

New Progress in the Theory and Model of Carbon Black Reinforcement of Elastomers

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ABSTRACT: The author proposes a new concept with a new interface model for carbon black reinforcement of elastomer, based on stress analysis. The new model consists of double uncrosslinked polymer layers of different molecular mobility, the inner glassy hard (GH) layer, and the outer sticky hard (SH) layer surrounding a carbon particle. In this report, the most essential and fundamental three subjects in the carbon black reinforcement are discussed. Large stress increase with filler content and increasing strain amplitude results from the strong stress concentration generated around carbon particles and its transmission to the whole system. The great increase in tensile stress is only possible when the stress-hardened superstructure produced in the SH layer under large extension supports the large stress concentration. The super structure is the network of carbon

particles interconnected by strands of oriented and extended molecules, together with a craze-like phenomenon forming numerous microvoids. Stress softening, called the Mullins effect, mainly results from the buckling of the strand of oriented molecules. Thus, the large and instant stress reduction takes place in unloading, in which the main load-bearing force is the entropic, contractile force of matrix cross-linked rubber. During long periods, the extended molecules in the uncrosslinked SH layer will considerably relax and return to their original entropic state. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 60–67, 2005

Key words: carbon black; reinforcement; elastomers; interface model; crazing

INTRODUCTION

The addition of carbon black significantly improves the physical and mechanical properties of elastomers; that is, it greatly increases the modulus, tensile strength, tear strength, fatigue resistance, and wear resistance of unfilled elastomers. This improvement is called “carbon black reinforcement” and has been widely discussed. Nevertheless, most proposed theories, ideas, and models deal only with a part of the above phenomena, rather than addressing the overall phenomena to give an unified and synthetic concept; that is, no one could systematically answer the following fundamental questions with a clear concept: (1) why does stress increase so greatly with filler content and with increasing strain amplitude?; (2) why does the filled system support such a great stress up to rupture?; (3) why does the stress decrease so instantly and vastly in unloading and why is the stress restored gradually at longer times and more quickly at high temperature?

In the previous paper,¹ the author summarized the phenomena concerning carbon black reinforcement so

far given and made clear the questions to be answered to understand the essence of carbon black reinforcement. Moreover, he picked up some interesting experiments published recently and proposed a new concept for carbon black reinforcement of elastomers. In this report, the author will develop his argument, particularly focusing on molecular behaviors in the interface layers and the formation of a superstructure to support the great stress concentration during loading and the buckling of the superstructure in the unloading process.

MECHANICS OF THE STRESS INCREASE IN CARBON BLACK-FILLED ELASTOMERS

The addition of carbon black increases the stress of unfilled rubber vulcanizates over all strain amplitudes. Figure 1 is typical of stress–strain curves of filled rubbers (SBR filled with HAF carbon black) given by Chikaraishi,² with the volume fraction of carbon black. It is well known that the stress increase by filling at small extension (i.e., modulus increase) agrees well with the Guth equation³ for coarse carbon black. The authors analyzed this phenomenon with FEM^{4,5} and showed that the great stress concentration occurred around the carbon particles and then was transmitted to the whole system, resulting in the increase of the average stress of the system. In the case of fine carbon black, the stress increase is a little larger

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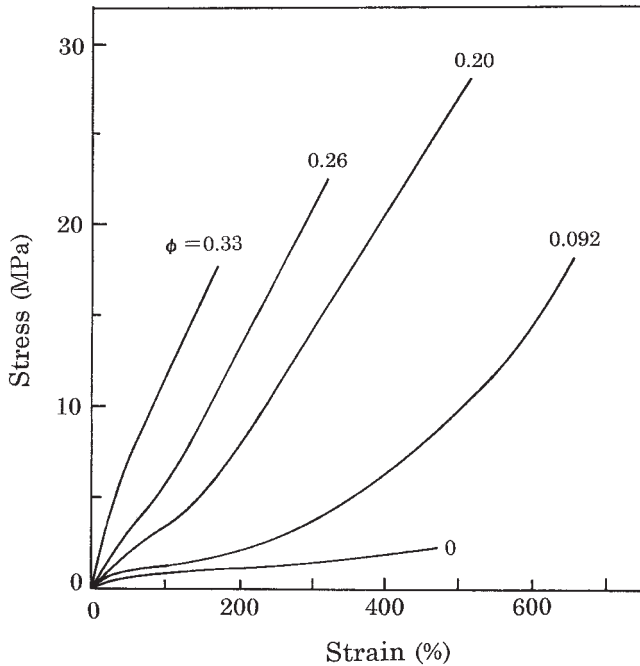


Figure 1 Stress-strain relation of HAF carbon-filled SBR in a simple extension.²

than that given by the Guth equation. This is also reasonably explained with FEM analysis by considering a 10% increase in the diameter of the carbon particle produced by the glassy carbon gel.⁵

Another important point in the stress increase produced by filling with carbon black is that the stress increase becomes much larger as extension increases; that is, the larger the strain amplitude, the greater the

degree of stress increase, as shown in Figure 1. The author also showed with FEM analysis that the stress concentration factor α and the maximum stress concentration factor α_{max} greatly increase as extension increases; the magnitude of α_{max} is 2.31 at 10% but 4.93 at 200% strain, for example.

Figure 2 shows the plots of the degree of the stress increase against strain, where the degree is defined by $\sigma(\epsilon)/\sigma_0$, where $\sigma(\epsilon)$ is the stress at arbitrary strain and σ_0 is that at a standard small strain for each carbon content. All curves for filled rubbers, except the case of $\phi = 0.092$, gave almost the same quantitative relation.

On the other hand, if we adopt α_{max}^2 as a representative expression of the stress field surrounding carbon particles, we can plot it against strain. The dashed line in Figure 2 shows the relation between α_{max}^2 and strain and coincides considerably with the plots of $\sigma(\epsilon)/\sigma_0$ against strain. This indicates that the stress concentration generated around carbon particles governs the stress of the carbon-black filled system over all strain amplitude. Mechanism of the great increase of tensile strength in carbon-filled elastomers

MECHANISM OF THE GREAT INCREASE OF TENSILE STRENGTH IN CARBON-FILLED ELASTOMERS

Necessity of the superstructure including microvoids to sustain the great stress concentration

Stress concentration itself is universally generated in inhomogeneous structures and then the strong stress concentration occurs in any systems filled with other

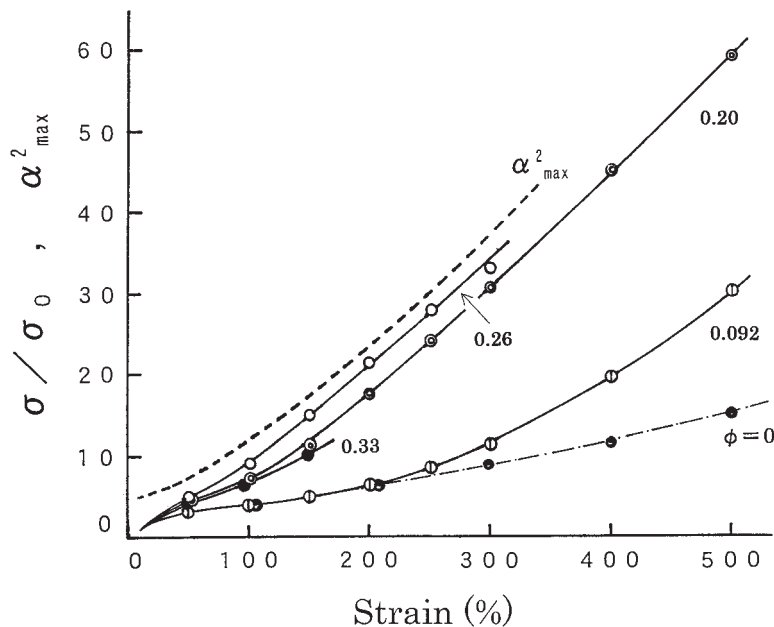


Figure 2 Strain dependence of the ratio $\sigma(\epsilon)/\sigma_0$ and α_{max}^2 .

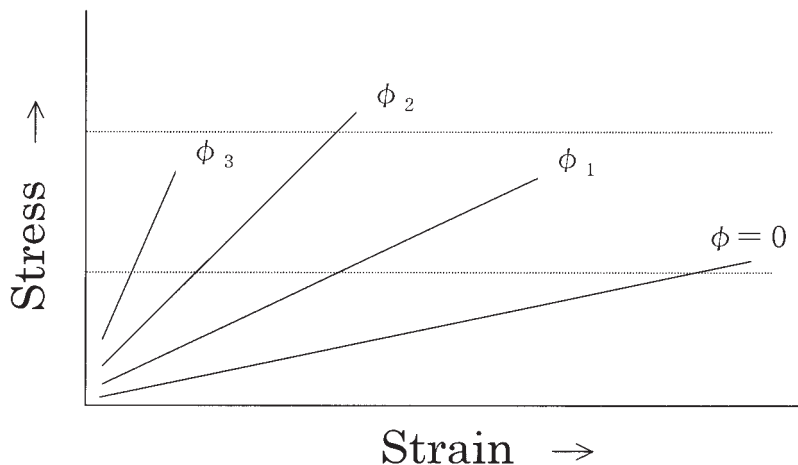


Figure 3 Schematic representation of stress strain curves of glass-bead-filled rubbers.

fillers too. Figure 3 is a schematic representation of stress–strain curves of glass-bead-filled rubbers. Although the large stress is gained by filling, tensile strength will not be so improved, being at most double or triple that of unfilled rubber. This means that the filled system can't support the larger stress concentration and breaks easily. In contrast, in carbon black reinforcement, the tensile strength is significantly improved. It reaches more than 10 times that of unfilled rubber with the best choice of filler content, as shown in Figure 1. Of course, this indicates that the structure formed in fine carbon-filled rubbers is so strong as to support the great stress concentration generated around carbon particles.

Recently, Chikaraishi² observed the volume expansion (nearly 10%) in fine carbon-black-filled SBR (the same system as Figure 1) at large extension, in which no eyeball separation was observed. It is generally known that in coarse carbon-black-filled rubbers, the eyeball separation takes place at the interface between the surface of carbon particles and the rubber matrix at large extension,⁶ and as a result, the volume of the system considerably increases. However, Chikaraishi's result showed that even in fine carbon-black-filled rubbers, the volume greatly increased without eyeball separation. This means that the volume expansion in a fine carbon-filled system must have resulted from the formation of microvoids (not macro-voids) in the system; it did not induce fracture of the system and produced the great increase in tensile strength.

Similar phenomena to the microvoid formation in carbon-black-filled rubbers

It is well known that crazing in glassy thermoplastics is a process of molecular orientation and microvoid formation. In the state of triaxial extension at a crack tip as shown in Figure 4, molecules are pulled out

from a strain-softened, liquid-like polymer layer and highly oriented, thus making a bundle of molecules, i.e., a fibril (its diameter being 5–10 nm). Of course, the bundles support the large stress concentration at the crack tip in a craze. At the same time, a series of microvoids (a few tens of nanometers) are produced between the fibrils. We know of another example for void formation. Figure 5 schematically shows that many macrovoids are formed in a rubber layer constrained between two metal disks. This situation is similar to the case of crazing, i.e., the state of triaxial extension under large extension. Macrovoids thus formed, of course, drastically decrease the tensile strength of the system.

Now returning to the stress analysis of carbon-black-filled rubber, Figure 6 shows the contour map of the stress concentration factor α generated in a rubber layer sandwiched between two adjacent rigid particles

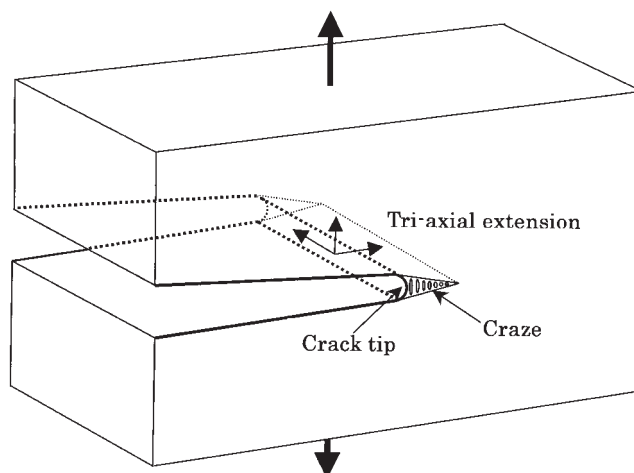


Figure 4 Schematic representation of craze formation in triaxial extension.

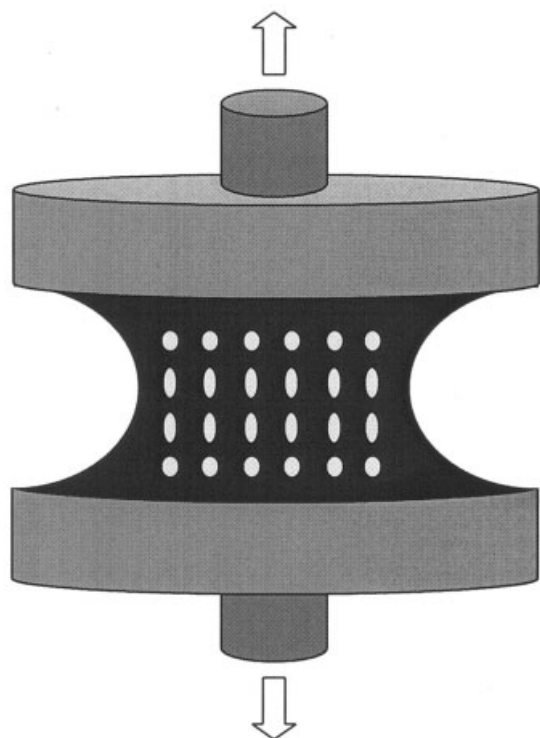


Figure 5 Schematic representation of macrovoids formation in triaxial extension.

($\phi = 0.2$), extended to vertical direction (10% strain). The maximum stress concentration appears between the rigid particles and the strong interaction is recognized between the adjacent particles like a strand of stress concentration. This constrained area is obviously in the state of triaxial extension, meaning that crazing or a craze-like phenomenon will easily take place there in fine carbon-black-reinforced rubbers.

Proposal of a new interface model

Preceding the proposal of a new interface model, we summarize the characteristics of the carbon gel (i.e., bound rubber) surrounding the carbon particles, produced in a mixing process of carbon black and rubber. Bound rubber consists mainly of two polymer phases of different molecular mobility.⁷⁻¹³ In the tightly bound phase, molecules are strongly adhered to the surface of carbon black and then the molecular mobility is strictly constrained, i.e., in the glassy state, its thickness being 0.5–2 nm. In the loosely bound phase, molecules are a little more constrained than those in unfilled rubber vulcanizate. Although many interface models¹⁴⁻¹⁶ have been proposed, most of them are too qualitative and we can hardly connect them to the mechanics and mechanism of carbon black reinforcement of elastomers.

The author proposes a new interface model (Fig. 7) concerning the carbon black reinforcement of elas-

tomers, combining the information about the bound rubber and the volume expansion under large extension with the mechanical and dynamic treatment based on stress analysis. This is a double-layer model consisting of the inner polymer layer of the glassy state (glassy hard or GH layer) of thickness 2 nm and the outer polymer layer, whose molecular motion is considerably constrained (sticky hard or SH layer), of thickness 3–8 nm. Thus, the total thickness of the GH and SH layers is 5–10 nm. The 2 nm thickness of the GH layer is about 10% of the diameter of a fine carbon particle (about 20 nm), but only a few percent of that of a coarse carbon black (100–200 nm). The total thickness of the GH and SH layers is nearly 5 nm for fine carbon black and 10 nm for coarse carbon black. Figure 8 is a more detailed representation to show molecular packing in both layers according to their molecular mobility.

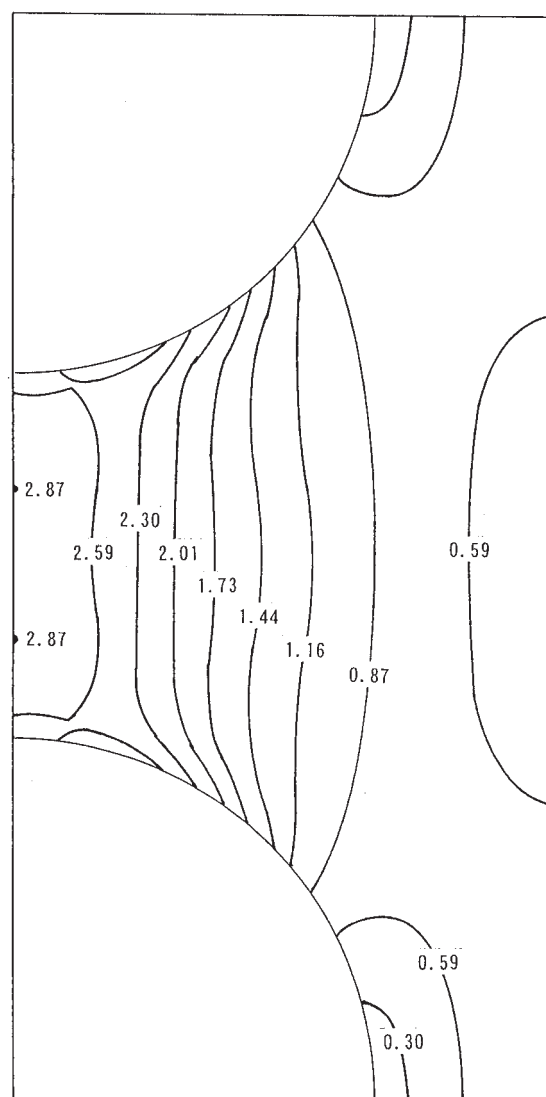


Figure 6 Contour map of α around adjacent particles along the extension direction at $\epsilon_0 = 10\%$ and $\phi = 0.2$.

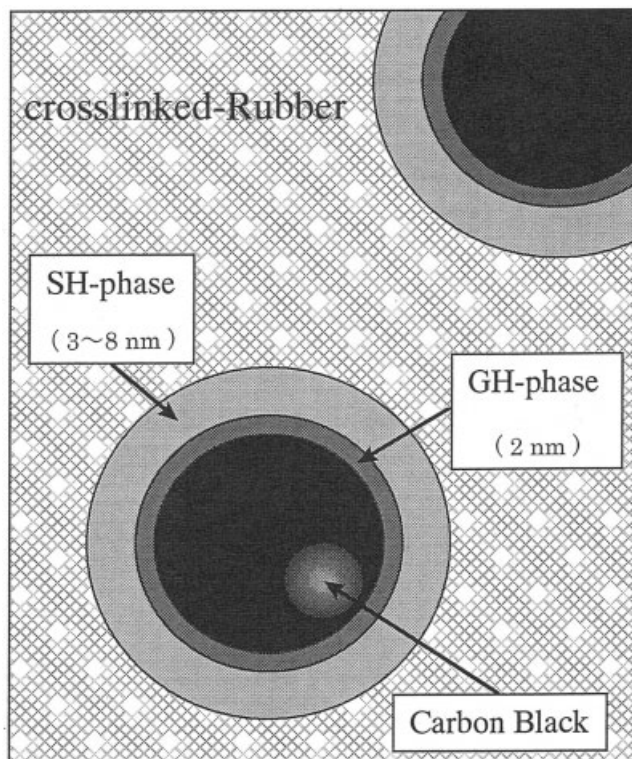


Figure 7 A new double-layer interface model consisting of a GH layer and a SH layer

The GH layer plays a role only to increase the effective diameter of a carbon particle, whose contribution to the stress increase of the system is kept constant over all strain amplitude. This means that the GH layer does not relate to the marvelous stress increase at large extension. On the other hand, the SH layer scarcely plays a role in stress increase at small extension (because it is slightly harder than matrix rubber vulcanizate), but plays a very important role at large extension through the structural stress hardening of the SH layer, discussed below.

Formation of the supernetwork structure to sustain the very large stress concentration

Now we consider molecular behaviors in the SH layer and its stress hardening under large extension. Here the author introduces two assumptions: (1) crazing, or a craze-like phenomenon, takes place in the SH layer; (2) there are very few or no crosslinks in the SH layer. The first assumption will be easily acceptable from the above explanation. The second will also be reasonably understood, considering that a big sulfur particle is outside of the bound rubber during mixing. In addition, the melted sulfur is quite difficult to dissolve into the bound rubber in the vulcanization process at high temperature, because the bound rubber is insoluble even in good solvents.

Anyway, these assumptions make the following behaviors possible. Under large extension ($\sigma \leq 0.2$), molecules in the SH layer slide, orient, and extend along the extension direction and produce strands of oriented-molecules, as shown in Figure 9. In this process, there appear numerous microvoids on the track that molecules have slid out of.

On the other hand, by combining Figures 6 and 7, we understand that the SH layers surrounding two adjacent carbon particles (fine carbon black) are overlapped and adhere to each other when the volume fraction of fillers is more than 0.20–0.25, as shown in Figure 10. Thus, the interconnected SH layers construct the network of the strands of oriented molecules, as shown in Figure 11. This superstructure is expected to be strong enough to support the large stress concentration around carbon particles, despite the fact that it includes numerous microvoids, as well as crazes. Of course, the interconnected structure produced after mixing (Fig. 10) is almost as soft as matrix crosslinked rubber but it changes to the hardened and strengthened superstructure under large extension (Fig. 11).

Fukahori and Seki¹⁷ investigated the thermodynamic characteristics of carbon-black-filled and unfilled natural rubbers by measurement of the temper-

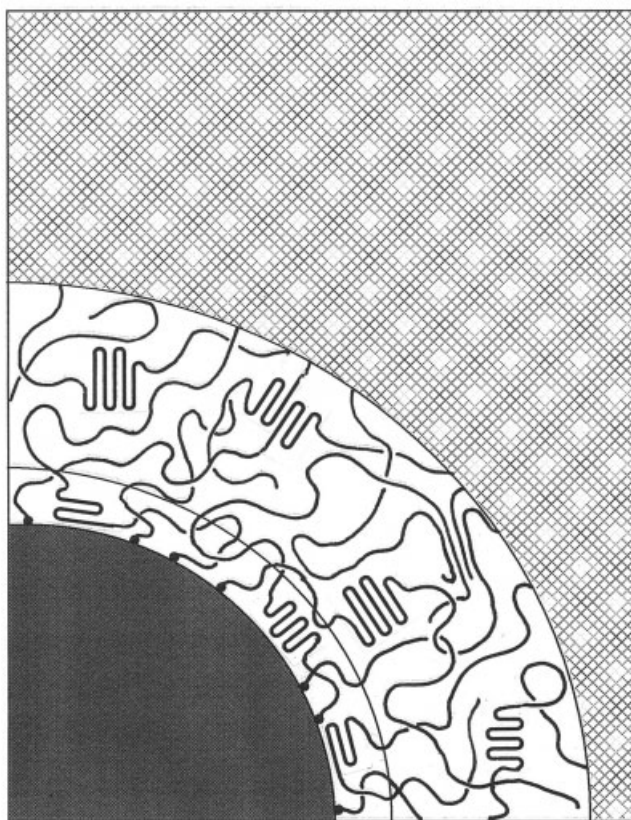


Figure 8 Detailed molecular structures in the GH and SH layers as vulcanized.

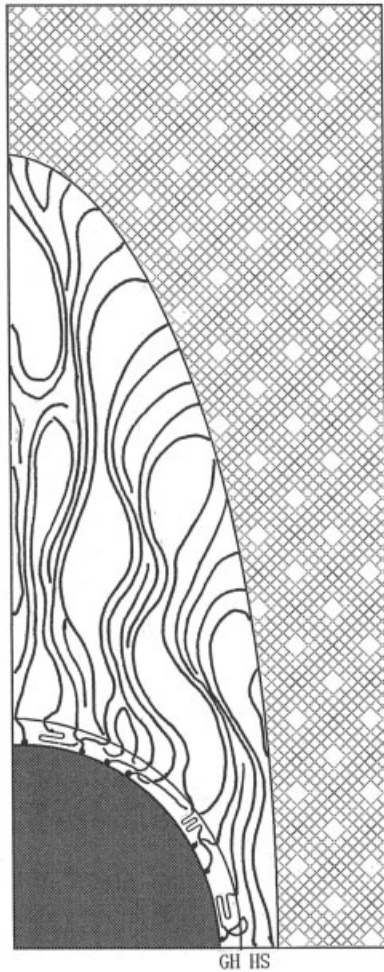


Figure 9 Molecular movements within the SH layer under large extension.

ature and strain amplitude dependence of the stress-strain relation of these systems. They concluded that carbon-black-filled rubbers behave rather entropically at small extension, but they become energetic at large extension. Now, we can easily understand this phenomenon from the formation of the strands of oriented molecules under large extension. That is, when the SH layer is as soft as a matrix rubber vulcanizate at small extension, the matrix rubber (the largest volume fraction in the system) supports the main stress of the system, but at large extension the oriented, energetic SH layer sustains almost all of the stress of the system.

MECHANISM OF STRESS SOFTENING (MULLINS EFFECT) IN FILLED ELASTOMERS

Stress softening, called the Mullins effect¹⁸⁻²⁰ is very interesting and important when we consider the carbon black reinforcement of elastomers, because it closely ties to the energy dissipation in fracture, thus the great resistance to crack growth in fatigue and wear. The Mullins effect includes a lot of phenomena,

as schematically shown in Figure 12; (1) large and instant stress reduction takes place in the first unloading; (2) the stress slightly increases in the second loading; (3) the stress returns to the original stress level when a strain exceeds that of the first loading; (4) the stress gradually recovers to a considerable degree of the original stress at long periods and more quickly at high temperature and in good solvents. Although many ideas and theories have been proposed,²¹⁻²³ we can hardly say that the above phenomena have been resolved, systematically and synthetically.

Now we try to consider the mechanism of stress softening of carbon-black-filled rubber based on the new interface model. First, we must have insight into the buckling of the extended and oriented molecular bundles in the first unloading, as shown in Figure 13.

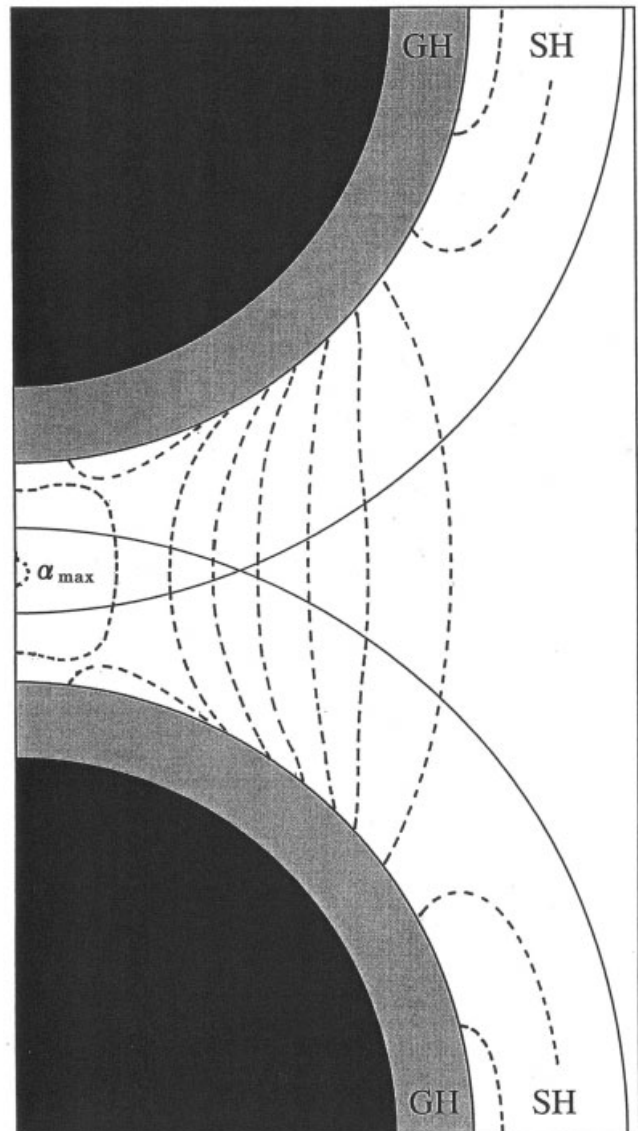


Figure 10 Overlapped SH layers in triaxial expansion along extension direction at $\epsilon_0 = 10\%$ and $\phi = 0.2$.

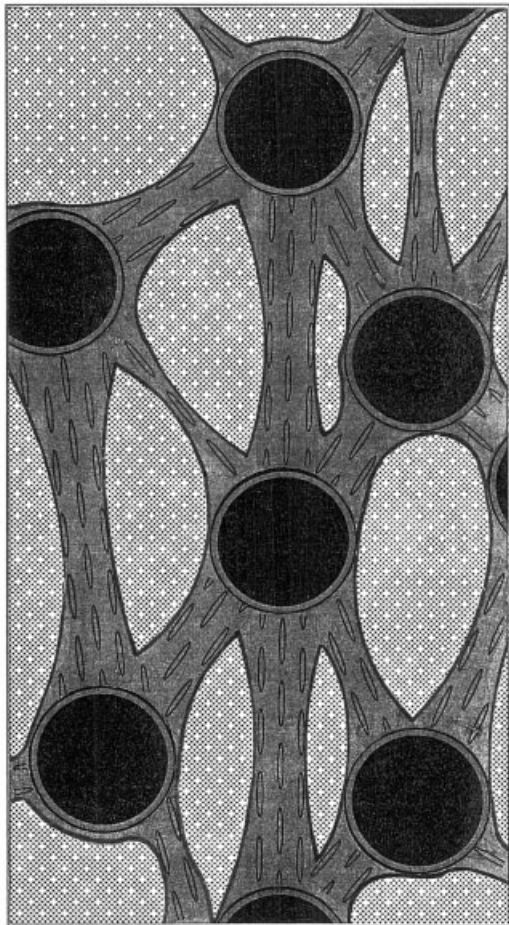


Figure 11 Supernetwork structure of carbon particles interconnected by strands of oriented molecules.

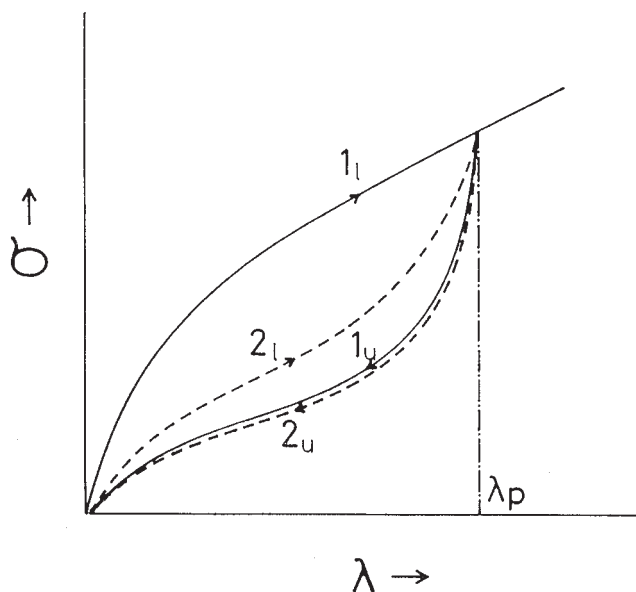


Figure 12 Schematic representation of the Mullins effect: loading (first, 1l; second, 2l) and unloading (first, 1u; second, 2u).

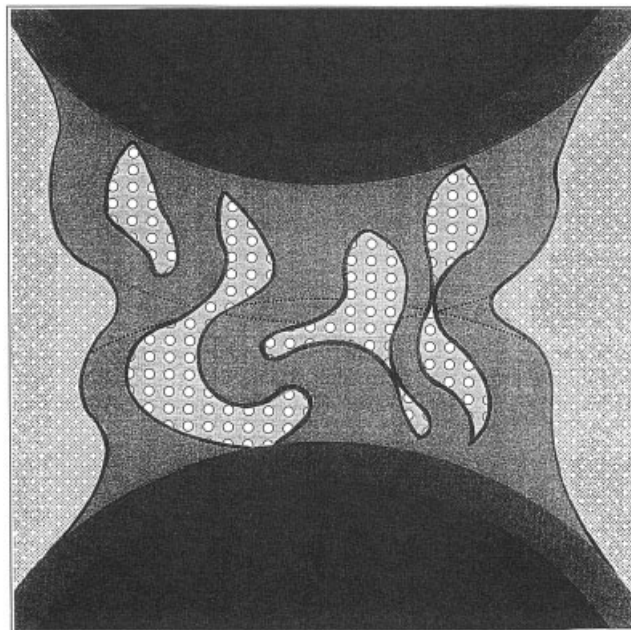


Figure 13 Buckling of extended and oriented molecular bundles.

This behavior takes place just in the beginning of unloading; thus the stress decreases so rapidly, much faster than usual stress relaxation due to viscoelastic molecular motion. In the unloading process, the buckled bundles can hardly hold the stress of the system, and instead, matrix crosslinked rubber mainly supports the stress. Therefore, the degree of stress reduction in unloading will be much larger than that generated in usual stress relaxation. In the second loading, since there is time for the buckled bundles to shrink slightly, the stress becomes a little larger than in the first unloading. Of course, the main load-bearing part is also the matrix crosslinked rubber in the second loading.

When the extension exceeds the strain level of the first loading, since the buckled bundles return to the first extended state again and are extended more under larger extension, the stress increases depending on the original stress-strain relation. During long periods or at higher temperature, the extended and buckled molecules will considerably relax and enter a much higher entropic, i.e., amorphous, state.

Recently, Soos²⁴ measured the stress recovery during annealing as a function of temperature using stress-softened specimens of SBR filled with various types of carbon black. His result showed that the activation energy of the stress recovery was approximately 10 kcal/mol (≈ 42 J/mol) for all carbon blacks. Of course, such low activation energy corresponds to flow or dispersion of liquids or molecules; that is, the stress recovery takes place in accordance with free molecular rearrangement of uncrosslinked molecules.

Moreover, the above result also supports the concept of molecular slippage and orientation in the uncrosslinked SH layer on a vast scale under large extension. The fundamental idea discussed here was given in Ref. 25.

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