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Interfaces in Composites. Reinforcement of Elastomers by Carbon Black

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ABSTRACT

Basic features of carbon black—aggregation of particles into structure, particle size and morphology, and surface activity—are reviewed. Carbon black reinforcement of vulcanizates is first examined in the example of tearing, and the influence of hysteresis is considered. The dynamic properties of vulcanizates containing two major types of reinforcing carbon black are compared.

While particle size gives the best correlation with tensile strength of vulcanizates, surface activity is shown to be the key to reinforcement. The role of these properties of carbon black in dissipating rupture energy is discussed.

The relation between work to tensile break and hysteresis to break in gum rubbers can be applied to black-reinforced vulcanizates by use of a strain amplification factor. The complication introduced by stress-softening is explained in terms of localized stress relaxation. Abrasion reinforcement can also be explained in terms of hysteresis.

The Flory-Rehner relationship of modulus of elasticity of swollen vulcanizates to physically-effective cross-linking

applies to unswollen vulcanizates only after prestressing. Black-reinforced vulcanizates involve application of the strain amplification factor.

The concept of mobile linkages to rubber chains at the surface of black particles is related to the influence of strain magnification and strain rate magnification in the reinforcing mechanism. These linkages result in formation of "shell" rubber adjacent to carbon black particles. The slippage of rubber chains relative to carbon black aggregates allows stress-sharing by highly-stressed chains. Bound rubber results from reaction of elastomer free radicals generated during mastication with carbon black.

There is a relation between bound rubber and reinforcement which is fully developed only after vulcanization. Formation of bound rubber results from the surface activity of carbon black rather than its structure. Its contribution to reinforcement of the vulcanizate may be as important as cross-linking.

AGGREGATION OF CARBON BLACK

Particles of reinforcing blacks are aggregated in a 1° structure consisting of some scores of particles fused together by carbon linkages. By electron microscopy, Hess and co-workers [1] have been able to show fibrous crystallites and continuous but bent graphite layers that link carbon particles into 1° structure.

Furnace black manufacturers can vary 1° structure at will, and high structure gives improved abrasion resistance for a given mean particle diameter. New furnace blacks giving higher reinforcement for a given surface area have a reduced aggregate size and narrower distribution of particle size. Blacks of different structure differ in the number of particles in the aggregates rather than in anisometry.

Electron microscopy indicates some breakdown of aggregates during milling with rubber, but Cabot workers [2] and Voet [3] have shown that 1° structure is not reduced by milling. This infers the presence of a weak 2° aggregation arising from Van der Waals forces.

Another concept recently proposed by the Cabot group [4] is that 1° aggregates occlude rubber, thus restricting its deformation. This occluded rubber may account for some of the effects of 1° structure. The greater the number of black particles in an aggregate, the greater the void volume within it. The extent of occluded rubber in the void volume has a strong influence on viscoelastic properties of the rubber compound, such as die swell.

SURFACE ACTIVITY AND PARTICLE SIZE

There is not a clear relationship between surface area (I_2 or N_2 adsorption) and spherical particle diameter (electron microscopy) of carbon

black. This divergency arises from the fused nature of the aggregates and the access limitations of the internal surface to rubber chains. The greater the surface area for a particular black concentration, the higher the tensile strength, especially with amorphous rubbers such as SBR.

It has long been noted that tearing failures of black-reinforced NR vulcanizates are not in a similar direction to the initial cut—a "knotty" tearing effect. A stick-slip fluctuation of the tearing force was later identified [5] with knotty tearing. This was attributed to formation of a strengthening structure at the tip of the tear.

"Knotty" tearing is also a feature of black-reinforced SBR vulcanizates and is associated with a negative gradient with increased rate of tearing. Originally attributed to structural changes within the vulcanizate, this has now been challenged by a concept of hysteresis as the major factor in tear resistance.

The original emphasis on small particle size as the essential factor in black reinforcement of rubbers is still the most viable. The size of 1° aggregates in a black-SBR compound has been compared with particle size in their relation to tensile strength, with particle size giving the best correlation [1]. While aggregate size gave the best correlation with tensile strength of NR compounds, these are not much strengthened by black because of the crystallization characteristic on extension.

Surface activity is possibly the key to black reinforcement. This represents the affinity the black has for its surrounding rubber matrix. Calorimetric studies of heat of adsorption [6] show there is a distribution of energy sites on the black surface. These can be reduced by heat treatment of the black, with subsequent reduction of tensile strength of black compounds.

Recent work from Donnet's school at Mulhouse [7] has indicated that reinforcing properties of carbon black are due to the most reactive of four bound hydrogen forms on the particle surface and not, as previously supposed, to oxygenated surface groups. Heat treatment of experimental blacks in conjunction with radioactive tritium labeling with model compounds pointed to a very small amount of the most reactive hydrogen as being the key surface factor. This is only about 12% of the total small hydrogen content, and it is proposed that a hydrogen exchange takes place between carbon black and rubber chains. Irrespective of the groups involved, this concept leads to the proposition that reinforcement depends on the number of bonded particles and particle interfaces rather than the surface area available for bonding rubber.

THE ROLE OF HYSTERESIS

Thus the number of particle interfaces and aligned rubber chains between particles are the important factors determining whether tearing

is diverted or stopped. This is consistent with the concept of multiple internal failures in front of the tip of a tear; also with the creation of extra interfacial surfaces by filler particles to dissipate tearing energy [8].

While finer-particle blacks increase both reinforcement and hysteresis, this correlation does not prove that the increase in reinforcement is due to hysteresis. The role of particle size is one of distributing the reinforcing agent as hysteresis centers.

There is a clear increase in road abrasion resistance as primary structure is increased for a specific concentration and particle size of carbon black [9]. This appears to be due to the increased modulus of the tread compound, in the same way as the belt breaker of radial ply tires stiffens the road contact area compared to cross ply tires.

It is generally accepted that rubber failure originates at flaws which develop into microtears and ultimately lead to rupture. Mullins has proposed that hysteresis associated with stress relaxation broadens the tear tip and that multiple failures at carbon particle interfaces contribute to hysteresis without causing catastrophic flaws [8]. Andrews [10] has shown that during propagation of a simulated flaw, the stress at the tip is less than before propagation. This stress reduction increases with the hysteresis of the rubber.

Hysteresis is known to be a factor influencing the strength of viscoelastic materials [11] and a relationship for several gum rubbers has been obtained:

$$U_b = KH_b^{2/3}$$

where U_b is the work to tensile break and H_b is the hysteresis to break. Harwood and Payne [12] applied this approach to reinforced rubber by inserting a strain amplification factor X :

$$U_b = K(H_b/X)^{2/3}$$

where X is the ratio of strains in gum and filled rubbers at equal applied stress.

A complication is introduced by the stress-softening effect (Mullins), most of which occurs in the elastomer phase of reinforced vulcanizates. But the hysteresis associated with this softening must ultimately be relevant to stress relaxation at the tip of a growing flaw as the prestress approaches the rupture point. Note the steepness of the initial part of the retraction curve (Fig. 1). This implies that hysteresis due to substantial stress relaxation will result from small localized retractions due to breaking of black constraints. Another source of hysteresis may be provided by occluded rubber

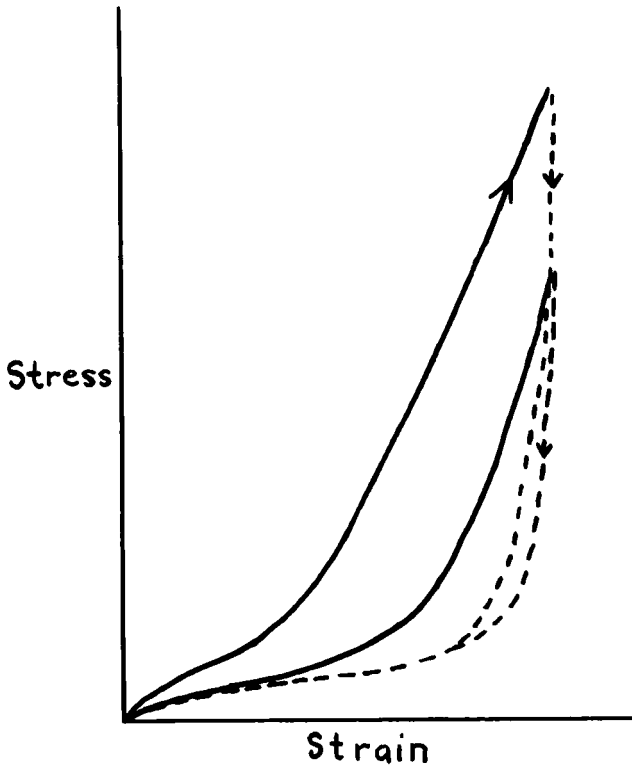


FIG. 1. Stress-strain curves of tire tread vulcanizate sequentially extended to and retracted from 300% elongation.

being pulled from within black aggregates under the influence of an external force.

Most of the hysteresis loop is not necessarily associated with tensile at breaking point. The correlation of U_b with H_b shows that total hysteresis depends on breaking stress and strain ratios, not that tensile strength reinforcement is due to hysteresis.

Abrasion resistance is another form of reinforcement and for the role of hysteresis two basic mechanisms must be considered [13]:

- "pattern" abrasion: due to cutting and tearing on sharp road asperities
- "fatigue" abrasion: due to growth of microtears from repeated deformations caused by local adhesions on smooth surfaces

Changes in dynamic loss modulus E'' have been shown to relate to changes in "fatigue" resistance at operating temperatures.

Changes in loss modulus, E'' , due to the presence of reinforcing blacks, can also be used to show that both hydrodynamic and viscoelastic mechanisms are present [27]. Low-temperature tests result in loss modulus values of black-reinforced vulcanizates having a peak in the region of the elastomer T_g with the peak displaced toward higher temperatures due to the presence of carbon black.

At elevated temperatures, increased black concentration significantly increases E'' but decreases the loss compliance $E''/(E^*)^2$, with the magnitude dependent on the particular reinforcing black.

The area under the peak at T_g can be taken as a measure of the viscoelastic response of the cross-linked rubber network as reinforced by the black. These relative areas for different carbon blacks are in line with surface activity, particle size, and structure of reinforcing carbon blacks.

The modification of the rubber network by black is equivalent to increased cross-link density, with the changes in E'' at both low and elevated temperatures increasing with surface activity of the black.

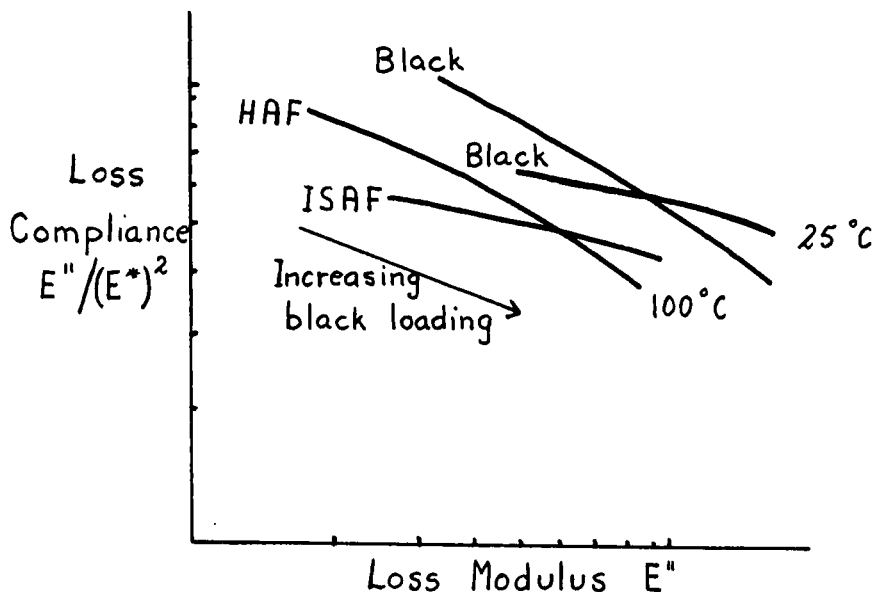


FIG. 2. Loss compliance $E''/(E^*)^2$ as a function of loss modulus E'' for various loadings and temperatures of HAF and ISAF black NH vulcanizates.

From the reduction in loss compliance $E''/(E^*)^2$ with increasing temperature, it appears that its magnitude is dependent mainly on the aggregates of black particles forming a structure. That is, there is a hydrodynamic effect under the compressive conditions which this term represents.

NETWORK REINFORCEMENT THEORIES

For a polymer network at equilibrium in solvent, Flory and Rehner [14] related the polymer fraction of the swollen volume to the molecular weight (M_c) of the chains between cross-links, even if a solvent interaction parameter was required.

For measuring cross-linking by the modulus of elasticity, G , they also derived a relation of G to physically effective cross-linking, in effect, to $1/M_c$. But for unswollen rubber, this does not accurately describe the variation of stress with the extension ratio. Reinforced rubbers must first be prestressed to obtain some correlation at lower elongations.

The appropriate extension ratio for reinforced rubbers involves application of the strain amplification factor. In F. Bueche's theory [15], some network chains are short and thus highly strained in stretched rubber. It is presumed that such highly stressed chains are broken by prestress softening.

Another theory, developed by Dannenberg [16] of the Cabot group, involves mobile linkages at the surface of black particles (Fig. 3). The criterion of prestressing is strain-energy input. The effective concentration of a particular black must include allowance for the occluded volume in black aggregates and for irregular black structure. At low energy inputs there were effects of black concentration and polymer type, and of differences in stability between polysulfide and C—C cross-links. At high energy inputs these differences tended to disappear.

Eirich [17] considers insufficient emphasis has been placed on the influence of strain magnification and strain rate magnification in the reinforcing mechanism. Strain magnification between filler particles when the matrix is extended is due to the nondeformable nature of the particles in the deformable rubber matrix. Shear rate magnification of rubber chains around the tip of an advancing crack permits the rubber to reach the highly-resistant area of the failure envelope.

While the cross-link density of the vulcanizate has a significant influence, the nonuniform nature of the network reduces the opportunity for energy dissipation. Eirich claims this effect is compensated by the affinity of widely dispersed reinforcing carbon blacks for rubber, so that greater strain can be applied before microflaws start to propagate.

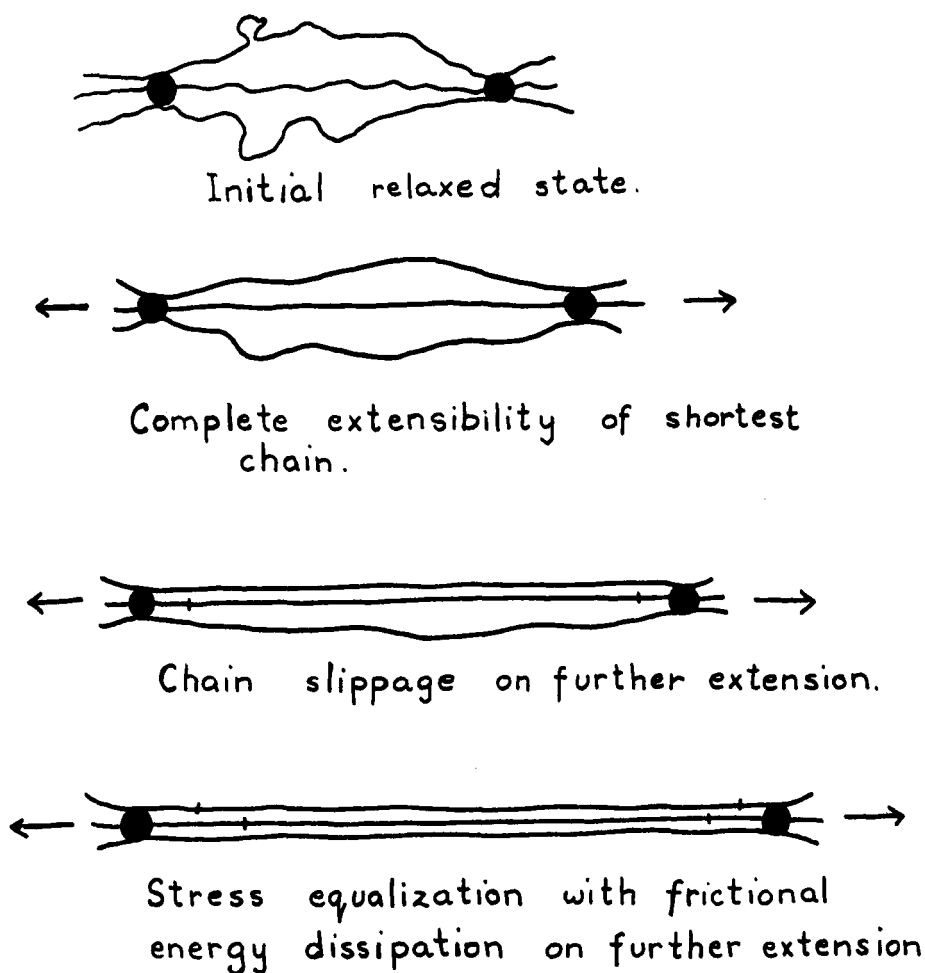


FIG. 3. Molecular slippage model of black reinforcement mechanism (after Dannenberg).

He now supports Dannenberg's concept of mobile linkages on the surface of black particles as a means of stress equalization and alignment of rubber chains around the particles. He proposes moving the slippage area some 10's of Å away from the particles to enable high energy dissipation in the rubber chains.

Kraus [18] showed that stress softening is a function of rate and

temperature and that the WLF transform technique is applicable. According to Rigbi of the Cabot group, stress softening and its recovery are highly temperature sensitive processes. Softening arises from an increase in network M_c due to slippage of rubber chain molecules relative to carbon black aggregates.

Kraus [19] also investigated swelling of black-reinforced SBR in relation to the Flory-Rehner equation for effective cross-linking ($1/M_c$). The contribution of carbon black to cross-linking was found to be roughly proportional to the degree of cure, while the number of apparent strong linkages contributed by the black were not dependent on surface area. This suggested that filler-induced linkages are mainly between rubber chains and the number is relatively small.

In addition, there is evidence [20] of a higher concentration of black rubber linkages near carbon particles than in the matrix itself. This concept of "shell" rubber may also involve occluded rubber in primary aggregates of particles.

The wide application of black reinforcement in unswollen rubbers has resulted in considerable attention to network theory for this field. In Blanchard's theory [21], hard regions are formed by highly deformed rubber and strain interaction with the black particles, as well as being broken down by the initial prestretch.

Mullins and Tobin [22] postulate a "hard" rubber phase with deformations occurring mainly in "soft" regions. Strain hardening at strains below the prestress is attributed to:

1. Tightening of short rubber chains between near particles (after Bueche).
2. Strain alignment of chain segments, leading to them being "strain structured" between particles and with crystallization in NR.
3. Slip rearrangements giving greatly increased alignment and stress sharing by highly stressed chains (after Dannenberg).

Bartenev [23] pointed out that increased orientation of rubber molecules in black-reinforced networks may divert tearing by distributing the stress over many molecules. If carbon blacks reinforce by bringing into play cohesive forces and steric resistances in stretched rubber, there will be hysteresis when such intermolecular forces are overcome. However, while labile structures must result in hysteresis, and hysteresis can provide rubber reinforcement, all sources of hysteresis may not be significant in reinforcement.

BOUND RUBBER AND REINFORCEMENT

Bound rubber, or carbon gel, results from milling carbon black and rubber and shows up as the solvent-insoluble fraction. Gessler [24]

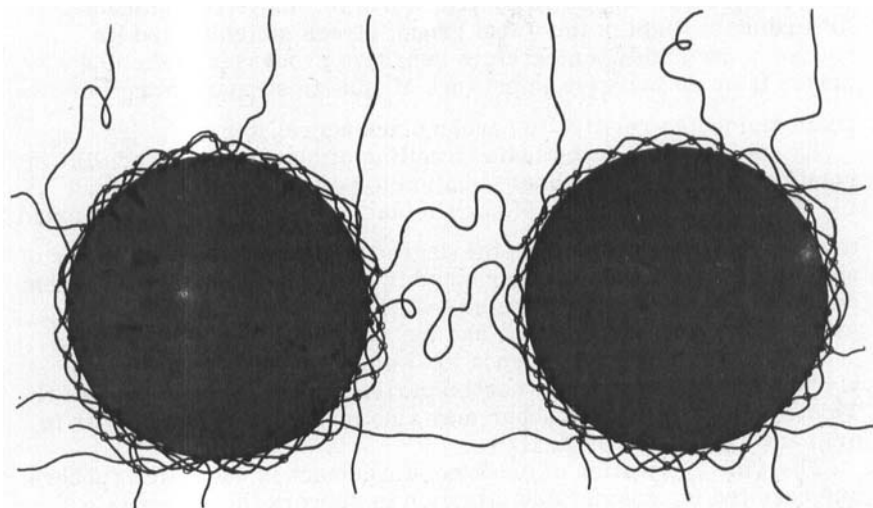


FIG. 4. Dimensional schematic of bound rubber model (after Gessler). A shell of immobilized rubber chains results from multisegment attachments to the carbon particle surface (\circ) and through interchain entanglements (\bullet).

established a relation between bound rubber and reinforcement in butyl rubber compounds containing carbon black. This was dependent on reactive groups on the black surface and on the level of butyl unsaturation.

Elastomer adsorption on the black surface would tend to produce a more ordered state of elastomer segments in the vicinity of black particles than in the remaining elastomer network (Fig. 4). Electron microscope and NMR studies [25] have confirmed the existence of this layer of immobilized elastomer surrounding black particles. While it is identified with bound rubber, a contributing process may be due to occlusion involving black aggregates.

Cabot workers have recently supported the existence of a three-phase system, i.e., black particles, to which are adsorbed a layer of immobilized rubber, all surrounded by a matrix of unbound rubber.

There is also the non-Newtonian behavior of unvulcanized rubber compounds to be considered, i.e., the dependence of relative viscosity η/η_0 on shear rate. The relative viscosity of black-reinforced compounds tends to decrease as the rate of shear increases. This may be explained by orientation under shear due to the presence of bound rubber, as opposed to rigid black particles. Furthermore, capillary rheometry shows the net effect of addition of black to NR is that the compound behaves similarly to a rubber of much higher molecular weight.

Watson [26] showed that cold milling of NR causes formation of free radicals which, in the presence of black, can result in chemical bonds to the black. Electron spin measurements point to carbon black acting as a radical trap. Sullivan and Wise [25] found that radicals appear to form from the shearing action in mastication of black-reinforced rubbers and then react with the black to form stable free radicals.

Recent studies [27] of the influence of thermal and mechanical history on bound rubber content of an HAF black NR compound have been made to simulate the influence of processing variables. This study utilized capillary rheometry for η_a , apparent viscosity at 100°C; GPC for polydispersity of chloroform-soluble phase; insoluble residue after cyclohexane extraction, as percentage on weight of black, for bound rubber (BR); and cyclohexane absorbed by small cube of compound, as percentage on weight of insoluble rubber, for volume swelling (VS).

Typical results are summarized in Fig. 5. Initial mixing of the black with premasticated NR reduces the molecular weight and narrows its distribution. The indication is that higher molecular weight chains selectively undergo scission to form bound rubber.

The compound was then subjected to heat under static or under milling conditions, with significant effects on volume swelling and apparent viscosity, although in opposite directions. It is inferred that heating in the absence of milling leads to some build-up of molecular weight (particularly \bar{M}_n) in the soluble rubber phase, with little change in bound rubber. On the other hand, hot milling increases volume swelling and reduces the apparent viscosity. This is attributed to scission of rubber chains bridging the bound rubber and soluble rubber matrix phases.

If the initially treated samples are then subjected to the other treatment, bound rubber is this time affected, although in opposite directions. Hot milling of the sample, previously heated statically, reduces both bound rubber and apparent viscosity, with an increase in volume swelling. This infers that some chain scission has occurred in the soluble rubber phase, as shown by the drop in \bar{M}_n , and also some scission in the rubber chains immobilized in the bound rubber, including chains bridging the two phases.

By contrast, static heating of the hot-milled sample increases both bound rubber content and molecular weight of the soluble rubber phase. This indicates formation of more bridging between the two phases. The extensive differences in properties brought out by this study point to the importance of considering these factors in the processing of rubber compounds.

It has been postulated that bound rubber and the swelling index are related to reinforcement only by their common dependence on the specific surface of black. Equilibrium swelling of vulcanizates [30]

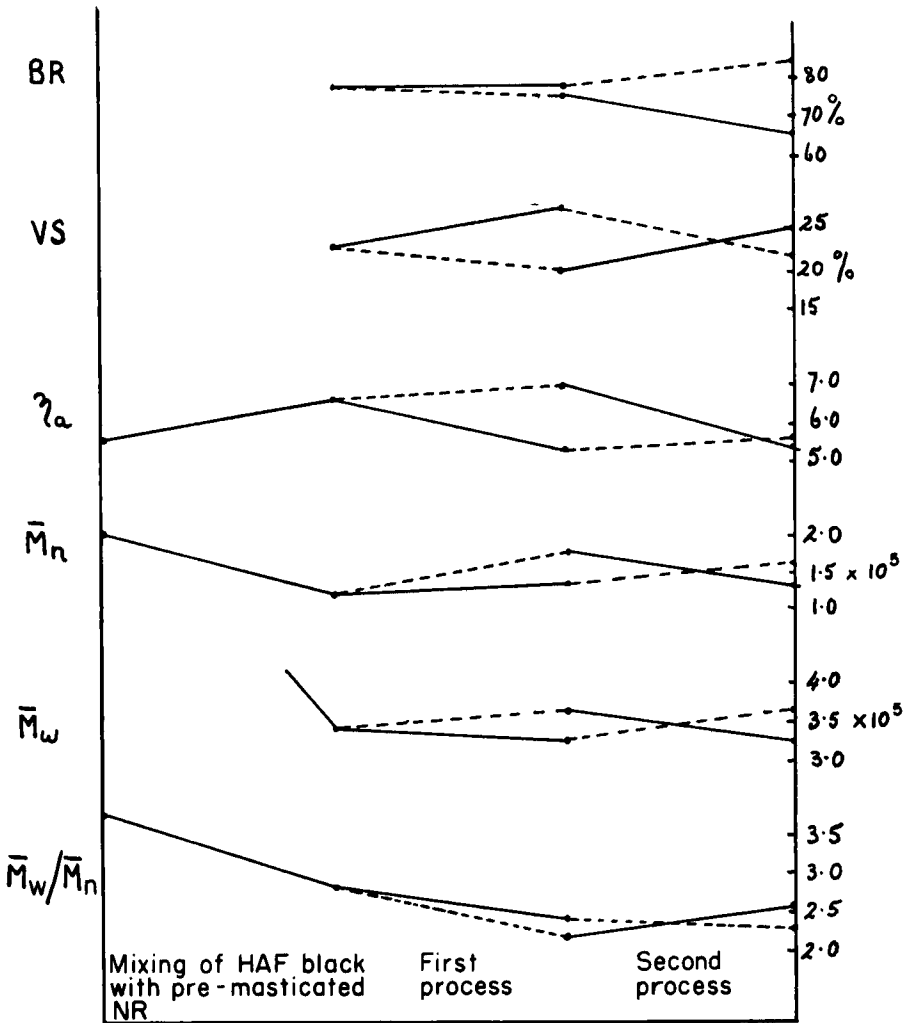


FIG. 5. Influence of processing history on HAF black NR compound. (--) Hot pressing, 40 min at 150°C. (—) Hot milling, 15 passes at 150°C.

has indicated that curatives tend to concentrate in the rubber phase, which has excess cross-links compared to an equivalent gum vulcanizate. Bound rubber content is directly related to excess cross-links, and no additional sulfur cross-linking is considered to occur within the bound rubber phase.

To reconcile bound rubber data with vulcanized properties, it was suggested that the chemical contribution to reinforcement occurs through curing rather than during milling. This postulate was confirmed for black-reinforced SBR by showing that free radicals are initiated by heating SBR in the absence of sulfur, as well as by milling.

In addition, Lewis [29], by use of radioactive-labeled sulfur in specially prepared blacks, was able to show that bound surface sulfur enters into the rubber matrix by reaction or exchange with curative sulfur or accelerator complexes. This is in line with Gessler's concept of 1° bonds being formed between the black surface and rubber chains.

Gessler [28] was able to demonstrate that breakdown of carbon black structure during mixing provides free radicals for bound rubber formation. This occurs only at high black concentrations, where the higher shearing forces during mixing are sufficient to cause breakdown of black structure. His results also indicate that the larger amount of occluded rubber in 1° aggregates of high structure blacks is not important in determining bound rubber.

These results confirm that the full potential of the contribution of bound rubber to reinforcement is not developed until vulcanization. Control of the formation of primary chemical links between black and rubber in bound rubber provides a convenient means of controlling the effect of carbon black reinforcement on the final physical properties of the vulcanizate. Its contribution may be as important as cross-linking.

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