

# Review

## Polymer–filler interactions in rubber reinforcement

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The reinforcement of elastomers by finely divided fillers, particularly carbon black and silica, is fundamental to the rubber industry. Optimal reinforcement appears to involve both physical and chemical interactions. From a consideration of the effects of particle size as such, it appears that reinforcement, in the sense of tensile enhancement, will occur with any very finely divided filler. Physical factors prevent escape of the polymer from the filler surface (vacuole formation) but allow stress delocalization through interfacial slippage. Occasional stronger bonds may be introduced advantageously to facilitate dispersion, reduce particle/particle interactions, and optimize practical properties relating to resilience and durability. Several lines of evidence suggest that only a minor amount of strong bonding is necessary or desirable, such that polymer/filler slippage can occur, under stress, over most of the interfacial area.

### 1. Introduction

Synthetic elastomers used in the rubber industry are amorphous high polymers having low glass transition temperatures, so that the chains are thermally mobile under the temperature conditions to be encountered in service. The primary chains have molecular weights typically in the region of 200 000 to 500 000 weight average. Cross-links are introduced during the vulcanization process, the molecular weight between cross-links being typically of the order of 5000 to 10 000. Vulcanization changes the material from a formable, viscoelastic substance to a highly elastic product capable of returning essentially to its original shape following very large deformations.

As applied to an amorphous (non stress-crystallizing) elastomer such as styrene–butadiene rubber (SBR), the vulcanization process yields resilient products having elastic properties but very little strength. Strength properties are introduced by the addition of “reinforcing” fillers, with carbon black being by far the most commonly used. The phenomenon of reinforcement is essential to the rubber industry, and is the subject of a very large body of literature. The contributions of many highly competent workers have yet to produce a consensus as to the fundamental nature of reinforcement. Existing theories of reinforcement number seven or more as delineated, for example, by Dannenberg [1], and in no case has a theory been expressed in simple or readily comprehensible terms. One of the major problems, from an investigative standpoint, is the difficulty of dissecting the vulcanized product so as to define conditions at the polymer–filler interface as they exist under service conditions. This difficulty applies most strongly to the question of polymer–filler bonding,

which is perhaps the single most controversial element of the subject. If, as many have postulated, chemical interaction occurs between carbon black and hydrocarbon elastomers during the mixing and/or vulcanization steps, then the rubber industry has been practising reactive processing of filled polymers for at least 80 years. The present paper will discuss some aspects of the elastomer–filler interface, with reference partly to physical effects, and partly to the utility and extent of strong bonding in practical systems.

### 2. The reinforcement phenomenon

For the purposes of this discussion, the term “reinforcement” will refer simply to the striking changes in stress–strain properties (extension to break as conventionally measured at room temperature) brought about by the presence of reinforcing particles in the vulcanizate. These changes are: (i) an increase in modulus, or stress at a given strain; (ii) an increase in elongation at break for vulcanizates having a “practical” degree of cross-linking ( $M_c$  in the region of 5000 to 10 000); and (iii) as a consequence, an increase of an order of magnitude in the tensile strength. These changes are illustrated in Fig. 1, which compares two SBR vulcanizates that are identical except for the presence or absence of 50 p.h.r. (parts by weight per hundred parts of rubber) of N220 carbon black in the compound recipe. The increase in modulus is, of course, to be expected, qualitatively at least, because the carbon black particles are rigid; the puzzle resides in the ability of the carbon black to permit a much increased elongation at break and, hence, an enormous improvement in the ultimate strength of the composite.

Reinforcement in a practical sense may be con-

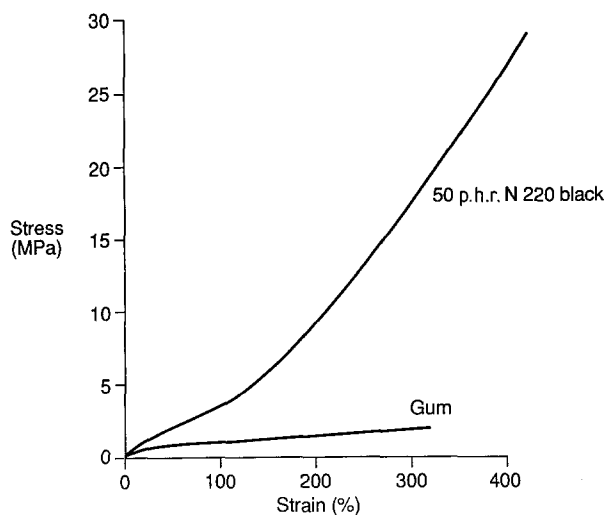


Figure 1 Gum: SBR 1502, 100; zinc oxide, 3; stearic acid, 1.5; Santoflex 13, 0.5; Santoflex 77, 0.5; Sundex 8125, 3; DPG, 0.3; Santocure NS, 1.2; Sulphur, 2. Black: Same formulation with addition of 50 p.h.r. N-220 carbon black. Press cure: 40 min at 153°C.

sidered in other terms, such as abrasion resistance or other measures of durability; and the issue can be further complicated by emphasis that may be placed, quite properly, upon relatively moderate improvements or differences in behaviour of which the literature takes note in practical contexts. These finer distinctions often tend to obscure the principal phenomenon, which is the remarkable difference (for non-stress crystallizing elastomers) between the non-reinforced, or "gum" vulcanizate, and the reinforced composite.

### 3. Reinforcing materials – effect of particle size

The list of particulate materials that have been shown to produce reinforcement effects, in the sense described above, is considerable. It includes carbon blacks, graphitized carbon blacks [2], precipitated silicas and silicates [3], anhydrous silicas [4], esterified silica [5], lignin when co-precipitated with SBR from solution as sodium lignate [6, 7], or when recovered by a "laundering" process to provide a product dispersible in dry rubber [8, 9], starch derivatives including zinc starch xanthate [10, 11], and particulate condensation resins of the urea formaldehyde or melamine formaldehyde types [12, 13].

These materials represent a broad diversity with respect to the chemical nature of their surfaces, but have the common feature of extremely small particle size. One is therefore drawn toward the hypothesis that any solid material will reinforce rubber provided it can be obtained in a very finely divided state and can be dispersed in the polymeric matrix. Such a hypothesis is by no means new, indeed it must occur to anyone interested in the subject of reinforcement. Thus Schmidt [14], in 1951, reported very strong reinforcing effects in SBR using colloidal stannic oxide, silica, Prussian Blue, polystyrene and casein, concluding that "small particle size of the pigment is of prime importance in elastomer reinforcement, whereas the chemical nature of the pigment appears to be of secondary importance".

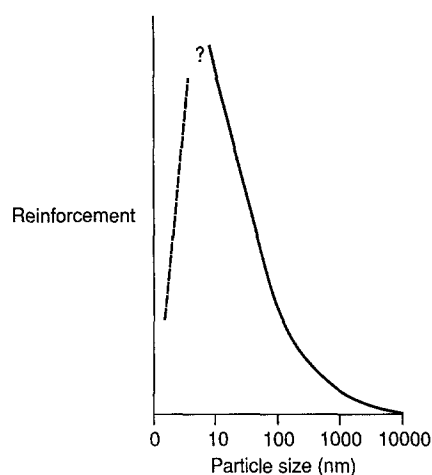


Figure 2 Schematic illustration of the effect of particle size on rubber reinforcement.

Although this hypothesis cannot be proven fully by experiment, there being no means for testing all imaginable materials, there is, nevertheless, good evidence that small particle size is a necessary requirement, and very likely the predominant requirement, for the reinforcement effect in rubber. In the carbon black field, there is a gradation of properties from the thermal blacks, with particle diameters above 300 nm, which show little reinforcement, through the "semi-reinforcing" furnace grades, with particle diameters in the region of 100 to 200 nm, thence to the "high abrasion" furnace grades (about 40 nm) and finally to the "intermediate super-abrasion" or "super-abrasion" grades with primary particle diameters below 35 nm. (The particle sizes are those of Studebaker [15]. Moderately different values are given in the literature, depending on the measurement used, but the distinctions are not such as to affect the present discussion.)

In categorizing non-black fillers, Wagner [16] distinguishes "diluent" fillers (e.g. soft clays) having particle sizes in the region of 1000 to 8000 nm, "semi-reinforcing" fillers (hard clays, zinc or titanium oxides, precipitated calcium carbonates) with diameters from 100 to 1000 nm, and "reinforcing" fillers (precipitated calcium carbonates, silicas, calcium silicates or silico-aluminates, or anhydrous silicas) with particle diameters in the range of 10 to 100 nm.

Referring specifically to calcium carbonates, Delfosse ([17–19], see also [20]) described the 1000 to 5000 nm range as "diluent", 100 to 1000 nm as "semi-reinforcing" and less than 100 nm as "reinforcing". The properties in this case refer to natural rubber, which is not classifiable as an amorphous elastomer; however, the data indicate very large increases in tensile and tear strengths as the particle size is reduced below 50 nm.

Thus, for all cases a high degree of reinforcement, and a very high dependence of reinforcement on particle size, are observed in the primary particle size range of 10 to 100 nm. The region below 10 nm appears to be largely unexplored. There must be some state of subdivision below which the properties would be more akin to a molecular solution than a dispersion of solid particles. This suggests that a maximum must

be present in the relationship between reinforcement and particle size; if so, its location has yet to be determined. The question is illustrated schematically in Fig. 2.

#### 4. Interfacial effects consequent upon small particle size

It is surprising, given the above observations, that the literature on rubber reinforcement is devoted so much to surface chemistry, and so little to the possible physical effects of particle size (and surface area) as such. Gent and Tompkins ([21], see also [22]), however, pointed out that the pressure required to maintain a gas bubble in a liquid becomes very large as the bubble size is reduced, and suggested that this effect might be relevant to the behaviour of rubber in relation to small solid particles. It is of interest to pursue this line of thought in greater detail, because it offers the possibility of insights that depend, to a first approximation, solely upon particle size. For the purposes of this discussion, the rubber is considered to behave as a hydrocarbon liquid, and the intermolecular forces (for the hydrocarbon and carbon black cases) are considered to be predominantly of the London dispersion type (see [23]). In the notation,  $\gamma$  is the surface tension; the subscripts l and s refer to liquid and solid, respectively, and the superscript d denotes that portion of the surface tension due to London dispersion forces. Values of the surface tension of hydrocarbon polymers are in the region of  $30 \text{ mN m}^{-1}$  [24].

For a gas bubble at equilibrium (Fig. 3a), the tension normal to a line around the circumference is balanced by the internal pressure:

$$\pi r^2 P = 2\pi r \gamma_l$$

whence

$$P = 2\gamma_l r^{-1}$$

where  $P$  is the internal pressure and  $r$  is the radius of the sphere. The dependence of pressure on bubble diameter is shown in Fig. 4. The pressure is seen to rise rapidly for bubble diameters below 50 nm, and to enter the order of magnitude characteristic of the

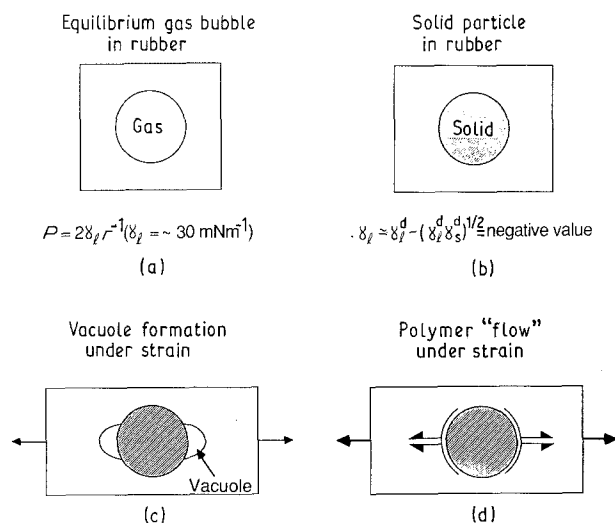


Figure 3 Spherical inclusions within "liquid" rubber medium. The sequence (a), (b), (c), (d) refers to the order of discussions in the text.

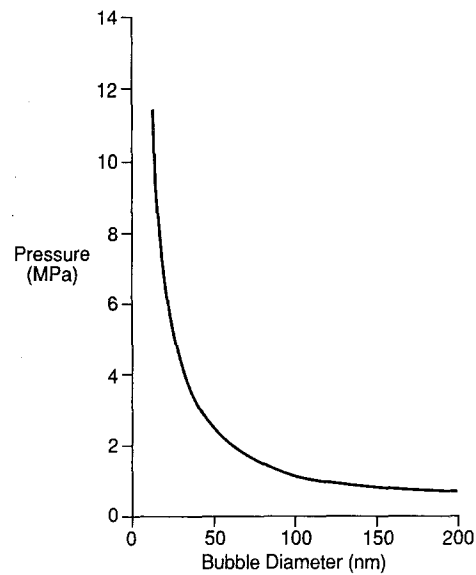


Figure 4 Calculated pressure within an air bubble, at equilibrium, in a liquid medium, assuming a surface tension of  $30 \text{ mN m}^{-1}$ .

forces required for large deformations in vulcanized rubber.

When, instead of air, the enclosed space is filled by a solid particle (Fig. 3b), the situation changes entirely. The liquid is now attracted to the solid surface as well as to itself. The resultant surface tension, considering the liquid in isolation, is approximated [23] by

$$\gamma_l - (\gamma_l^d \gamma_s^d)^{1/2}$$

If the dispersion component of the surface energy of the solid is greater than that of the liquid, as is normally the case, then the surface tension of the liquid, considered in isolation, is negative. Taking  $\gamma_s^d$  for graphite as  $110 \text{ mN m}^{-1}$ , for example [23], the surface tension of the polymer at the interface comes to  $-27 \text{ mN m}^{-1}$ . Thus, the polymer wets and adheres to the surface, being held by moderate intermolecular attractive forces, but is not pressured against it as was the case with the gas bubble.

The final and most interesting part of the thought process arises when we now attempt to separate the polymer from the filler surface (Fig. 3c). As soon as separation occurs, the conditions of Fig. 4 are once again pertinent. However, there is now no mechanism (high internal gas pressure) to sustain an equilibrium; the state of separation is prohibited by the magnitude of the surface tension forces tending to collapse the bubble. (These forces are actually supplemented, in the present case, by atmospheric pressure, although this factor is very small compared to the surface tension factor.)

From these considerations it seems evident that separation of the polymer from the surface of particles having a small radius of curvature is prohibited. Under deformation, the polymer molecules may be free to move with respect to the filler surface, if held only by weak intermolecular attractions (Fig. 3d); but escape from the surface in the sense of vacuole formation is ruled out by surface energy considerations.

An example illustrating the effect is shown in Fig. 5 [25]. This compares vacuole formation (measured by density changes observed upon stretching specimens

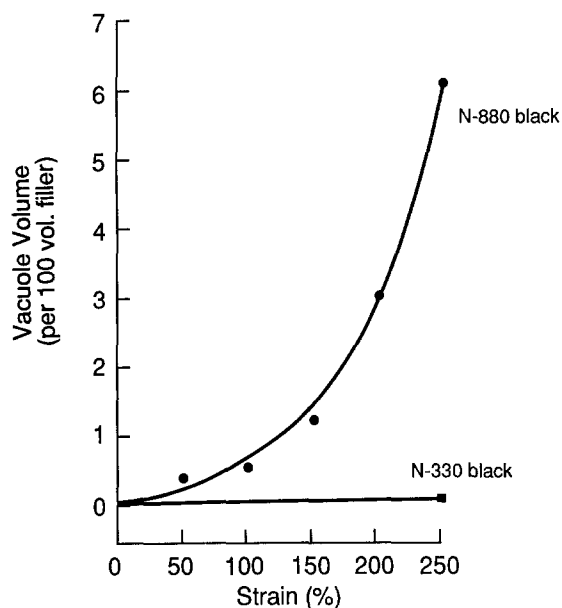


Figure 5 Vacuole formation in black-filled butyl rubber. Polysar Butyl 301, 100; carbon black, 50; zinc oxide, 5; stearic acid, 3; MBTS, 0.5; TMTD, 1.0; sulphur, 2.0. Press cure: 50 min at 145°C.

immersed in ethanol) for two grades of carbon black compounded at 50 p.h.r. in vulcanized butyl rubber. A substantial volume increase occurs with N-880 black (particle diameter about 300 nm) while little or no effect is observed with a reinforcing black (N-330, 44 nm) under the same conditions.

### 5. Reinforcement as a stress delocalization mechanism

The sliding of elastomer molecular segments across the filler interface is a mechanism for the conversion of elastically stored energy into heat (hysteresis) and for the partial relief of excessive stresses in localized areas. Movement of the particles, rotationally and otherwise, can also be envisioned as a stress delocalization mechanism. Such processes are similar to those proposed by others, notably Dannenberg [26].

Grosch *et al.* [27] showed that, for amorphous elastomers, the work required to extend and break a vulcanizate specimen increases with the hysteresis according to an empirical relationship of the form

$$U_B = KH^C$$

in which  $U_B$  is the energy to break, and  $H$  the hysteresis (determined by the difference between the areas under the stress-strain curves upon extension and retraction, in specimens elongated nearly to the breaking point). This type of relationship was shown to be universal for amorphous elastomers,  $C$  being nearly  $2/3$  in all cases tested, and  $K$  also showing similar, although not identical, values for the various elastomer types. The relationship holds for reinforced and unreinforced specimens, extended to break at various temperatures, or swollen to various degrees with a solvent. In the case of carbon-filled compounds, "stress softening" (a term derived from earlier work by Mullins [28], and referring to a pronounced lowering in the stress when a filled vulcanizate is extended a second time to strains lower than that of the first extension) was considered to be "a major source of

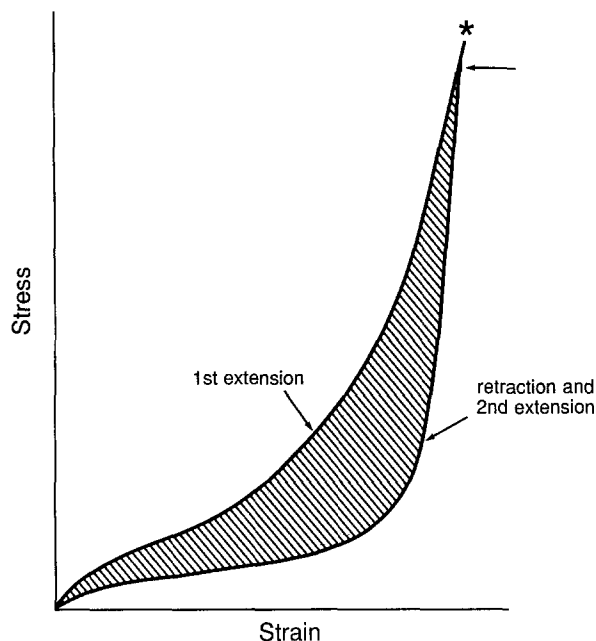


Figure 6 Simplified schematic diagram showing two successive stress-strain curves in a reinforced amorphous elastomer, the first extension being nearly to break, and the second extension to break.

hysteresis in these rubbers". A simplified schematic diagram is shown in Fig. 6.

For the case of HAF black compounded at 30 p.h.r. in SBR, Bueche [29] showed that the "stress-softening" effect following high extensions is permanent (at room temperature) in the sense that it does not recover after solvent-swelling and then drying the vulcanizate; internal breakage or permanent rearrangement of some kind must have occurred. (It appears that high extensions are required to demonstrate this effect in unequivocal terms. Harwood *et al.* [30], working at moderate strains, found little distinction between the behaviour of filled and unfilled SBR vulcanizates.)

From the above observations, it seems reasonable to suppose that movement of the elastomer molecules with respect to the filler interface occurs when the local stresses are sufficiently high, and that the required local stresses are less than those required to rupture polymer chains. The absence of significant chain breakage was demonstrated by Dannenberg and Brennan [31], who measured equilibrium solvent swelling after pre-extension of carbon black-reinforced SBR vulcanizates. The slippage is a mechanism for energy dissipation (hysteresis) and for delocalization and redistribution of stresses on a microscopic or submicroscopic scale. Internal flaws in the form of vacuoles are prohibited by interfacial energy factors in the case of very small particles and cannot, therefore, act as sites associated with catastrophic failure.

Hysteresis cannot be viewed as a direct contribution to high tensile strength in the context of reinforced rubber. A sample that has been pre-strained nearly to breaking is now effectively a new substance that is not very highly hysteretic; yet it retains its high breaking strength when strained a second time. The initial hysteresis is then a measure of internal energy-absorbing adjustments that have led to a more uniformly distributed capacity for load-bearing in the direction of the initial strain.



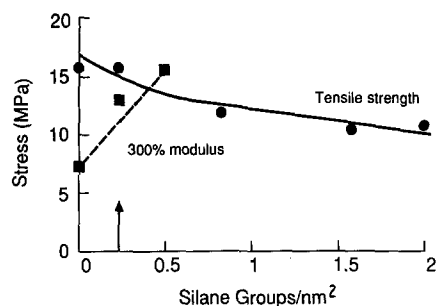


Figure 8 Modulus and tensile strength as functions of filler-polymer bonding in the model system of Fig. 7. Arrow indicates region of "practical" vulcanizate properties.

silica, Cab-O-Sil M5 (Cabot Corp.), having a surface area of  $200 \text{ m}^2 \text{ g}^{-1}$ . Compounds contained 30 p.h.r. of the modified products. The curative level was varied in each case so as to establish the point corresponding to maximum network density as determined by swelling. Data pertinent to the present discussion are shown in Table I.

The inactive, esterified silica, due presumably to its very fine particle size and ease of dispersion in the hydrocarbon polymer, provides respectable strength properties, similar to what one obtains in conventional polybutadiene vulcanizates with a reinforcing carbon black. Surface bonding to the extent of 0.45 sites/ $\text{nm}^2$  more than doubles the 300% modulus and reduces the elongation at break to 300%. The reduction in curative level, in this instance, was about 10%, hence this proportion of the reactive chain ends became attached to the filler surface rather than to a tetrafunctional curative molecule. The relative contribution of polymer-filler bonds to effective network density, as compared to the contribution of polymer-polymer bonds, is obviously very high in systems of this kind.

A further increase, to 0.82 sites/ $\text{nm}^2$ , produces a reduction in tensile strength and a low elongation at break. A desirable balance of properties, to the extent that they can be judged from stress-strain data, would correspond to about 0.2 sites/ $\text{nm}^2$  for this system. This is further illustrated in Fig. 8, which shows the broader trends in modulus and tensile values. The region of "practical" vulcanizate properties is indicated by the vertical arrow; its location represents about 10% of the filler reactivity range that was covered in this study. In considering this evidence, one should recognize that the network density within the bulk of the rubber decreases as the degree of filler bonding increases; the implications regarding more conventional systems are most meaningful at the low end of

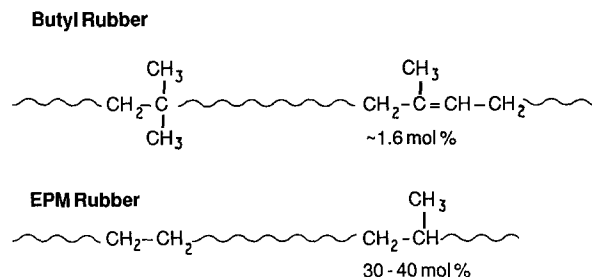


Figure 9 Elastomers of limited chemical reactivity.

the interaction scale, where the bulk network density is not much affected.

## 6.2. Butyl rubber and EPDM

The interaction between carbon black and butyl rubber was studied extensively by Gessler [36] and others over a period of many years. Large changes in "bound rubber", modulus properties, and resilience at low rates of deformation were demonstrated, depending upon modifications to the carbon surface, or the use of "promoters" and "heat treatment" procedures intended to induce bonding between the polymer and filler during the mixing process. Butyl is an interesting case with respect to the present discussion, because the degree of possible interaction is limited by the concentration of reactive sites present in the polymer (Fig. 9). The backbone is polyisobutylene, which contains only primary and secondary hydrogen atoms and is chemically very inert. It degrades under free radical attack and is, therefore, incapable of cross-linking by free radical mechanisms. Isoprene groups are present to permit vulcanization, and have been proposed by Gessler [36] to be capable of reacting with carboxylic groups on the carbon surface, by an ionic mechanism, to form ester linkages or alkylates.

The concentration of isoprene units in the most commonly used grades of butyl rubber is about 1.6 mol %, representing 0.028 mol isoprene units per 100 g polymer. About one-third of these take part in a sulphur curing reaction [37]. Because this proportion applies approximately also to bromobutyl [38], and to various curing systems in butyl rubber [39], it appears likely that the remaining sites are prevented from uniting, either because of restrictions of movement imposed upon them by the network, or because of low "yields" in the vulcanization reactions. Recent halobutyl curing studies [40, 41] have shown higher efficiencies, although still only in the region of 50%. If it is assumed for the butyl rubber case that the

TABLE I Model system

Terminally reactive polybutadiene	100		
Modified fumed silica	30		
Tert-amine curative	As required for maximum cure		
Cure: 48 h at 60° C			
Reactive sites/ $\text{nm}^2$ filler surface	Tensile strength (MPa)	Elongation at break (%)	Modulus at 300% (MPa)
0	15.7	550	7.1
0.21	15.7	340	13.3
0.45	15.2	300	15.2
0.82	11.5	210	-

network density is similar in gum and black-reinforced vulcanizates, then the isoprene units available for black interaction amount to about 0.018 mol per 100 g polymer. Taking the case of N-330 black, with a surface area of  $81 \text{ m}^2 \text{ g}^{-1}$ , this gives a value of 2.7 potential bonding sites per  $\text{nm}^2$  of carbon black surface.

This figure would seem to represent an absolute upper limit for the case in question, because it assumes that all isoprene groups not used in vulcanization can contact the carbon surface and, once having done so, can react to form linkages at 100% yield. This is a most improbable circumstance, considering that few types of reactions are known that can be used efficiently to modify polyisoprene. The surface of carbon black carries carbonyl groups, lactones, phenolic and carbonyl sites [42]. Efficient reactions between such structures and isoprenic moieties are unknown. The value of 2.7 is, therefore, high in all probability by at least an order of magnitude; yet there is no question that stress-strain properties characteristic of high reinforcement are realized in butyl rubber vulcanizates. Similar considerations apply to other polymers carrying a limited number of active sites, particularly EPDM (Fig. 9). This class of elastomers appears to have received relatively little attention from the standpoint of reinforcement fundamentals. It is clear, however, from early literature [43] that gum vulcanizates are weak, and that reinforcement effects very similar to those found in SBR are readily obtained by the addition of conventional loadings of carbon black. No special treatments appear to be necessary for this purpose. EPM rubber, containing no third-monomer unsaturation, and vulcanizable only by free radical processes, is also reinforced efficiently by carbon black.

### 6.3. Interaction of functionalized polymers with precipitated silicas and silicates

The reinforcement of rubber with precipitated silicas produces vulcanizates with high tensile strength and excellent resistance to tear and flex cracking. Resilience and abrasion resistance, however, are poor compared to carbon black reinforcement, and the vulcanizates have a characteristic stiffness or "boardiness". The vulcanizates exhibit low 300% modulus values and high tensile set following break. The characteristic stiffness arises from the high degree of affinity between the silica particles; they tend to aggregate within the rubber matrix to form a three-dimensional reticulate structure. The essentially continuous nature of this structure has been demonstrated very clearly through the study of water absorption behaviour in *cis*-polybutadiene [44].

The stiffness imparted by silica can be observed readily in unvulcanized mixtures, containing only rubber and silica, by measuring the initial slope (Young's modulus) of suitably prepared sheet specimens [45]. In nitrile rubber, the stiffness is not present in mixtures prepared on a cold mill and handled subsequently at room temperature. It develops very quickly, however, upon heating to temperatures typical of the vulcanization process, such that the stiffness is already present before the polymer network has a

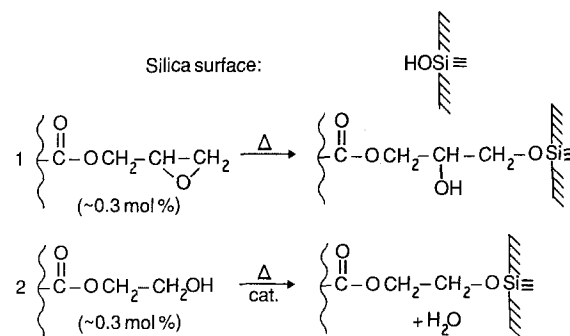


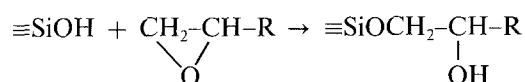
Figure 10 Schematic representation of functionalized polymers for silica reinforcement.

chance to form. In SBR [46] reticulation occurs noticeably at room temperature over a few days, and is very rapid at curing temperatures.

In order to assist in the particulate dispersion of the silica particles, and in order to maintain the particulate dispersion during cure, it is desirable to form bridges between filler and polymer during the mixing process. Work in these laboratories was directed toward establishing economical methods for accomplishing this by using polymers that carry a small concentration of functional groups capable of interacting chemically with the silica surface. Two types of reactions were studied for this purpose. These are illustrated in Fig. 10.

#### 6.3.1. Polymers with epoxy groups

The reaction of epoxy groups with silica has been mentioned in the literature [47], but has received very little quantitative attention. Work with small molecules is complicated by the fact that polymerization of the epoxy compound is initiated at the silica surface [48]. The probable reaction, referring to a high polymer carrying a few epoxy groups, is



To effect the desired interaction, a combination of heat and shear is necessary. For exploratory work, it is convenient to use micro compounding and testing procedures [49]. For routine purposes, a milling procedure of 3 min with the rolls at  $150^\circ \text{C}$  was used in the present work, although shorter treatments may be adequate for efficient systems.

Data illustrating the effects of epoxy concentration are listed in Table II. All of the polymers are nitrile rubbers having about 34% bound acrylonitrile by weight. The control compound, without epoxy functionality, is a commercial product, KRYNAC 34.50. The data show that hot milling as such does not alter the properties typical of silica reinforcement. Young's modulus is high, reflecting the stiffness of the compound, 300% modulus is low and tensile set is high. These properties can be influenced somewhat by varying the state of cure, but the general shape of the stress-strain curves obtained with silica remains fundamentally different from that characteristic of carbon black [45].

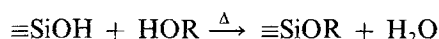
At the level of 0.035 mol epoxy groups/kg polymer, using the hot milling procedure, the 300% modulus is

increased to a level characteristic of highly reinforcing carbon black, but the Young's modulus is not much reduced. At a level of 0.07 mol, the Young's modulus is reduced profoundly, the 300% modulus is very high, and tensile set is greatly reduced. As a single index showing the changes in the shapes of the stress-strain curves, the ratios of 300% modulus values to Young's modulus values are included in the table.

The silica in question had a surface area of  $143 \text{ m}^2 \text{ g}^{-1}$ . At a loading of 50 p.h.r. in the polymer, and assuming that all epoxy groups react at the silica surface, the resulting concentration of bonding sites is  $0.6/\text{nm}^2$  of surface. Because the "yield" of the bonding reaction is unlikely to approach 100%, the actual concentration of bonding sites must be somewhat lower, and possibly much lower, than this value. With respect to 300% modulus as such, it is notable that an epoxy concentration of 0.035 mol/kg polymer ( $0.3/\text{nm}^2$  of surface) is sufficient to bring silica into the range normally characteristic of highly reinforcing carbon blacks when hot milling is applied.

### 6.3.2. Polymers with hydroxyl groups

The esterification of silica with alcohols is well known:



Exhaustive esterification has usually been done under conditions that would be far too extreme for practical application to rubber. For example, Chahal and St Pierre [50] used temperatures up to  $300^\circ \text{C}$  in the esterification of pyrogenic silica. Ballard *et al.* [51] used 2 h treatments in the temperature region  $225$  to  $300^\circ \text{C}$  to complete the esterification of silica with *n*-butanol. However, it has been observed [52] that this reaction can be catalysed by amines to the extent that it will occur appreciably even at room temperature.

The application of this reaction to the reinforcement of styrene-butadiene rubber has been reported [46]. Some previously unpublished results using precipitated silica are listed in Table III. The first two compounds in this table are based on a commercial SBR (KRYLENE 1502), while the others are experi-

mental polymers. The differences in peroxide levels used for curing arise from differences in the stabilizers present in the polymers. As in the previous cases, it is the overall shape of the stress-strain curve, rather than the state of cure, that is important in interpreting the data.

The data show, in the case of SBR, that hot milling of the control polymer has some effect in reducing the Young's modulus value. A further large reduction occurs when the polymer is functionalized with 0.04 mol hydroxyl groups/kg. The use of the amine catalyst produces further improvements, such that the overall relationship between low strain and high strain moduli is now within the range characteristic of carbon black reinforcement. Increasing the functionality produces a further substantial reduction in the Young's modulus value relative to 300% modulus.

In view of the effects observed at the 0.04 mol/kg level, and considering once again that a complete reaction of the available sites is very unlikely, this evidence also places the bonding requirement in the region below  $0.3/\text{nm}^2$ .

It should be noted, parenthetically, that the bonds formed between the silica and the functionalized elastomers are prone to hydrolysis under very mild conditions; this impairs the practical use of such an approach to the enhancement of silica reinforcement in rubber.

### 6.4. Silane coupling reactions

The foregoing sections have discussed relevant experience gained in these laboratories. In the mineral filler field, there is a very large literature on the use of silane coupling agents, notably mercaptosilanes for the case of unsaturated elastomers such as SBR, to bring about coupling between polymer and filler during processing and/or vulcanization (Fig. 11). Silane-treated mineral fillers have been available commercially for many years. Pre-treatment of the filler is considered to provide the highest efficiency in the use of the coupling agent; it also obviates storage and handling problems (odour, moisture sensitivity) that are present when a

TABLE II NBR-epoxy terpolymers

	Compound no.				
	1	2	3	4	5
Epoxy groups (mol/kg polymer)	0	0.035	0.035	0.07	0.07
Compound hot milled*	Yes	No	Yes	No	Yes
Tensile strength (MPa)	31.2	29.2	32.5	27.5	33.4
Elongation (%)	680	660	560	630	450
Young's modulus (MPa)	15.9	15.0	12.0	14.8	5.8
300% modulus (MPa)	5.7	7.8	14.9	8.8	20.6
Tensile set (%)	25	23	15	15	7
Ratio 300% mod./Young's mod.	0.36	0.52	1.25	0.59	3.58
Recipe:	Polymer		100		
	Silica <sup>†</sup>		50		
	Dicumyl peroxide (40%) <sup>‡</sup>		1.5		
Press cure:	30 min at $160^\circ \text{C}$				

\* 3 min at  $150^\circ \text{C}$  before curative addition.

<sup>†</sup> HiSil 233. Precipitated silica, particle size 22 nm. PPG Industries Ltd.

<sup>‡</sup> DiCup 40C. Dicumyl peroxide on calcium carbonate carrier, 40% active. Hercules Inc.





direct line of evidence, based on functionalized NBR or SBR polymers, places upper limits in the region of about  $0.6/\text{nm}^2$ , assuming complete reaction of available sites; and because complete reaction is exceedingly unlikely for these cases, the value of about  $0.2/\text{nm}^2$  is consistent with this experience as well. A similar order of magnitude applies to experience with silane coupling agents. It is notable also that Rivin *et al.* [57] in a study of strong bonding in relation to sulphur vulcanization systems, arrived at an estimate of 0.07 strong bonds/ $\text{nm}^2$  carbon black surface, based on small molecule chemisorption studies.

If we consider a methylene group as a typical unit of an elastomeric chain, and assign to it an area of  $0.05 \text{ nm}^2$  approximately, the number of units per  $\text{nm}^2$  is then 20. Taking the number of chemical attachments as  $0.2/\text{nm}^2$ , the proportion unbonded is 19.8 out of 20, or 99%. Granted that segments in the immediate vicinity of the bonding sites will be restricted in their motion, this result nevertheless indicates that most of the polymer at the filler surface will be held only by interfacial forces of the London dispersion type. This will permit motion relative to the surface when the rubber article is subjected to the large strains encountered in practical use.

The case of SBR carrying the large terminal groups with hydroxyl and *t*-amine sites is distinctive. Although there is only one such group per chain, the estimated size of the groups is such that the carbon black surface coverage amounts to about 40% of the available area, assuming that all interactive sites can reach the surface. If, however, the interactive forces are much weaker than would be the case with covalent carbon-carbon bonding (as seems likely) then movement at the interface may be expected to occur under conditions of high strain in this system as well.

## 8. Conclusions

1. From the evidence available, it appears that reinforcement effects will be imparted to rubber by any particulate solid of very small particle size and moderate or high surface energy.

2. In the particle size region below about 50 nm, separation of the rubber from the filler surface (vacuole formation) is prevented by surface tension effects dependent only on the radius of curvature of the filler particles. However, movement of the rubber relative to the filler surface is restricted, in the absence of chemical bonding, only by relatively weak interfacial forces.

3. A degree of strong bonding is desirable in practical vulcanizates to assist in dispersing the filler particles and to impart an optimum balance of resilience, abrasion resistance, and durability.

4. The degree of strong (covalent) bonding desirable in practical vulcanizates appears to be of the order of 0.2 bonding sites/ $\text{nm}^2$  filler surface. Most of the polymer in contact with the filler surface is capable of moving with respect to the surface when high stresses are applied.

## Acknowledgements

The author thanks E. J. Buckler for helpful discussions,

and Polysar Limited for permission to publish. This paper was presented at the symposium on "Interaction of Fillers During Processing of Rubber and Plastics", Division of Colloid and Surface Chemistry, American Chemical Society, 3rd Chemical Conference of the North American Continent, Toronto, 5 to 11 June, 1988.

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*Received 7 October 1988  
and accepted 26 April 1989*