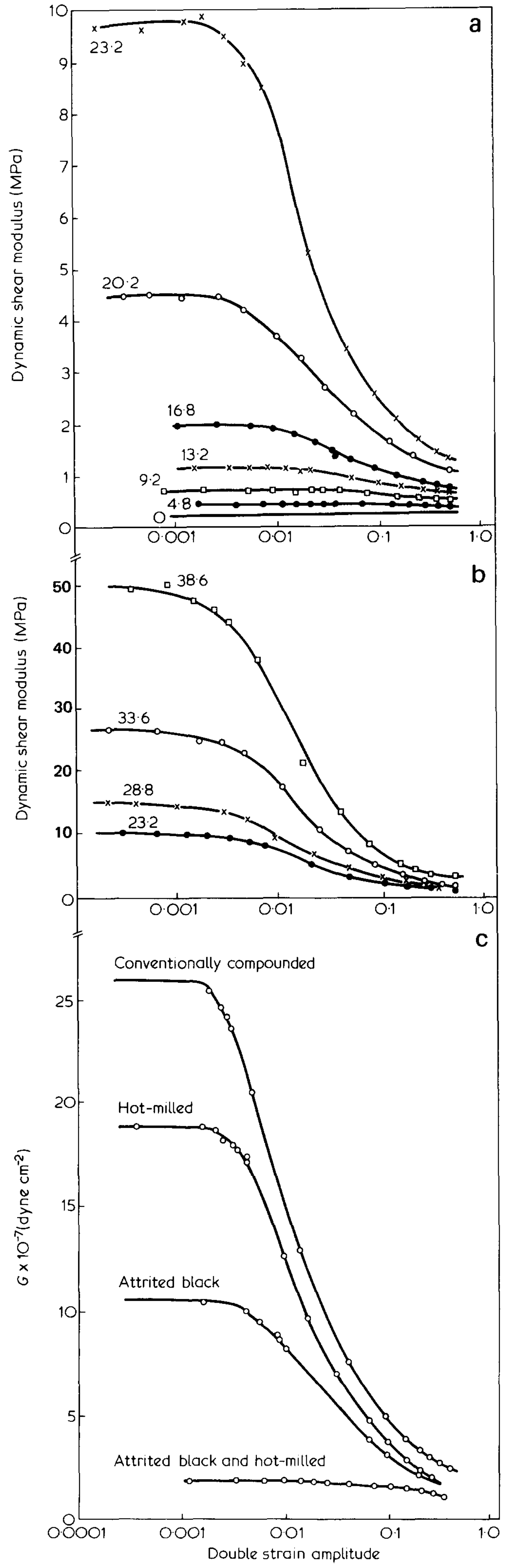


Figure 4 Effect of amplitude on dynamic shear modulus of butyl rubber vulcanizates filled with (a) 4.8 to 23.2 volume % of HAF black; (b) 23.2 → 38.6 volume %; (c) effect of hot milling and attrition on the height of the dynamic modulus curve HAF in butyl rubber. [Reproduced by kind permission of Wiley–Interscience from Payne, A. R. 'Reinforcement of elastomers' (Ed. G. Kraus) 1965, Ch 3 ©]

shown by Gessler[30]. Attrition and hot milling virtually eliminated the effect (*Figure 4c*). Another support for the carbon network concept is that electrical conductivity follows the same pattern as the elastic modulus. At low amplitude when the carbon network is still intact, conductivity is high, but it diminishes rapidly at higher amplitudes in conjunction with the elastic modulus[31] as the carbon network is broken.

The loss modulus, G'', plotted vs. amplitude shows a maximum occurring at the inflection point of the elastic modulus vs. amplitude curve[32]. At this point, the effect of increasing amplitude is maximal, the network will reform itself with time and so it appears evident that these mechanical losses are caused by carbon aggregates interacting with carbon aggregates. It is logical that this effect also exists at higher degrees of deformation since the higher amplitudes can only be reached by way of lower and intermediate amplitudes.

The existence of filler networks is well-known for fumed silica. Here it is utilized to stop liquids from flowing by 'gelling' them with only a few percent of a high-structure fumed silica. Oil is made into grease by such an addition. These silica aggregates hold together by hydrogen bonding between silanol groups on their surface. These bonds are most pronounced in non-polar solvents when there is no competition for the silanol bonding. Therefore the gelling effect is maximal in hydrocarbons and minimal in solvents such as water and alcohols.

EFFECT OF FILLER-PROPERTIES ON REINFORCEMENT

Amount of filler

The most effective way to show the difference between a reinforcing and a non-reinforcing filler is by means of the stress–strain curves at increasing loadings as shown in *Figure 5* (after van Rossem[33]). Much more pronounced is the reinforcement with non-crystallizing synthetic rubbers such as SBR. This is shown by *Figure 5c*. There is an optimum loading for reinforcement properties such as tensile strength and tear and abrasion resistance whereas stiffness increases steadily and elongation decreases at higher loadings. The optimum loading varies for different fillers and different rubbers as shown in *Figure 6*. The optimum occurs because the reinforcing effect (surface effect) is counteracted and finally dominated by a dilution effect (volume effect).

Filler characteristics

The following filler characteristics are of importance for the properties of the compound.

(1) Particle size, which determines the surface area per unit weight and with that the total solid–elastomer interface per cm^3 of compound.

(2) Specific surface activity per cm^2 of surface area.

(3) Shape and structure, as determined by the void volume under standard packing conditions, and porosity of

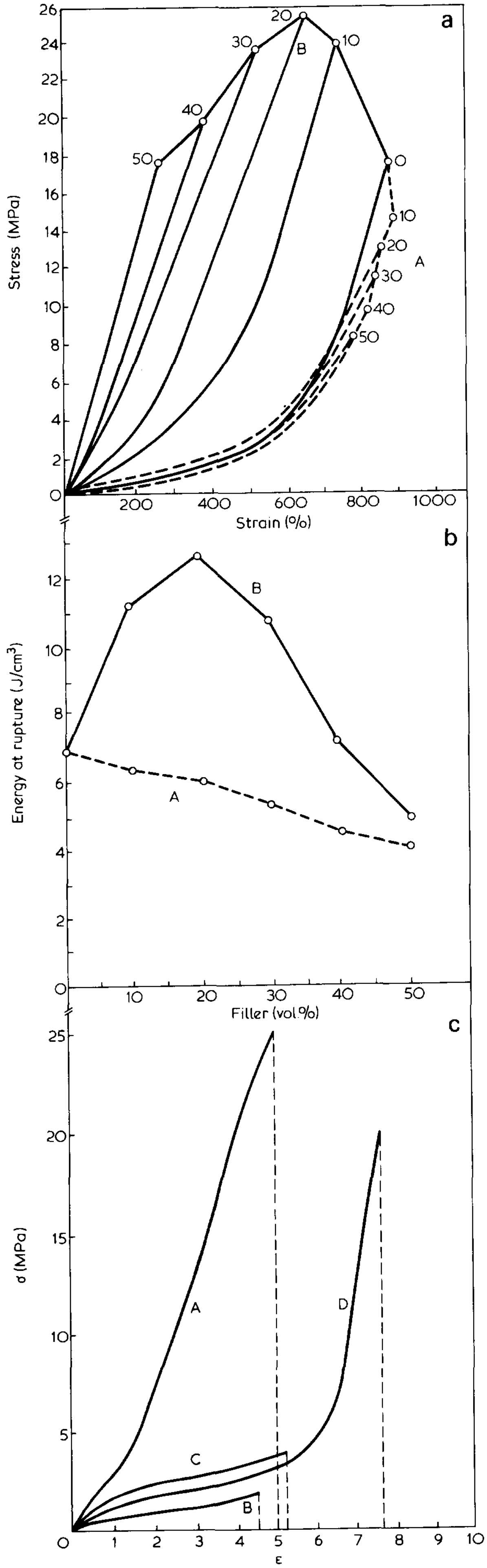


Figure 5 (a) Stress–strain curves of basic natural rubber compound with increasing volume percentage of (a) barytes, and (b) EPC black; (b) change of energy at rupture with increasing volume percentage of (a) barytes and (b) EPC black, courtesy Prof. A. van Rossem. (Ref. 33); (c) typical stress–strain curves of carbon-black-reinforced SBR vulcanizates, (A), unfilled vulcanizate (B), filled with large particle inert filler (C), filled with graphitized carbon black (D). [Reproduced by kind permission of Rubber Division, American Chem. Soc. from Kraus, G. *Rubber Chem. Technol.* 1978, **51**, 315 ©]

the particles, usually referring to pores of very small size.

These properties are usually not independent, so that their product rather than their sum determines final behaviour.

Particle size and surface area. For units of uniform size there is a direct relationship between surface area and particle size: a cube of 1 cm^3 of unit density has a surface area of 6 cm^2 g^{-1}. Cut it in half in each of the three directions and one has created 2 additional surfaces of 1 cm^2 each cut in each direction so now the total is 12 cm^2 and the cube size is ½ cm. The specific surface area is then 6/½ if the density is unity, that is 12 cm^2/g.

Similarly it can be shown that for 1 g of uniform spheres of diameter '*d*' the surface area, $SA = 6/d\rho$ where ρ = density of the filler = 1.85 for carbon black.

Traditionally the surface area of a filler is expressed in m^2 g^{-1}, its particle diameter in nm (10^{-9} m). In these dimensions the equation becomes, for carbon black,

$$SA = 3200/d.$$

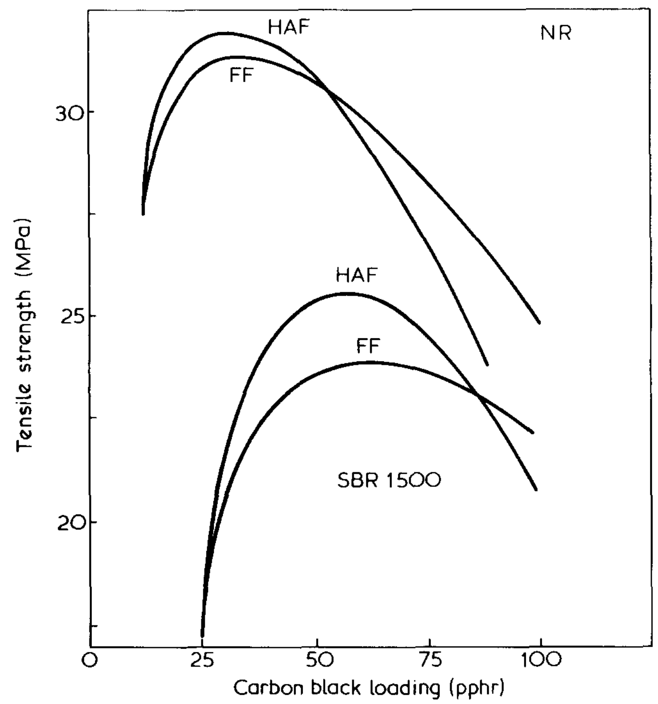


Figure 6 Optimum loading of HAF and FF black in natural rubber and SBR-1500. [Reproduced by kind permission of the Plastics and Rubber Institute from Boonstra, B. B. 'Rubber Technology and Manufacture' (Ed. C. M. Blow) 1971, Ch 7 ©]

Although filler particles are not all spherical in shape and not uniform in size, the equation gives a good approximation of average particle size if surface area is known and *vice versa*. Surface area is easier to measure than particle size and is more relevant. It is the filler property with the largest variation and therefore the most important factor in reinforcement. Coarse fillers may have surface areas of 1 m^2 g^{-1} or less, while precipitated silica is made to 225 225 m^{2}g^{-1}, fumed silica to 400 m^{2}g^{-1}, carbon blacks to 1000 m^{2}g^{-1}. Rubber grade blacks may vary from 6 to 250 m^{2}g^{-1}, a factor of more than 40. Neglecting the fact that not all of the measured surface area is available, one can calculate that a compound with 50 phr of ISAF (N220) has about 35 m^2 of filler–elastomer interface per cm^3.

Table 1 gives a survey of properties of carbon black compounds and shows a rapid decline in reinforcement as the surface area of the carbon black decreases.

Table 2 shows a similar list for inorganic fillers in natural rubber. Here the decline of reinforcement as the filler surface area decreases is not as clear since NR is a self-reinforcing elastomer. Its self-reinforcement is due to crystallization on stretching. The decline in reinforcement is still visible in the tear resistance. In practice the surface area is measured by determination of the adsorption isotherm for nitrogen according to Brunauer, Emmett and Teller (BET)[34]. The volume of nitrogen necessary for a monomolecular layer on the surface can be detected on the isotherm and from the dimensions of the nitrogen molecule the surface area can be calculated. As will be discussed later, the method has to be modified in case of porous fillers.

Simpler methods have also been developed for control such as the adsorption of iodine and CTAB[35] (cetyltrimethylammonium bromide); the first is more sensitive to impurities on the surface, the second measures specifically the outside area (see section on porosity below).

Filler surface activity. The activity of the solid surface, which is important for the interaction with the vehicle and reinforcement of the composite, is mainly of a physical nature particularly in general purpose hydrocarbon rubbers. The polar groups (OH) on the surface of many mineral fillers (clays, whiting, barytes, silicas, etc.) interact with polar rubbers such as chloroprene (CR) rubber, nitrile rubber (NBR) or acrylate type rubbers (ACM and ANM). Too strong an interaction, such as chemical bonding between filler and elastomer, is undesirable as demonstrated by Morton *et al.*[36] with synthetic filler particles which were either reactive or non-reactive. The reactive particles (which contained unsaturated crosslinkable groups) imparted lower tensile

Table 1 Effect of particle size of carbon black at 50 phr on main properties of SBR

Old type	ASTM designation	Surface area (m^2/g)	Average particle size (nm)	Tensile		Relative laboratory abrasion	Relative roadwear resistance
				p.s.i.	MPa		
SAF	N110	140	20–25	3600	25	1.35	1.25
–	N234	120	24–29	3400	24	1.30	1.24
ISAF	N220	120	24–33	3300	23	1.25	1.15
–	N375	90	30–35	3400	22	1.24	1.14
HAF	N330	80	28–36	3200	22.5	1.00	1.00 Standard
FEF	N550	45	39–55	2600	18.5	0.64	0.72
GPF	N660	37	50–60	2300	17	0.55	0.65
SRF–NS	N774	28	70–96	2100	15	0.48	0.60
FT	N880	14	180–200	1800	12.5	0.22	
MT	N990	6	250–350	1400	10	0.18	
No filler		–	–	400	3	–	–

Table 2 Particle size of fillers. Effect on tensile strength and tear resistance of natural rubber vulcanizates

		11.5 volumes				23 volumes				46 volumes			
				Crescent Tear				Crescent Tear				Crescent Tear	
Filler	Particle diameter (nm)	Tensile (p.s.i.)	MPa	lb/in.	kg/cm	Tensile (p.s.i.)	MPa	lb/in	kg/cm	Tensile (p.s.i.)	MPa	lb/in.	kg/cm
Whiting	550	3350	24	62	11	2870	20	67	12	1950	14	90	16
Barytes	500	3430	25	118	21	2840	20	106	19	2000	14	–	–
$MgCO_3$	410	3830	27	90	16	3130	22	112	20	2360	17	168	30
Lithopone	230	3920	28	123	22	3550	25	157	28	2800	20	258	46
Dixie Clay	200	3840	27	78	14	3410	24	112	20	2640	19	151	27
ZnO (ordinary)	130	3920	28	179	32	3630	26	342	62	2700	19	330	59
ZnO (fine part.)	90	3900	28	325	58	4010	28	420	76	3160	23	448	81
Frantex B[a]	65	4340	31	39	70	4410	31	62	11	3770	27	78	14
Silene EF[b]	43	4020	29	319	57	3630	25	398	72	–	–	–	–
Hi–Sil[c]	25	4170	30	409	73	3800	27	470	85	–	–	–	–
Cab–O–Sil[d]	14	4550	32	–	–	–	–	–	–	–	–	–	–
None	–	4650	33	40–100	7–18	–	–	–	–	–	–	–	–

[a] Modified clay; [b] Precipitated calcium silicate [c] Precipitated silica [d] Fumed silica

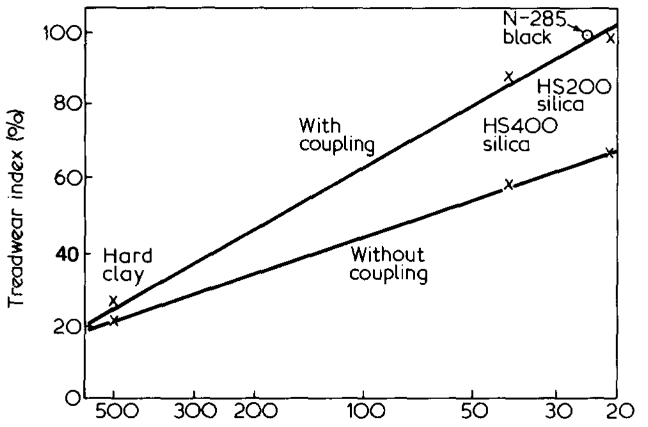


Figure 7 Improvement in treadwear of silicas of various particle size and clay in SBR by the use of a coupling agent (mercaptopropyl triethoxysilane)[37]

Table 3 Effect of black-graphitization on major properties in SBR-1500

	N220 (ISAF)	
	Original	Graphitized
Surface area, N_2 (m^2/g)	108	88
Oil absorption, ($cm^3/100$ g)	133	154
Extrusion shrinkage, (%)	39.6	43.5
Mooney viscosity (100°C)	73	76
Scorch (135°C min)	18	20
Dispersion (%)	99	98.2
Tensile strength (MPa)	27.6	22.8
Modulus (300%, MPa)	10.3	2.9
Abrasion loss (Laboratory)	67	142
Elongation (%)	630	750
Hardness, shore A	68	65
Torsional hysteresis	0.204	0.297
Pelleted bulk density (lb/cu. ft) (g/cm^3)	22.6(0.36)	24.4(0.39)
Bound rubber (%)	18	0.4–2
Propane adsorption (cm^3/g) ($P/P_0 = 0.001$)	0.93	0.31
H_2O adsorption (55% rh %)	1.85	0.0

strength than corresponding particles that had no surface groups capable of reacting with the elastomer.

On the other hand, the surface activity of some fine particle silicas towards hydrocarbon rubbers is so low that surface treatment with certain silanes (which react with surface hydroxyl groups of the filler) results in considerable improvement in strength properties. This is shown in *Figure 7*[37]. The silane used here is mercaptopropyltriethoxysilane $(C_2H_5O)_3Si(CH_2)_3SH$. The ethoxy groups react with free hydroxyl groups on the silica surface, splitting off alcohol. The mercapto group can react with the elastomer during vulcanization. Another coupling agent is bis-(3-triethoxy silylpropyl) tetrasulphide $(C_2H_5O)_3$ $Si(CH_2)_3$ $S{-}S{-}S{-}S(CH_2)_3$ $Si(OC_2H_5)_3$[38].

Attempts to improve further the interaction of carbon black and hydrocarbon elastomers such as natural rubber and SBR have not met with success. Surface treatments by reactive chemicals such as chlorine, nitric acid, sulphuric acid and oxidants have either impaired reinforcement properties or left them unaffected. However, the effect of the surface activity can be clearly demonstrated by deactivating the surface. In the case of carbon black this can be done very simply by heating to high temperatures (1500°–3000°C) excluding air. All surface oxygen and hydrogen is driven off and since carbon is a simple element with a triple point of about 3800°C at 2000 p.s.i., all that can happen to it at these temperatures is recrystallization. This actually occurs and is first noticeable at the surface. Since it is the surface which comes in contact with the polymer, this surface graphitization has a profound effect on rubber properties. The annealing of the carbon aggregates begins at about 1200°C and is complete near 1500°C. Its result is growth of the carbon crystallites and repair of flaws in the crystallographic structure (which were due to the extremely fast formation of carbon black aggregates in the flame and lack of time for formation of perfect crystallites). The carbon black crystallites recrystallize, with their turbostratic arrangement of honeycomb-like layers of carbon atoms, starting at the surface, into larger more ordered, units with few or no lattice flaws. These flaws, which may consist of a carbon atom missing or an unmatched valency, because an adjacent C atom is bound to a hydrogen or otherwise satisfied, form the active spots on the carbon black surface and with their disappearance a large part of the reinforcing capability is lost. The results which are very revealing are shown in *Table 3*. It is of interest to note that tensile strength has decreased only some 15% but, while surface area and oil absorption have not significantly diminished, the 300% modulus has dropped to about a quarter of the corresponding level of the non-treated black compound, abrasion losses have almost

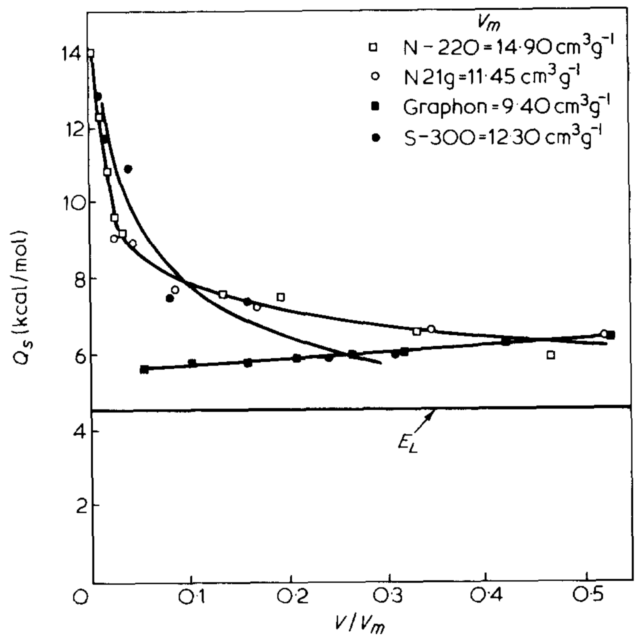


Figure 8 Heat of adsorption of propane on carbon blacks as a function of coverage. [Reproduced by kind permission of the American Chem. Soc. from Taylor, G. and Atkins, J. H. *J. Phys. Chem.* 1966, 70, 1678 ©]

tripled, and hysteresis has increased. The loss in 300% modulus is not due to lower structure since the oil absorption value is increased, indicating higher structure (probably because the annealed aggregates are stronger and not broken down as much during measurement). The reduced surface activity is reflected in lower water adsorption and propane adsorption. After the graphitization process the carbon surface still has a distinct adsorptive activity[40,41]. This is illustrated in *Figure 8*, showing adsorption of propane on various blacks with a surface area of about 100 m^2g^{-1}. It shows that for the original carbon black the first few percent surface coverage has adsorption energies of 38 kJ/mol, the later ones only 25 kJ/mol. The first represents the most active sites and as coverage increases, less and less active sites are filled. Beyond 25% coverage, the energy of adsorption stays practically constant and is of the same order of magnitude as that for graphitized black. The latter shows a slow increase which is due to the contribution of the energy of liquefaction as subsequent propane molecules close ranks with those already present on the surface. This picture is of the greatest importance for understanding the mechanism of reinforcement and the unique position of carbon black compared with mineral or organic fillers.

Further elucidation of this mechanism is provided by the adsorption energy profile of the surfaces of active and graphitized carbon black and mineral fillers such as clay, whiting and some silicas. These profiles are shown in *Figure 9* and are based on the theory of mobile adsorption of de Boer[41] and Ross and Oliver[42]. The Figure represents a schematic of the potential troughs of a molecule such as propane adsorbed on various points of the surface. In *Figure 9a* the reinforcing black shows pits where the adsorptive energy (V_A) is high (flaws in the lattice), and many sites of intermediate energies (V_B and V_C); all of the surface has an adsorptive energy of at least V_m so that to move a molecule from point A to point B one needs an activation energy V_A. The molecule is then still adsorbed but free to move over the surface where it is held by the adsorptive energy V_m. This is the adsorptive energy of that part of the surface which does not have flaws or other active sites.

Figure 9b represents the surface of graphitized blacks where the deep energy troughs have disappeared and a rather uniform adsorption energy V_m exists over the entire surface with only small ripples which are of the order of magnitude of the kinetic energy RT (about 2.5 kJ/mol at room temperature). Adsorbed molecules can move freely over the surface since the required activation energy is of the order of the kinetic energy of a free molecule.

Figure 9c shows typical adsorption on fixed sites. Those adsorbed molecules which have the required activation energy to leave the energy trough are then completely free of the surface; this is the situation that may prevail at many mineral filler surfaces. The energy of adsorption may be quite high. In this respect, calculation by Wake on measurements of Smith *et al.* are interesting[43]. He showed that the total heat of adsorption of cyclohexane, benzene, etc., per cm^2 of surface was higher for barium sulphate and calcium carbonate than for carbon black (steam or vacuum treated). The entropy of adsorption of butane on fixed sites at 300K would have to be 38 e.u. and for mobile adsorption 12.0 e.u. For butene on carbon black an experimental value of 13.8 was derived, close to that for mobile adsorption. His conclusion: hydrocarbons such as butane and butene show mobile adsorption on carbon black. We may therefore expect that segments of the elastomer macromolecule will also be attached to the carbon surface by mobile adsorption.

This may well be a unique property of the carbon black surface responsible for its reinforcement of hydrocarbon rubbers: a number of adsorptive sites of varying energy content superimposed on a uniform surface of a relatively lower but constant adsorptive capacity.

Shape and structure:

Shape. (a) The simplest form of a filler particle is a sphere or the nearest approach to it, when the dimensions in all three directions are approximately equal.

The two other possibilities for non-convoluted (i.e. convex) filler particles are:

(b) dimensions in two directions are significantly larger than in the third direction – platelets.

(c) dimensions in two directions are much smaller than in the third one. The particles are acicular, approaching rods or needles or in the extreme case fibres.

The effect of these fillers on final composite properties such as viscosity, etc., increases as the shape changes from spherical to platelets to needles, assuming approximately identical surface area and surface activity. Of course the last is difficult to realize, but *Figure 10* shows the effect for three mineral fillers where these conditions are approximately idenfilled. It shows that the increase in Mooney viscosity with loading is much greater with Attapulgus clay which is acicular, than with ASP-400 clay whose particles are platelets. Ato-

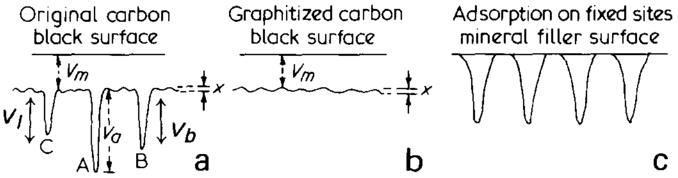


Figure 9 Types of adsorptive surface profiles. (a) Original carbon black surface, active spots A, B and C have high adsorptive energies V_A, V_B, V_C etc; (b) graphitized black shows a rather uniform surface with adsorptive energy V_m (monolayer) with small undulations due to the proximity of surface atoms; (c) adsorption on fixed sites

mite, with spheroid particles, with no pronounced geometrically dominant direction, shows the smallest rise.

According to Voet and Suriano[44] the relation is expressed by the empirical equation:

$$\log \eta_r = kv$$

in which v is the volume ratio of filler to vehicles and η_r is the relative viscosity. The constant k is the shape factor. The figure shows the highest shape factor for the acicular Attacote whereas ASP 400 shows a k only slightly more than unity and the Atomite line has a slope of practically unity. Similar effects are found for the 25 and 50% modulus of the vulcanizates of these compounds.

The ultimate in shape factor is reached with 'short' fibres as fillers. Here the ratio of length to diameter (aspect ratio) lies between 50–800. The most suitable are fibres with aspect ratios of 50–200[45,46]. These can be nylon, Kevlar, glass, carbon (graphite), cellulose or asbestos. A much-used length is 6.4 mm (¼ in). When used as a filler in elastomers they impart very high stiffness and at the same time the elongation is greatly reduced, particularly in the direction of the fibres if these are oriented in the test piece. The reinforcement is not of the type defined in the section on type of filler above; there is no increase in energy at rupture. Due to the drastic reduction in elongation there is actually a decrease in total rupture energy and of strength on cross-section at break, the product of tensile strength and extension ratio, i.e.:

$$\left(1+\frac{\text{elongation}}{100}\right)\text{Ts} = \text{Ts on actual cross-section at rupture}$$

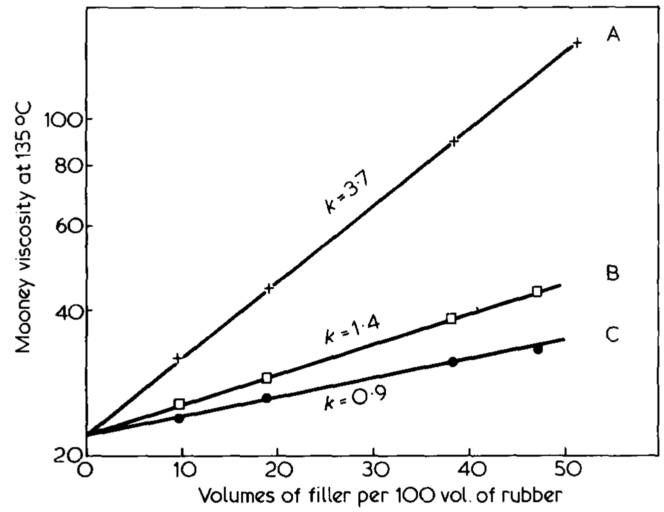


Figure 10 **Mooney viscosity as a function of volume loading for particulates of 3 different shapes, rods, platelets, and spherical clumps. A, Attacote rods; B, ASP-400 platelets; C, Atomite, spheroids**

The composites are used as an engineering material for intricately-shaped articles where reinforcement with continuous fibres (belts, hose, tyres) cannot be used. Adhesion to the elastomer is a key problem and often requires surface treatment with chemical bonding agents. *Table 4* shows some of the properties of short fibre reinforced NR (from O'Connor[46]).

Structure. In the case of carbon black a more complicated factor, 'structure', takes the place of differences in shape. Structure is a property introduced in 1944 by Sweitzer and Goodrich[47] to account for differences in rubber properties imparted by different blacks of the same particle size or surface area.

The unit of importance in carbon black is the primary aggregate, built up by the fusion or sintering of the primary particles in the flame. Each of the primary particles is built up from crystallites on the outside and less organized material in the interior. The crystallites on the surface are platelets, oriented mainly parallel to the surface of the particle. Particle size is still often measured or calculated from surface area. The latter is an approximation which is allowable since a relatively small percentage of the area of each particle is lost by fusion to others, forming an aggregate. Surface area is a more meaningful criterion than particle size. For rheological properties it is the aggregate that counts. These aggregates can be either compact or voluminous and highly branched out (dendritic). This has a profound effect on the viscoelastic behaviour of compound and vulcanizate. A classification of the morphology of aggregates has been given by Medalia[48] based on 'anisometry' and 'bulkiness' of the aggregate. Together these define the structure. *Figure 11* gives a few examples of the method. Analysis on this basis, even with automated image analyses, is a lengthy process. A practical way of determining 'structure' is by measuring the void volume. This is done by mixing a weighed amount of black with a liquid such as dibutyl phthalate (DBP). The first additions of DBP leave the black as a dry powder but

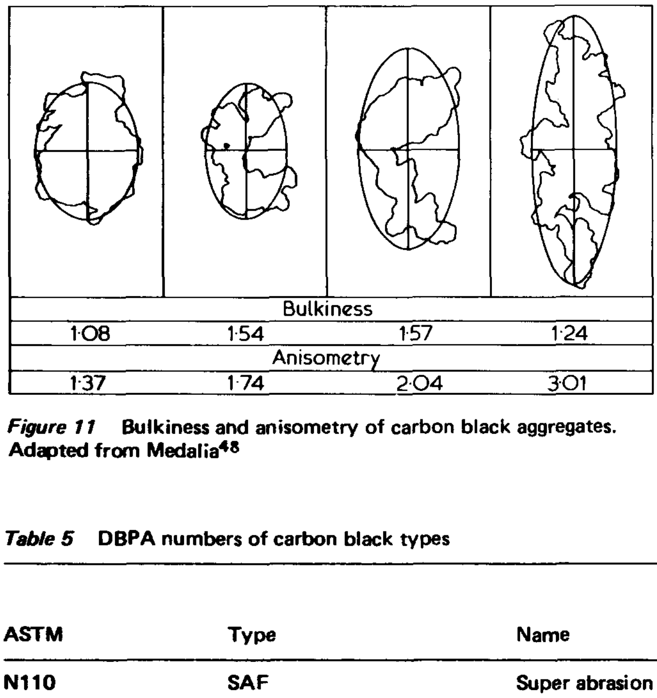
Table 4 **Effect of fibre content on properties of natural rubber composites**

								Before processing			
Fibre	Fibre volume %	Orientation fibre	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Tear Resist. (N/m)	Hardness Durom A	Fibre length (mm)	Fibre diameter (mm)	*L/D* ratio	In composite *L/D* ratio
None (carbon black present)	–	–	6.4	24	460 .	54	75	–	–	–	–
Glass	22.9	Longt.	50	16	27	41	90	6.4	0.013	490	17
		Trans.	21	7.4	80	23					
Carbon	23.5	Longt.	53	15	30	40	90	6.4	0.008	790	–
		Trans.	20	7	87	24					
Cellulose	24.4	Longt.	149	24	10	7	94	2.0	0.012	167	100
		Trans.	40	9	38	30					
Kevlar	24.0	Longt.	200	21	10	97	97	6.4	0.012	530	111
		Trans.	48	11	33	50					
Nylon	24.5	Longt.	107	25	27	113	93	6.4	0.025	250	180
		Trans.	35	11	45	14					

when more of the fluid is added, coherent lumps develop and at the end-point the viscosity of the mix rises sharply as one coherent mass is formed. The end-point is quite sharp and occurs when all the voids between and in the aggregates are filled with DBP. The value is not very much influenced by surface area or surface activity. Uniform spheres in closest packing would leave 26% of void space – in random packing 36%; this value becomes much larger if units of irregular and branched structures are packed. The more branched the structures are, the higher is the void volume. The values for carbon black are usually expressed in cm^3 of dibutylphthalate per 100 g of black. To compare with the figures above, 100 g of black (of density 1.85 g/cm^3) occupies only 54 cm^3, so that a dibutylphthalate absorption (DBPA) value of 100 cm^3/100 g is 185 cm^3 of DBP/100 cm^3 of black and equals 65% void volume.

A few typical DBPA values are shown in *Table 5* expressed in cm^3 DBP/100 g of black. In a number of cases deviations from the expected behaviour occur which are due to the difference in fragility of the carbon structure.

One has to consider that the dendritic structure is much higher at the moment of formation in the flame than in the final product. This structure is constantly reduced by handling, pelletization, densification, and finally by mixing with the elastomer. In this last operation very high shear forces develop which can destroy a large part of the structure of some blacks and a smaller part of others if these have a stronger, more persistent structure[49]. Therefore, the DBPA test is not always indicative of the structure that remains after mixing with the elastomer. To compensate for this to some extent, dry carbon black can be compressed under high pressure to break some of the branches of some aggregates, push others into each other (compacting) and thus reduce the structure. According to the 24 M4 test[50] the carbon black is compressed four times under 24 000 p.s.i. pressure. After each compression the carbon cake is broken up and put into the compression apparatus again; after the fourth compression the DBPA is determined. The difference between the original DBPA value and the one after compression gives an idea about the strength of the structure of the particular black (see *Table 5*).



	Bulkiness		
1·08	1·54	1·57	1·24
	Anisometry		
1·37	1·74	2·04	3·01

Figure 11 **Bulkiness and anisometry of carbon black aggregates. Adapted from Medalia[48]**

The DBPA test is rarely used for fillers other than carbon black. Precipitated silica can be manufactured to have a DBPA of 225 cm^3/100 g; for fumed silica, values as high as 640 cm^3/100 g can be found. The measurement is less precise than for carbon black and has less meaning for the silica-filled rubber properties. Sometimes fluids different from DBP are used for silica and silicate fillers to obtain a clearer end-point.

Porosity. The aggregates of certain carbon black types contain pores, cracks and fissures. The degree of porosity can be measured by the 'internal surface area'. The BET nitrogen adsorption method[51] measures all areas accessible to the nitrogen molecule which is much smaller than hydrocarbon molecules, particularly segments of an elastomer chain molecule. Many pores, cracks and cavities are not accessible to the polymer segments. The N_2 adsorption method then results in a much larger area than has meaning for the rubber compound.

To determine the outer surface a variation of the BET method is applied known as the '*t*' method of Lippens, Linsen and de Boer[52]. The principle is best illustrated by

Table 5 **DBPA numbers of carbon black types**

ASTM	Type	Name	DBPA (cm^3/100g) Orig.	DBPA (cm^3/100g) Crushed
N110	SAF	Super abrasion furnace	115	99
N234	–	Improved ISAF	125	101
N220	ISAF	Intermediate super abrasion furnace	116	100
N219	ISAF-LS	Intermediate super abrasion low structure	78	76
N375	–	Improved HAF	114	97
N330	HAF	High abrasion furnace	103	90
N326	HAF-LS	High abrasion furnace low structure	72	68
N339	–	Improved HAF	121	100
N472	XCF	Extra conductive furnace	185	135
N550	FEF	Fast extruding furnace	120	86
N660	GPF	General purpose furnace	91	77
N650	GPF-HS	General purpose furnace high structure	122	86
N774	SRF-NS	Semi-reinforcing furnace non-staining	70	59
N880	FT	Fine thermal	35	–
N990	MT	Medium thermal	30	–
	Acetylene black	Conductive black	>200	70
Silica	Precipitated	(SA 120–140 m^2/g)	200–220	–
	Precipitated	E.P. (SA 47 m^2/g)	200	–
	Fumed	130–150 m^2/g)	520	
		200 (m^2/g)	560	
		325 (m^2/g)	610	–
		380 (m^2/g)	640	–

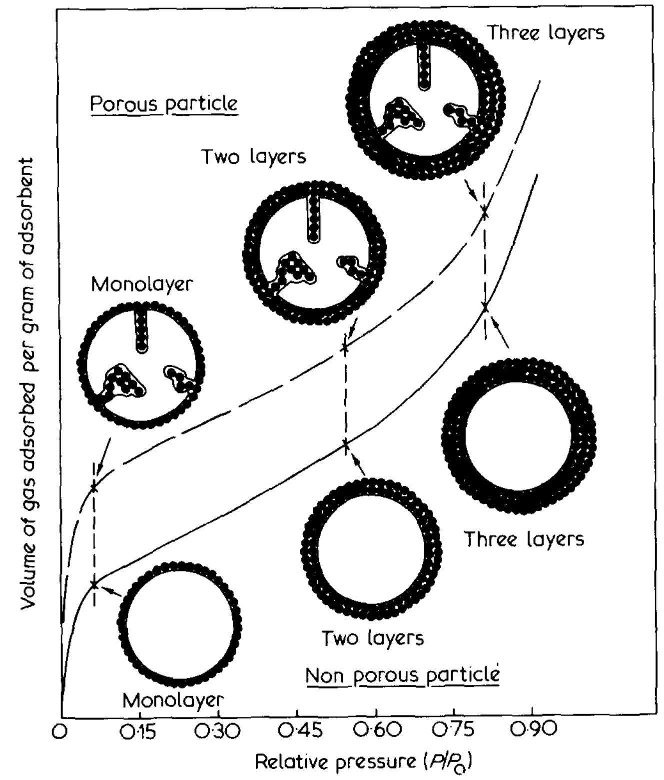


Figure 12 Illustration of the principle of surface area determination of the 't' method. [Reproduced by kind permission of the Plastics and Rubber Institute from Medalia, A. I. *Plast. Rubber Proc.* Vol 3 ©

Figure 12 borrowed from Gessler, Hess and Medalia[53]. After the first monolayer has formed, filling the pores, the amount of nitrogen necessary for the second layer is determined. From this value the outer surface is calculated.

Most rubber grade blacks are non-porous as is shown in *Table 6*. An exception is the conductive black N472 (Vulcan XC-72) and blacks made for paint, ink and lacquer applications. Porosity is the result of partial oxidation; since the rate of oxidation is much faster parallel to the crystal layer planes than perpendicular to them, certain regions of the carbon black particle are specifically attacked. Particularly the inside which is less crystallized is easily attacked by oxygen or oxidative agents which eat their way into the interior along certain paths, starting at the edges. Porosity has two effects. One is that porous particles tend to adsorb more accelerator and therefore retard the vulcanization. The second is that porous particles weigh less than solid ones so that for a given weight loading, there are more porous particles and aggregates than there would be solid ones. Therefore their average interaggregate distance is smaller which leads to higher conductivity. Thus the conductive black N472 is much more porous than other rubber blacks.

Effect of fillers on type and density of crosslinks

Reinforcing fillers resemble additional chemical crosslinks in their effect on a rubber vulcanizate. They increase modulus and reduce elongation and swelling in solvents. Modulus and swelling in a pure gum vulcanizate are measures of crosslink density. However, addition of fillers increases permanent set and creep, whereas higher chemical crosslink density results in lower creep and remaining set after deformation. In addition, all filled vulcanizates exhibit a negative temperature coefficient contrary to the theory of kinetic elasticity, which requires the elastic tension to be proportional to the absolute temperature.

If we consider the filler, particularly carbon black, as a multiple crosslink it must be a very transient type of crosslink, capable of rearrangements. This is consistent with the mechanism of reinforcement explained below. Apart from this, the presence of a filler influences the vulcanization reaction particularly sulphur vulcanization. Lorenz and Parks[54] and Westlinning[55,56] have shown that the rate of crosslinking and induction period with dicumyl peroxide is independent of the amount of carbon black of the HAF type. Porter[57] showed a similar case for a curing system with low sulphur and high acceleration level. In the standard sulphur–accelerator formulation, however, both induction period and rate of crosslinking are affected by the presence of carbon black. According to studies by Moore[58] the ratio of the various types of sulphur crosslinks is influenced by carbon black.

In the case of silica, completely different effects play a role. With precipitated silica, the surface silanol groups react with the zinc oxide in the recipe forming zinc silicate, thus deactivating the most reactive sites on the surface[59,60]. Leaving out the zinc oxide results in better vulcanizate properties but the viscosity of the unvulcanized compound is impractically high. Glycols are used to alleviate the problem. Coarse fillers leave the crosslinking unaffected unless they are of a strongly acidic or alkaline nature.

Summary of filler properties and their effect on final vulcanizates

The carbon black properties which influence compound and vulcanizate properties can be summarized as follows in

Table 6 BET and *'t'* surface areas for some carbon blacks and mineral fillers

Non-porous fillers carbon blacks			Surface area		
ASTM	Type		BET (m^2/g)	't'	DBP ($cm^3/100g$)
N110	SAF	Rubber-grade	138	138	115
N234	–	blacks are all	123	122	127
N220	ISAF	essentially	118	117	116
N375	–	non-porous	95	94	114
N330	HAF		82	82	103
N550	FEF		44	43	120
N774	SRF–NS		28	28	70
N880	FT		14	14	40
N990	MT		6	6	30
Acetylene black			60		>200
Fumed silica (high S.A.)			380	387	640
(medium S.A.)			207	215	560
(low S.A.)			45	45	–
Fumed alumina			94	96	–
Precipitated silica			125	129	200
Porous carbon blacks					
N472	XCF		243	143	185
Medium Colour black			214	165	122
High colour black			527	359	121
S301 (medium processing channel black)	MPC	Obsolete	113	92	95

* Using the FT (fine thermal black) curve for master curve

order of importance

Higher surface area

Increases	Decreases
Dispersion time	Elongation at break
Viscosity	Fatigue life
Bound rubber	Extrusion shrinkage (small effect)
Abrasion resistance	
Tensile strength	
Modulus and hardness (small effect)	
Electric conductivity	
Hysteresis	

Higher specific surface activity

Increases	Decreases
300% Modulus	Hysteresis
Abrasion resistance	
Adsorptive properties (bound rubber)	

Higher structure (persisting in the compound)

Increases	Decreases
Incorporation time and degree of dispersion	Extrusion shrinkage
Viscosity	
Fatigue life (probably through better dispersion)	
Modulus and hardness	
Hysteresis (slightly)	
Abrasion resistance at high severity	

Higher porosity

Increases
Mooney viscosity
Electrical conductivity
Modulus

REINFORCEMENT MECHANISM: PRACTICAL SIGNIFICANCE

Reinforcement manifests itself in many ways. One of the most obvious examples is the increase in tensile strength and elongation of a random copolymer such as SBR. As a pure gum vulcanizate, this has only a strength of 350 p.s.i. (2.2 MPa) at room temperature; by the addition of 50 phr of a highly reinforcing carbon black this can be raised to over 4000 p.s.i. (30 MPa), a factor of 12 higher than the pure gum with a similar increase in rupture energy (see above). This criterion does not hold for natural rubber, of which a pure gum vulcanizate can be made having a tensile strength of 45–50 MPa (6000–7000 p.s.i.) at an elongation of 700%. The cause of this enormous strength is the very regular linear structure of the natural polyisoprene chain which, on stretching above 400% elongation, begins to crystallize where bundles of stretched-out chains run parallel. Up to 1/3 of the elastomer can be in the form of crystallites, which constitute areas of extra-strong cohesion between the elastomer chains. It is important that chains arrange and rearrange themselves under tension to accommodate the stresses and thus distribute them very uniformly. These crystallites carry out the same function as a reinforcing filler; therefore crystallizing rubbers such as NR, IIR, CR are already self-reinforcing and will be hardly reinforced by fillers, as judged by tensile strength or high-elongation modulus. There is a beneficial effect of carbon black on abrasion resistance at medium and high severity. Local high temperature and complex stresses hamper crystallite formation here. On the other hand, any particulate filler of adequate subdivision – that is, having sufficiently large surface area – will reinforce an elastomer such as SBR (or NBR) provided it is wetted by the rubber.

The most important reinforcement aspect is that of improved abrasion resistance which gives carbon black its unique position as a rubber filler. It finds its origin in the high affinity of carbon black for hydrocarbons, the property that has given rubber its name (from its use as an eraser to rub out pencil marks by adsorbing the graphite). The differential heat of adsorption of natural rubber on carbon black at low concentration is 26 J/g of black[61]. The cohesive energy density of polyisoprene in the layer next to the adsorbed one can be considerably less. The eraser demonstrates the principle, it picks up the pencil's graphite and disintegrates itself into small rolls. Although this is one of the causes of the unique action of carbon black on hydrocarbon rubber, it is not the only cause of its reinforcing capacity. The main cause is, in the author's opinion, the phenomenon of mobile adsorption in combination with points of higher adsorption capacity (active sites) that is the basis for the unique carbon black reinforcement. The principle is shown in the classical picture presented in *Figure 13*. The mechanism gives a natural explanation for the stress softening, the phenomenon that after prestressing to a definite elongation and relaxing, a second extension follows a stress–strain curve with much lower stresses up to the elongation of prestrain (so-called Mullins effect). It also explains the negative temperature coefficient of the tension of a black-loaded vulcanizate instead of the positive temperature coefficient of elastic stress required by the theory of kinetic elasticity. The slippage also contributes to the high hysteresis of black vulcanizates. It dissipates the energy which would otherwise be used for formation of cracks or growth of cracks. This last aspect opens a new view on the relationship between hysteresis and reinforcement (tensile

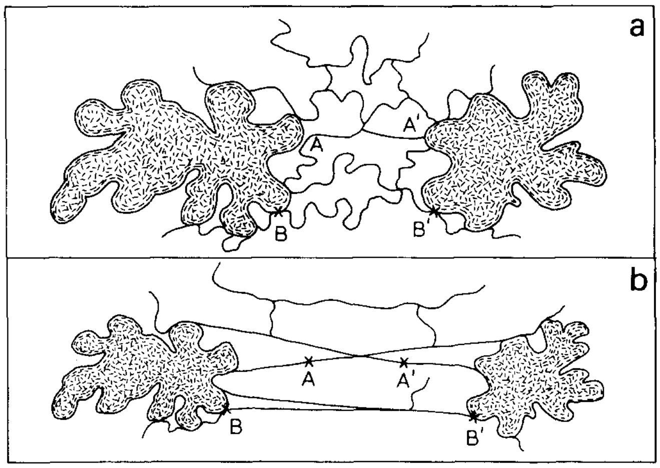


Figure 13 (a) Elastomer molecules between two adjacent carbon black aggregates at very low strain (along the axis connecting the two aggregates). The chain between A and A' is fully stretched. Chain between B and B' is still loosely coiled. (b) Same molecules and aggregates as under (a) but stretched some 300%. Chain AA' would have broken in case of fixed points A and A'. In this present case the chain has slipped at these points and former segment of attachment A and A' are now in the middle of the chain. Chain between B and B' is now also fully stretched so the full load is carried by several stretched chains

strength and abrasion resistance). These have been considered for many years as opposing factors, i.e. one could not be improved without deteriorating the other one. If one wanted higher tensile and abrasion resistance, one went to a higher surface area of black which gave the expected improvement but at the same time resulted in a higher hysteresis, an effect which seemed unavoidable.

In recent years, however, the view has gained ground that a large part of hysteresis at practical deformation levels is due to the interaction between carbon black aggregates themselves (see section on dynamic properties) and that it must be possible to influence this part of the hysteresis by carbon black properties without degrading the reinforcing action.

Stacy and coworkers[62] showed that for blacks of equal surface area, those with wider aggregate size distribution had lower hysteresis than those with narrow size distribution. The data have considerable scatter, but this is to be expected because of the other factors influencing hysteresis. High reinforcement plus low hysteresis is an ideal combination which tyre manufacturers have been wishing for. If the several hysteresis factors can be separated quantitatively it means an important step towards still better tyre tread material.

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