

A Molecular Explanation for the Origin of Bound Rubber in Carbon Black Filled Rubber Compounds

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ABSTRACT: Some of the theories that have been developed to explain the origin of bound rubber are critically reviewed and discussed with respect to published data. Theories for carbon black filled compounds and for silica–silicone rubber mixtures are considered; the phenomena involved are likely to be very different, with clear chemical aspects for the latter systems. A common feature emerges, however, from these theories: the area of the polymer–filler interaction site, which is generally considered as a fitting parameter in most approaches. This article concentrates on this aspect and suggests that, with respect to recent findings about the very surface of carbon black particles, an explanation for bound rubber can be offered that considers strong topological constraints exerted by the filler surface on rubber segments. Calculations of interaction site area made with experimental data give values close to a fraction of the half-lateral surface of the structural unit representative of the rubber considered. It follows that the bound rubber variation during storage can now be understood by considering a slow replacement of short rubber chains initially adsorbed on filler particles by larger ones, as demonstrated by calculated data. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 2257–2268, 1997

Key words: bound rubber; carbon black; elastomer; theory

INTRODUCTION

Filled rubber compounds are an interesting class of complex polymer systems, the flow properties of which are determined by their heterogeneous nature, the macromolecular character and the viscoelastic properties of the matrix, the interaction potential between ingredients, and the complex morphology that arises through a combination of the above aspects. Among the intriguing properties of such materials, bound rubber, that is, the portion of elastomer nonextractable by a good solvent, has been known for decades to be the major factor in reinforcement by active fillers such as carbon black. Bound rubber is indeed discussed

in several important reviews on carbon black reinforcement^{1–4} but mainly as a phenomenological aspect without clear explanation offered for its origin. For instance, the statement by Kraus¹ in his 1965 review that “bound rubber is not a single phenomenon, but a manifestation of many diverse effects” is still valid today but essentially reflects a poor understanding. Recently, a relationship between bound rubber and rheological properties has been demonstrated,⁵ suggesting that interactions between elastomer and carbon black strongly influence the flow behavior of such materials. How bound rubber is formed is thus likely the most critical aspect of compounding, with respect to the behavior of the resulting material in the subsequent processing steps.

Basic aspects of rubber compounding can be analyzed by considering the mixing of the two major ingredients in most formulations: the elasto-

mer and the filler. For the latter, a reinforcing black—and its inherent structural complexity—is representative of the most severe problems encountered in mixing. Thus, initially, one is dealing with two materials, completely different in their chemistry and physics. The elastomer has a macromolecular nature, behaves in a viscoelastic manner, and when introduced in the mixer, is at room temperature on the rubbery plateau of its modulus versus temperature function. If, for the sake of argument, the mastication of the rubber within the mixer could be reduced to the sole effect of a temperature increase, then one would have to consider a displacement on the $G(T)$ curve from the rubbery plateau toward the flow region. However, during mixing, filler particles are incorporated according to quite complex mechanisms, obviously, but along with a substantial increase in modulus, as a net result. After dump, the batch is cooled down, and again with a simplistic view, this corresponds to a return journey on the $G(T)$ curve from the flow region toward the rubbery plateau of the filled compound. During mixing, the filler has encountered severe changes in its physics, if not its (surface) chemistry. At the least, a size reduction is associated with the dispersion of the filler in the polymer matrix, and in certain instances, the extent of size reduction must be limited, otherwise, below a certain size, some of the benefits of the polymer–filler composition are lost. A classic example is offered by reinforcing carbon blacks, the size reduction of which must go from agglomerates to aggregates, with limited further breakage that would lead to colloidal particles without reinforcing capabilities. Although rather pragmatically developed, industrial mixing achieves this goal by applying on particles the adequate amount of stress, sufficient to break down agglomerates into aggregates, but essentially remaining below the internal cohesive forces of the latter.

In addition to filler size reduction and aggregate dispersion, strong interactions between the elastomer and the black take place during mixing, and it is recognized that they are of physical rather than chemical nature, as demonstrated by the effect of temperature on bound rubber measurements.⁶ A recent investigation on the surface morphology of carbon black particles with an atomic force microscope suggests that rubber–filler interaction is likely to reflect strong topological constraints exerted by the black complex surface on elastomer chains.⁷ The aims of this article are

to analyze some of the theories proposed for bound rubber in the light of our data and to propose a molecular explanation for the origin of bound rubber.

BOUND RUBBER THEORIES

Earlier Approaches

One of the earliest bound rubber theories was developed by Villars,⁸ who considered a gel of filler particles bonded by the largest polymer molecules. In this theory, it is assumed that segments of rubber molecule adhere to “elemental sites” assumed to exist on filler particles. The total carbon black area is considered to be divided into such elemental sites, the size of which is defined as the area occupied by one adsorbing rubber segment. In this respect, the size of the elemental site is an ad hoc parameter. For instance, Villars reports that the mean elemental area of around 30 nm² with natural rubber would correspond to an adhering rubber segment of up to 800 isoprene units, that is, about one-fifth of the weight-average molecular weight. Later, Kraus and Gruver⁹ tested this theory with narrow-distribution polybutadienes (40% *cis*-1,4, 52% *trans*-1,4, 8% *vinyl*-1,2; \bar{M}_w from 470 to 930,000 g/mol), found the theory inadequate, and on the basis of the observed dependence of bound rubber on the square root of \bar{M}_w , calculated the molecular weight distribution (MWD) of the (extractable) unbound rubber and obtained good agreement with gel permeation chromatography data. It is worth noting that Kraus and Gruver also proceeded to solution adsorption experiments by pouring “lightly crushed” carbon black pellets in an *n*-heptane solution of rubber. They observed a kinetic character of the adsorption process in such a manner that periods of up to 9–10 h were necessary before a plateau in the adsorbed quantity of rubber was reached. In agreement with similar experiments in the 1950s,^{10–12} they found that the higher the molecular weight of the gum rubber in solution, the higher the maximum adsorbed quantity on carbon black particles.

Meissner's Theory

In 1974, Meissner¹³ developed a theory of bound rubber that treats the effect as a random adsorption of structural units of polymer on “reactive

sites" assumed to exist on the filler surface. A major difference from the approach of Villars is that the size of the adsorbed polymer segment is fixed and identified with the structural unit of the polymer. No hypothesis was drawn as to the chemical or physical nature of such reactive sites, and the following equations were derived for the bound rubber fractions:

for monodisperse polymers:

$$BR = 1 - \exp\left(\frac{\bar{M}_w c S_p}{A_0 N_{Av}}\right) \quad (1)$$

for random disperse polymers:

$$BR = 1 - \frac{4}{\left(2 + \frac{\bar{M}_w c S_p}{A_0 N_{Av}}\right)^2} \quad (2)$$

where BR is the bound rubber fraction (g of bound polymer/g of total polymer in the formulation), \bar{M}_w is the weight-average molecular weight of gum polymer (g/mol), c is the filler concentration (g/g of gum polymer), S_p is the specific surface area of filler (m^2/g), N_{Av} is the Avogadro number (6.023×10^{23}), and A_0 is the area of one active site on the filler particle ($\text{nm}^2 = 10^{-18} \text{ m}^2$). As a matter of fact, the latter parameter is an adjustable one, because Meissner derives its value from experimental data (that is, bound rubber measurements). For instance, with natural rubber-HAF black systems ($\bar{M}_w = 2.6 \times 10^5$ g/mol; $S_p = 85 \text{ m}^2/\text{g}$), A_0 is found to be equal to 52 nm^2 , while for SBR1500-various blacks ($\bar{M}_w = 2.5 \times 10^5$ g/mol; $S_p = 35$ to $140 \text{ m}^2/\text{g}$), A_0 is found to be equal to 83 nm^2 . From the data of Kraus and Gruver on SBR-ISAF black systems (\bar{M}_w ranging from 0.5×10^5 to 4.2×10^5 g/mol; $S_p = 115 \text{ m}^2/\text{g}$), Meissner obtained $A_0 = 120 \text{ nm}^2$. However, after heating the SBR-ISAF black compounds (20 h at 90°C), Kraus and Gruver observed higher bound rubber, which consequently led Meissner to derive $A_0 = 52 \text{ nm}^2$. In a recent publication,¹⁴ Meissner calculated $A_0 = 112 \text{ nm}^2$ using the same data on BR and SBR compounds from Kraus and Gruver, $A_0 = 12 \text{ nm}^2$ from Cotten's data on SBR compound with 50 phr N347 carbon black ($S_p = 92 \text{ m}^2/\text{g}$),¹⁵ and $A_0 = 180 \text{ nm}^2$ from Shiga's data¹⁶ on ethylene-propylene rubber (EPR, saturated) and unsaturated ethylene-prop-

ylene rubber (EPDM) compounds with 80 phr FEF black ($S_p = 44 \text{ m}^2/\text{g}$).

With such a wide range, that is, 12–180 nm^2 , A_0 looks rather like an ad hoc parameter, and to clearly understand the relationships between bound rubber, surface of active site, and rubber molecular weight, as predicted by Meissner's equations, we calculated three-dimensional (3D) maps (Fig. 1) for a given level of 50 phr carbon black (that is, $c = 0.5$) with specific surface area $S_p = 100 \text{ m}^2/\text{g}$. As can be seen, the type of MWD marginally affects the 3D map obtained, despite the very different mathematical shape of both equations. Drastic variations in bound rubber are predicted when A_0 is below 60–80 nm^2 while \bar{M}_w is below 300–400,000 g/mol. Owing to the large size of most industrial gum elastomers, A_0 is thus the key parameter about which, unfortunately, no clear meaning was provided in Meissner's original theory.

In a recent publication, Karásek and Meissner¹⁷ suggested that, for a given polymer-filler system, A_0 be calculated from

$$A_0 = \frac{S_p M_0}{k N_{Av}} \quad (3)$$

where M_0 is the molar mass of the polymer structural unit and k is a constant. The latter is derived from the application of the Flory theory for polyfunctional crosslinking¹⁸ to polymer-filler gel systems. The idea is that interactions between filler particles and polymer chains generate a coherent gel-like structure embedded in the extractable elastomer. Therefore, the fraction of "cross-linked" units of polymer q_{cr} is proportional to filler fraction c , that is, $q_{cr} = kc$. The proportionality constant k has, however, to be derived by fitting experimental data. For instance, Karásek and Meissner obtained $k = 1.72 \times 10^{-4}$ and 1.68×10^{-4} , respectively, for NR and SBR compounds with fume silica ($S_p = 50 \text{ m}^2/\text{g}$; average particle size, 40 nm; aggregate structure). Accordingly, they derived A_0 equal to 32.0 and 32.5 nm^2 for the respective compounds. Using such data and eq. (3), one notes, however, that in order to obtain the reported values, they had to use $M_0 = 66.30$ and 65.77, respectively, for the molar mass of NR and SBR structural units (vs. 68.11 [C_5H_8] and 66.58 [C_4H_6 – C_8H_8 with 25% styrene]).

In his theory, Meissner also derived an equation for the MWD of the unbound rubber; that is

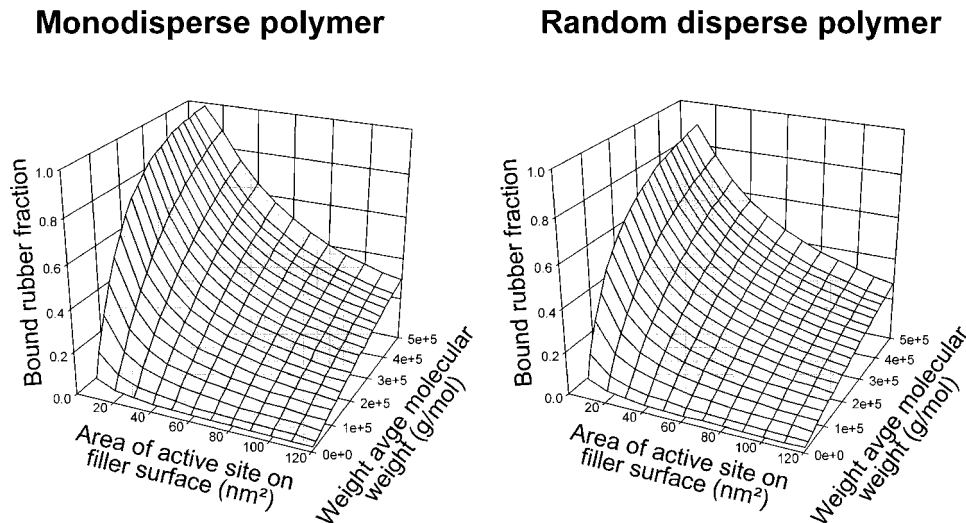


Figure 1 Effect of parameters in Meissner's bound rubber model.

$$w_E(y)dy = \frac{1}{1 - BR} w(y)e^{-qy} dy \quad (4)$$

where y is the number of structural units in a polymer chain, $w_E(y)dy$ is the weight fraction of polymer having y between y and $y + dy$, and q is the fraction of adsorbed structural units ($=M_0cS_p/A_0N_{Av}$). He then predicts that, with respect to the MWD of the initial gum rubber, the one of extractable rubber is shifted toward the lower molecular weight. Consequently, the bound rubber is made up of the largest rubber chains. This aspect of Meissner's theory is substantiated by certain published data.^{9,19}

Cohen-Addad's Approach

While obtained with speciality systems (that is, mixtures of silicone rubber and silica), the experimental results and theoretical developments of Cohen-Addad are worth consideration.²⁰ It has been known for a long time that silica-polysiloxane mixtures behave like permanent gels. Extraction experiments with a good solvent demonstrate that significant amounts of polymer are strongly adsorbed on silica particles. However, the mechanism of this adsorption has been identified and relies on the formation of hydrogen bonds between oxygen atoms on the polymer chain and silanol groups located on the silica surface. In such systems, bound polymer formation proceeds clearly through a chemical mechanism. A direct proof is offered by the fact that when treating silica sam-

ples with hexamethyldisilazane, silanol sites are converted into nonadsorbent trimethylsilyl groups; at equal silica fraction, the bound polymer level thus decreases accordingly.²¹ By considering that polysiloxane chains obey Gaussian statistics, Cohen-Addad derived the following relationship for bound rubber (it may be noted that Cohen-Addad's equations have been rewritten to comply with the formalism used in this article):

$$BR = \frac{\sqrt{\bar{M}_0}}{A_0} \cdot \frac{cS_p}{\varepsilon_a N_{Av}} \cdot \sqrt{\bar{M}_n} \quad (5)$$

where \bar{M}_0 is the average weight of one skeletal bond (equal to 37 g/mol for siloxane), A_0 is the average area (on the filler particle) associated with one hydrogen bond (equal to 0.55 nm² for the silanol group), $\varepsilon_a \approx 1$ is a numerical factor accounting for chain stiffness and surface coverage, and \bar{M}_n is the number-average molecular weight of the polymer; c , S_p , and N_{Av} have the same meaning as above. Using this equation, one calculates, for instance, that a mixture of polydimethylsiloxane (PDMS) ($\bar{M}_n = 325,000$) with 29 phr of fume silica ($S_p = 150$ m²/g) has a bound rubber fraction of 0.46, a value reasonably close to the experimental data (around 0.52 from Fig. 1 in ref. 20). The above equation predicts that bound rubber increases with the square root of the number-average molecular weight of the initial gum polymer, as experimentally observed. In this respect, Cohen-Addad's approach is similar

to observations of Kraus and Gruver with narrow-distribution polybutadiene, as discussed above. However, the interesting point here is the clear identification of the anchor site (one silanol group) and the anchoring element (one siloxane group), which is allowed by the recognition of the chemical nature of the adsorbing process. One notes, however, that the surface of the anchor site on the silica particle is at least 100 times smaller than the reactive site in Meissner's theory (0.55 versus 30–180 nm²).

In a recent publication, Cohen-Addad and Frebourg considered more common rubber-filler compounds by studying mixtures of low *cis*-1,4 polybutadiene (38% *cis*, 54% *trans*, 8% *vinyl*) with various levels of N220 ($S_p = 115 \text{ m}^2/\text{g}$).²² They developed an adsorption model in order to relate the bound rubber fraction with the number-average molecular weight of the gum. In agreement with the quantitative description already offered for PDMS-silica mixtures, they assumed that there are elementary interactions—of unspecified nature—between monomer units of the polymer backbone and the carbon black surface. At first, they considered that any single polymer molecule can bridge only two aggregates, while several elementary binding sites are involved in the interaction between one polymer molecule and one aggregate. Consequently, they established the following relationship for bound rubber:

$$BR = (1 - 2\beta) \left[\frac{n_B}{2\Psi(n)N_{Av}} \right]^2 \bar{M}_n^2 c^2 + 2\beta \left[\frac{n_B}{2\Psi(n)N_{Av}} \right] \bar{M}_n c \quad (6)$$

where β is the fraction of bound polymer chains involved in the bridging of aggregates (the other fraction of bound chains is just dangling and partly desorbed), n_B is the number of elementary interaction sites on the carbon black particle, $\Psi(n)$ is the average number of monomer units involved in the binding of one chain (note: n is obviously the average number of skeletal bonds in one chain); \bar{M}_n , c , and N_{Av} have the same meaning as above. Using this equation to fit their data with a master curve, Cohen-Addad and Frebourg obtained $\beta = 0.35$ and estimated that there are around 0.042 sites per nm² where polybutadiene chains are strongly bound to carbon black, inde-

pendent of the polymer molecular weight. This value is notably low because, providing the actual law of adsorption obeys Gaussian statistics, the number of contact points of one chain with the filler surface should be proportional to $\sqrt{\bar{M}_n}$. By considering that in the studied systems, there is a broad distribution of the enthalpies of the adsorption of monomer units (in contrast with silica-PDMS systems, where the interaction process is essentially chemical), Cohen-Addad and Frebourg draw the hypothesis that, would the enthalpy of the solvent-surface interaction be stronger than the enthalpies of adsorption, the washing process of filled rubber mixtures goes along with a partial elimination of chains from the adsorbed layer on filler particles. Using nuclear magnetic resonance analysis, they somewhat confirmed that in the polybutadiene-carbon black systems studied, less than 0.001 monomer unit per nm² is involved in the polymer-filler interaction process. In other words, on average, one monomer unit would be fixed per 1000 nm² of carbon black surface, a result that largely differs from the surface area derived from the application of Meissner's theory to bound rubber data, as we noted above.

THE NATURE OF RUBBER-FILLER INTERACTION

The Rubber-Black Interaction Site

In the author's opinion, most theories for bound rubber ignore, however, an important aspect: the effect of the chemical nature of the elastomer. It is indeed common knowledge that, at a given type and concentration of carbon black, bound rubber content is strongly dependent on rubber type. For instance, Leblanc and Hardy¹⁹ studied a number of compounds with various carbon blacks (N326, N330, and N347) and found that bound rubber content decreases according to the following ranking order: NR > polybutadiene > EPDM > EPR. They published the data showing that bound rubber fraction is actually dependent on the storage maturation time (at room temperature) of uncured compounds and suggested a two-step mechanism, first a variation in $\sqrt{\text{time}}$, followed by a constant value. Recently, Leblanc and Stragliati²³ reconsidered this model and proposed the following equation to fit BR – storage maturation data, that is

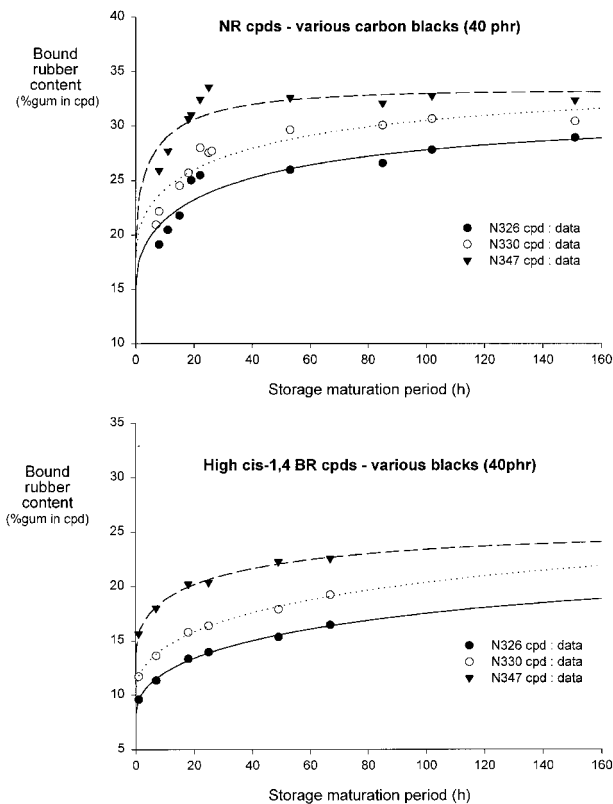


Figure 2 Variation of bound rubber with storage time (data from ref. 19); lines calculated with eq. (7). cpd, compounds.

$$BR_t = BR_0 + (BR_\infty - BR_0)(1 - e^{-k\sqrt{t}}) \quad (7)$$

where BR_0 and BR_∞ are, respectively, the initial and stabilized bound rubber fraction, t is the maturation time, and k is a fitting parameter. By non-linear regression, the parameters of this equation are obtained, namely, the stabilized BR value, with a de facto consideration for experimental scatter. Figure 2 shows this approach applied to some data previously published.

Using the stabilized BR values so derived from Leblanc and Hardy's data, the areas of active sites were calculated according to Meissner's equation for randomly dispersed polymers. Viscosity average molecular weight was measured on material cut from the bales as well as on gum samples masticated in an internal mixer up to a mixing energy of 1470 MJ/m^3 . Results are given in Table I, as are the specific surface areas for carbon blacks and the polymer molecular weights used in the calculations. As expected, results are strongly dependent on the molecular-weight values, particularly in the case of natural rubber, with its

known sensitivity to mastication. For synthetic elastomers, the differences in \bar{M}_v measured on samples cut from bales or after mastication are not significant. Despite some scatter, the logic behind Meissner's theory is indeed observed: higher bound rubber essentially arises from a larger area of reactive sites on filler particles. In addition—and this is not taken into account in the theory—for a given filler type (at constant level), A_0 is dependent on the chemical nature of the elastomer and generally tends to increase according to the sequence EPDM < EPR < polybutadiene < NR, as clearly seen from mean A_0 values.

To further develop the bound rubber theory, one has to pay attention to the nature of polymer-filler interaction. In other words, to attempt to answer two basic questions—(1) why do certain fillers strongly interact with polymer chains? and (2) how does the elastomer nature affect this interaction?—from the above theoretical considerations, it is possible to offer an explanation for rubber-carbon black systems. Indeed, using stabilized bound rubber fractions measured by Leblanc and Hardy on various rubber-black systems, we calculated the surface of the elementary adsorption site on the filler particle according to the approach of Cohen-Addad (Table II). Either the viscometric molecular weights, as measured on gum samples cut from the bale, or \bar{M}_v values, measured from masticated samples, were used in the calculation. In the case of ethylene-propylene rubbers, the molecular weight M_0 of the monomer units was calculated with respect to mean composition.

As can be seen, the results are sensitive to \bar{M}_v values used, but the calculated A_0 are very close, irrespective of the carbon black-specific surface area and the nature of the polymer. The mean value is 0.88 nm^2 with a standard deviation of 0.22. Because the bound rubber dependence on the chemical nature of the rubber is not seen in the A_0 values obtained, one concludes that the approach of Cohen-Addad implicitly takes into account this effect. With the series of systems studied, the only parameter referring to the nature of the rubber is the molecular weight of the monomer unit (plus, obviously, ϵ_a , the numerical factor accounting for chain stiffness and surface coverage, but this factor was taken to be equal to 1, in the absence of clear indication about its meaning). This, of course, conforms with a pure physical nature of the interactions between carbon black and general purpose elastomers, as suggested by earlier experiments of Ban et al.²⁴ and in agreement with recent data by

Table I Areas of Active Site on Filler Surface, Through Application of Meissner's Equation on Leblanc and Hardy's Data

Parameter	Elastomer Type			
	NR SMR 5CV	Polybutadiene 98% <i>cis</i> -1,4 NeoCis BR40 EniChem	EPR 42% PP Dutral CO 054 EniChem	EPDM 46% PP; 3.5% ENB Dutral TER 054/E EniChem
\bar{M}_v (from bale)	580,000	225,000	55,000	65,000
\bar{M}_v (masticated ^a)	330,000	230,000	65,000	50,000
N326 ^b compounds				
bound rubber (%) ^c	30.33	23.57	8.06	7.80
A_0 (nm ²) ^d	81.7–46.5	43.6–44.6	35.8–42.3	43.8–33.7
mean \bar{A}_0	64.1	44.1	39.1	38.8
N330 ^e compounds				
bound rubber (%) ^c	32.77	25.22	8.12	8.96
A_0 (nm ²) ^d	72.8–41.4	39.7–40.5	35.0–41.4	37.3–28.7
mean \bar{A}_0	57.1	40.1	38.2	33.0
N347 ^f compounds				
bound rubber (%) ^c	33.31	27.52	9.62	9.34
A_0 (nm ²) ^d	77.2–43.9	38.5–39.4	31.7–37.4	38.7–29.7
mean \bar{A}_0	60.6	39.9	34.6	34.2

^a In Banbury mixer up to 1470 MJ/m³ mixing energy.

^b N326: $S_p = 84$ m²/g.

^c From toluene extraction experiments; extrapolated to infinite storage time at room temperature.

^d First number is calculated with \bar{M}_v measured on rubber sample cut from bale; second number is calculated with \bar{M}_v measured on masticated sample.

^e N330: $S_p = 83$ m²/g.

^f N347: $S_p = 90$ m²/g.

Wang et al.,⁶ who demonstrated a drastic decrease in bound rubber with increasing solvent extraction temperature on SBR–carbon black compounds (17 blacks considered, from N110 to N762). With respect to the above discussion, it is clear that such interactions are likely to be topological constraints exerted on chain segments by the appropriate (geometrical) elements on the surface of filler particles.

Molecular Origin of Bound Rubber

Let us consider—in a very simplistic view—the likely dimensions of representative structural units of some diene elastomers. For instance, in natural rubber, the *cis*-1,4 structure is defined by two subsequent monomer units that determine a fiber dimension of 0.82 nm; if the backbone of such a structural unit is assimilated to a tube of 0.2-nm diameter (according to the average diameter of most atoms), the length of which equals the sum of the C—C and C=C bonds concerned (respectively, 0.154 and 0.135 nm), then one calcu-

lates* a half-lateral surface of 0.327 nm². The same reasoning leads to a similar value for *cis*-1,4 polybutadiene. While this might be purely coincidental, it is striking to see how *three times this value* (that is, 0.98 nm²) is close to the A_0 data given in Table II. This would indicate that, for a strong interaction to occur, the surface topology of a given carbon black particle must locally encounter the conformation of a chain segment equal to three structural units typical of the elastomer considered, as depicted in Figure 3 in the case of one motif of high *cis*-1,4 polybutadiene. By analogy with puzzle pieces, such an encounter would be possible, provided the polymer segment of structural units and the filler topological site have the corresponding reciprocal geometry, in the appropriate orientation, and at the right time. During mixing, the probability of such favorable events is obviously quite high. Once this topologi-

$$* \frac{\pi 0.2}{2} (5 \times 0.154 + 2 \times 0.135).$$

Table II Areas of Elementary Adsorption Site on Filler Surface, Through Application of Cohen-Addad's Equation on Leblanc and Hardy's Data

Parameter	Elastomer Type			
	NR SMR 5CV	Polybutadiene 98% <i>cis</i> -1,4 NeoCis BR40 EniChem	EPR 42% PP Dutral CO 054 EniChem	EPDM 46% PP; 3.5% ENB Dutral TER 054/E EniChem
\bar{M}_0	68.12	54.09	34.79	37.66
\bar{M}_v (from bale)	580,000	225,000	55,000	65,000
\bar{M}_v (masticated ^a)	330,000	230,000	65,000	50,000
N326 ^b compounds				
bound rubber fraction ^c	0.3033	0.2357	0.0806	0.0780
A_0 (nm ²) ^d	1.16–0.87	0.83–0.83	0.96–1.04	1.12–0.98
mean \bar{A}_0	1.02	0.83	1.00	1.05
N330 ^e compounds				
bound rubber fraction ^c	0.3277	0.2522	0.0812	0.0896
A_0 (nm ²) ^d	1.06–0.80	0.76–0.77	0.94–1.02	0.96–0.84
mean \bar{A}_0	0.93	0.77	0.98	0.90
N347 ^f compounds				
bound rubber fraction ^c	0.3331	0.2752	0.0962	0.0934
A_0 (nm ²) ^d	1.13–0.85	0.76–0.77	0.86–0.93	1.00–0.88
mean \bar{A}_0	0.99	0.76	0.90	0.94

^a In Banbury mixer up to 1470 MJ/m³ mixing energy.

^b N326: $S_p = 84$ m²/g.

^c From toluene extraction experiments; extrapolated to infinite storage time at room temperature.

^d First number is calculated with \bar{M}_v measured on rubber sample cut from bale; second number is calculated with \bar{M}_v measured on masticated sample.

^e N330: $S_p = 83$ m²/g.

^f N347: $S_p = 90$ m²/g.

cal interaction has taken place, it is quite obvious that, in order to release it, the free portions of the chain must exert on the constrained units not only sufficient stresses but also stresses in the appropriate direction. This process would require quite a high energy level to be statistically significant for bound rubber to vanish.

A_0 values obtained for ethylene-propylene rubbers are in the 0.9–1.0 nm² range. Therefore, by analogy with the above reasoning, one would conclude that C₂₄ segments are involved in the interaction with the black surface. However, because of the absence of a double bond, such segments have a higher flexibility and are consequently less prone to permanent topological interaction with the rigid filler surface. This would explain why EP rubbers exhibit lower bound rubber values.

Storage Maturation of Bound Rubber

We recently demonstrated that bound rubber is a complex function of mixing energy and storage

time,²³ but above a sufficient level of the former (in the 1900–2000 MJ/m³ range), only the latter effect remains significant. With respect to previous considerations (see previous section), these results can now be explained by considering that by the absorption of enough mixing energy by the compound, an optimal state of filler dispersion is achieved. With reinforcing black, this means that nearly all of the filler particles are in the form of aggregates, thus offering the largest black surface for topological interactions with chain segments of the matrix. Consequently, the variation of bound rubber during storage must be related to the evolution of one of the parameters that controls its level. With respect to Cohen-Addad's approach [eq. (5)], this can be either the average area of the interaction site on the filler particle, that is, A_0 , or the number-average molecular weight of the elastomer \bar{M}_n , or the factor accounting for chain stiffness and surface coverage, that is, ϵ_a (which was arbitrarily taken as 1). Because the meaning of the latter parameter is not clear at

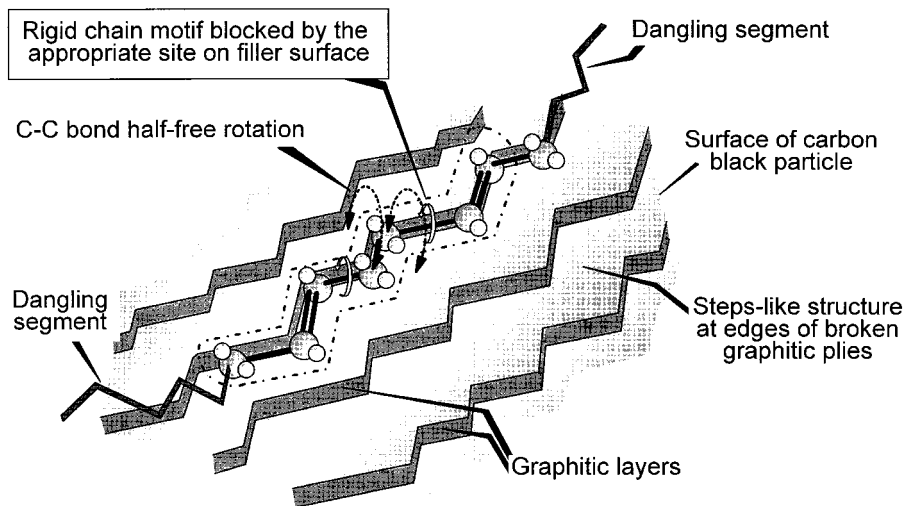


Figure 3 Pictorial view of rubber–filler interaction resulting from topological constraints when an elastomer motif conformation meets locally the surface structure of a carbon black particle.

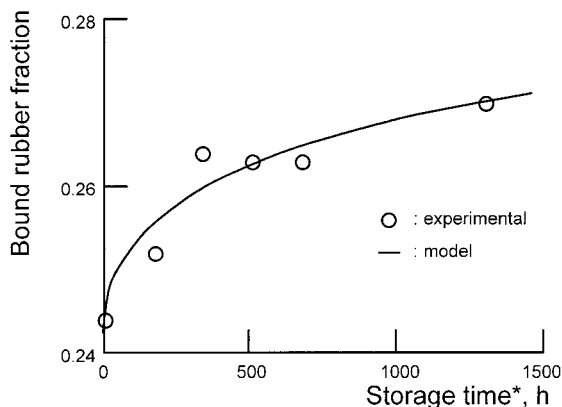
this stage, we will consider that it does not vary during storage and thus remains equal to 1.

Figure 4 shows the variation during storage of bound rubber for a single two-ingredient compound prepared with a mixing energy of 2420 MJ/m³, as previously reported.²³ Equation 7 is used to fit the data and yields the following parameters: $BR_0 = 24.24\%$, $BR_\infty = 28.60$, $k = 0.02694$. This allows one to calculate bound rubber values after any storage period, including $t = 0$, and to calcu-

late the corresponding A_0 data according to Cohen-Addad. Results are given in Table III.

As can be seen, the area of interaction site on filler particle is decreasing on storage. The area calculated at time $t = 0$ concerns the rubber–filler interaction at the dump, because it is achieved at the end of the mixing process. Results in Table III might look paradoxical because, at first sight, one does not see clearly how bound rubber could increase when the (average) interaction area on filler particles is decreasing. Obviously this arises directly from the mathematical form of eq. (5), and in the above application, it is implicitly

High *cis*-1,4 polybutadiene / N330 carbon black (50 phr)



* at room temperature, under argon atmosphere

Figure 4 Variation during storage at room temperature of a high *cis*-1,4 polybutadiene compound with 50 phr of N330 compounds [data from ref. 23, fitted with eq. (7)].

Table III Variation in Area of Bound Rubber Interaction Site During Storage at Room Temperature—High *cis*-1,4 Polybutadiene/50 phr N330 Carbon Black Compounds

Storage Time (hours)	Bound Rubber (%)	Interaction Site Area (nm ²)
0	24.24	0.788
1	24.36	0.784
2	24.41	0.782
5	24.50	0.779
10	24.60	0.776
50	25.01	0.763
100	25.29	0.755
500	26.25	0.727
1000	26.79	0.713
2000	28.03	0.681

considered that the number-average molecular weight \bar{M}_n of the elastomer remains constant because the value measured on gum rubber was used in the calculation. By essence, not all fractions of the elastomer in the compound are involved in bound rubber, and it is a common feature of all theories that the highest-molecular-weight chains do preferentially adsorb on filler particles. This was, for instance, stated in Meissner's theory and recently demonstrated by Leblanc and Stragliati with their extraction kinetics method.

Consequently, one should consider the actual molecular weight of the rubber fraction readily involved in bound rubber rather than the \bar{M}_n of the whole elastomer. This means that two possible explanations might be considered for bound rubber variation during storage: (1) the interaction site area increases during storage, as does the \bar{M}_n of adsorbed chains; (2) the interaction site area concerns a fixed number of representative structural units of the elastomer—say around 3, that is, five to six monomer units—but the \bar{M}_n of the adsorbed chains increases during storage. We note that both explanations implicitly consider that initially adsorbed short chains are progressively replaced by larger ones.

No data are available about a possible evaluation of the \bar{M}_n of bound chains during storage, and one doubts that such a measurement is possible. However, with respect to our reported work,²³ an acceptable model would read as follows:

$$\bar{M}_n(t) = \bar{M}_n(0) + [\bar{M}_n(\infty) - \bar{M}_n(0)](1 - e^{-bt}) \quad (8)$$

where $\bar{M}_n(0)$ and $\bar{M}_n(\infty)$ are the number-average molecular weights of bound rubber directly after compound preparation and after an infinitely long storage period, respectively, and b is a kinetic parameter. The events considered, that is, a substitution of short adsorbed chains by larger ones, occur in a bulk material, and therefore, the kinetic parameter b is likely to be quite low. Let us consider that over a very long storage period, \bar{M}_n in bound fraction varies by a factor of 2. Then, one can calculate how changing the value of b over several decades of time affects the change in \bar{M}_n (Fig. 5). A reasonable choice to proceed further seems to be $b = 0.0003$.

One can thus rewrite Cohen-Addad's equation in order to include a variation of \bar{M}_n , as follows:

$$BR(t) = \left[\frac{\sqrt{\bar{M}_0} c S_p}{A_0 N_{Av}} \right] \times \sqrt{\bar{M}_n(0) + [\bar{M}_n(\infty) - \bar{M}_n(0)](1 - e^{-bt})} \quad (9)$$

Let us consider explanation 1: bound rubber varies during storage because \bar{M}_n and A_0 do. Using the $BR(t)$ values in Table III, one does obtain the evolution of $A_0(t)$ from

$$A_0(t) = \left[\frac{\sqrt{\bar{M}_0} c S_p}{BR(t) N_{Av}} \right] \times \sqrt{\bar{M}_n(0) + [\bar{M}_n(\infty) - \bar{M}_n(0)](1 - e^{-bt})} \quad (10)$$

As shown in Figure 6, the interaction site area increases in such a manner that over a storage period of 2000 h, or nearly 3 months, the (average) number of structural units involved in bound rubber has increased from 2.4 to 2.8 (4.8–5.6 monomer units).

With explanation 2, bound rubber evolves with time because \bar{M}_n increases, but the site area remains constant and corresponds to a topological constraint exerted by the filler surface on a fixed number of structural units. Equation 9 is then used to calculate the variation of \bar{M}_n , using $b = 0.0003$ for the kinetic parameter. A comparison with experimental data is made in Figure 6, and it is seen that a good fit is obtained only when the found fractional number of structural units, that is, 2.4, is used. Using an entire number, for instance, 2 or 3, leads to an overestimation or underestimation of bound rubber, while the shape of the evolution versus storage time looks similar to experimental observations.

Both explanations thus allow equivalent results to be obtained, but it is clear that the determining aspect is the variation of \bar{M}_n during the storage period. Whether one would want to consider that A_0 remains constant or increases as well, is a secondary aspect with respect to the limited variation of this parameter, as deduced from the above modeling. An apparently intriguing point is that experimental data and the application of eq. (5) lead to the conclusion that a fractional number of structural units, instead of an entire number, are involved in rubber–filler interaction. This, however, is likely because *average* molecular weights are considered in the reasoning.

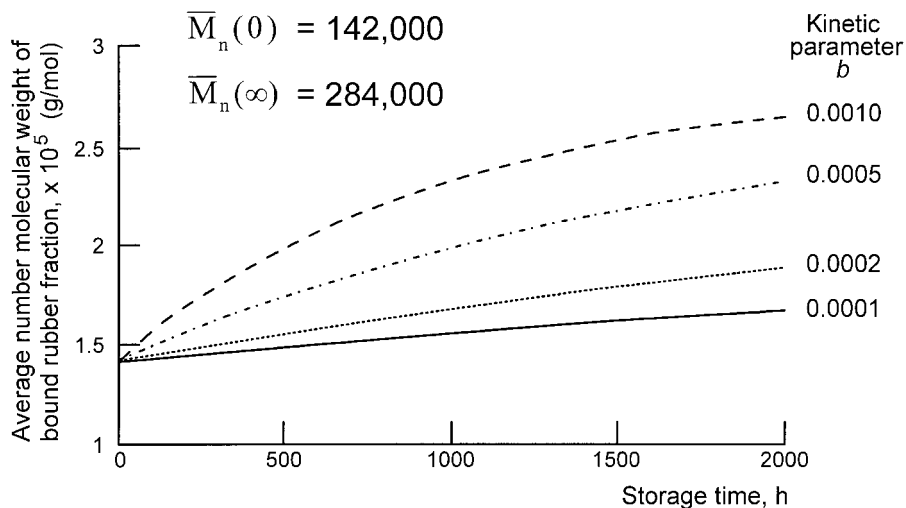


Figure 5 Modeling the variation during storage of the number-average molecular weight of the bound rubber fraction.

CONCLUSIONS

We are proposing a molecular explanation for the origin of bound rubber that is compatible with existing theories and is conforming to calculated quantities obtained when applying such theories to experimental data. The effect of the chemical nature of the elastomer on bound rubber is now understood, an aspect not considered in bound rubber theories. The role of chemical nature and unsaturation of the polymer on bound rubber is now clearer because it is not the double bond per

se that is the key element in the interaction but rather the local conformational stiffness it brings in the elastomer chain, in such a manner that strong topological interactions with filler surface are favored. This allows one to understand also why saturated elastomers do not exhibit strong interactions with high structure carbon blacks.

Another promising aspect of this work is the concluding hypothesis that the observed storage maturation of bound rubber could just reflect a slow replacement of short chains initially involved in bound rubber by larger ones. This process is obviously physically possible, but direct experimental proof is difficult to obtain.

High cis-1,4 polybutadiene / N330 carbon black (50 phr)

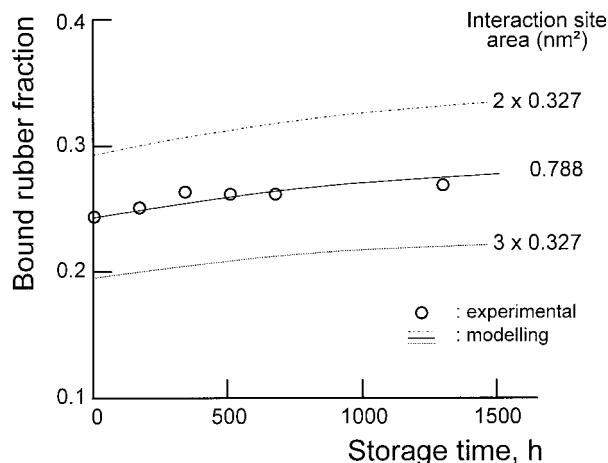


Figure 6 Modeling the variation of bound rubber during storage, as a result of \bar{M}_n changes of the bound chains.

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