Elastomer–Filler Interactions and the Rheology of Filled Rubber Compounds

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ABSTRACT: Strong interactions between elastomer and filler particles result in the so-called bound rubber (BdR), i.e. the fraction of polymer not extractable from uncured filled rubber compounds by a good solvent of the gum elastomer. BdR is an essential characteristic of uncured compounds and a key element in understanding the flow properties of such materials. After a brief review of works that demonstrate how BdR is involved in the particular morphology of uncured filled rubber compounds, the molecular origin of this phenomenon is explained. A kinetic extraction method to assess BdR is described that yields the absolute value of BdR with a compensation for experimental scatter. Results that further demonstrate how bound rubber is related with the rheological properties of filled rubber materials are reported. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 1541–1550, 2000

Key words: filled rubber compounds; bound rubber; carbon black; silica; rheological properties

INTRODUCTION

Bound rubber is the fraction of polymer that cannot be extracted from uncured carbon black filled compound by a good solvent of the gum elastomer. Above a sufficient filler level, in the 15–20% weight range, a highly swollen rubber–filler gel remains after all the free rubber has been extracted. This phenomenon is known for decades[1] and has been assigned a major role in reinforcement.[2] Because filler–elastomer interactions that are obviously involved in this phenomenon are likely to affect as well the flow properties, we have paid over recent years some attention to bound rubber.[3–5]

The aims of this paper are (1) to show how bound rubber is deeply involved in the particular morphology of uncured filled compounds, (2) to describe briefly a nonambiguous method to assess bound rubber, (3) to describe our view about the molecular origin of bound rubber, and (4) to report our most recent data that further demonstrate how bound rubber is related with the rheological properties of filled rubber materials.

MORPHOLOGY OF UNCURED FILLED RUBBER COMPOUNDS

When an elastomer and a reinforcing filler (e.g., carbon black) are mixed, they strongly interact and form a complex and heterogeneous structure. Rubber–filler interactions readily occur in the early stages of the mixing operation and the resulting structure can be best described as consisting of filler aggregates, covered by an inner shell of tightly bound rubber, and embedded in a loosely bound rubber region where limited chain motion is possible; the loosely bound rubber region forms "filaments," connecting the complex rubber–filler units. A third region of unbound and mobile rubber interpenetrates the three-dimensional soft network. Figure 1 is a representation
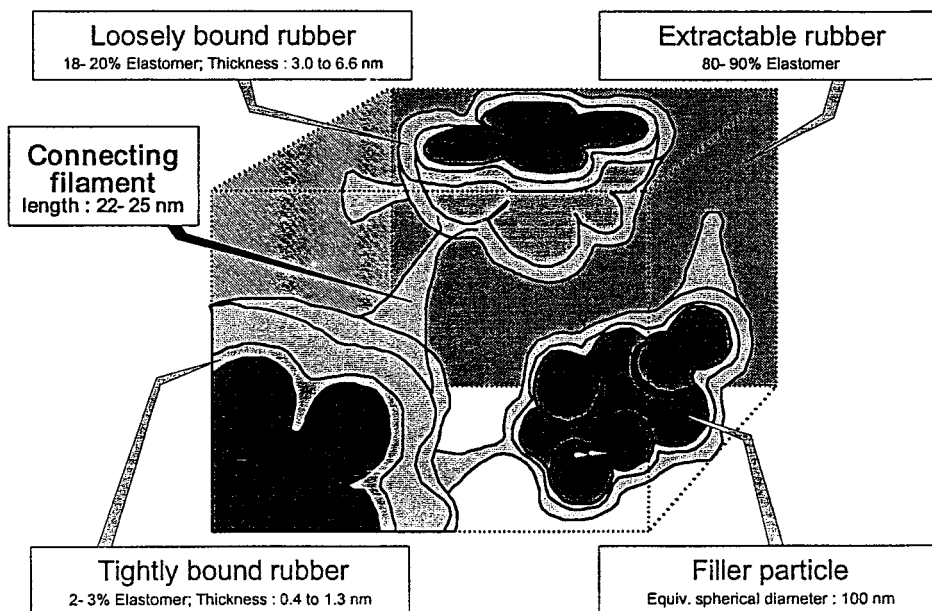
Figure 1 Morphology of uncured filled rubber compound.

of this complex structure, which was somewhat obvious in micrographs published around 24 years ago,[6] the details of which can be inferred from NMR measurements.[7] By modeling an optimum dispersion of carbon black particles as a face-centered cubic pattern, we calculated that the mean length of "connecting filaments" should be in the 25–50 nm range, an interesting result to be compared with the mean random coil diameter of a high molecular weight polymer (i.e., 50 nm).[8]

Under strain flow conditions, such a system exhibits a bulk behavior that reflects its particular morphology—namely, integration of a strain history with the memory of past deformations, both dampened however by microrelaxation processes due to the mutual influences of the rubber–filler units connected by the loosely bound filaments. For instance, a yield stress behavior is expected with consequently no linear viscoelastic domain. Indeed, at low applied stress, the system will essentially respond as a soft, deformable network. Once the yield stress is exceeded, each rubber–filler unit steadily moves from one equilibrium position to the other and basically the whole system exhibits then an overall bulk stable flow behavior. Moreover, a stationary layer at the wall of processing equipment is quite a physical impossibility because of the drag flow of the rubber–filler units, and therefore rubber compound can be expected to exhibit strong slippage effect, as indeed observed. Furthermore, under appropriate

conditions, for instance in converging flows, the complex rubber–black morphology is prone to strong flow induced anisotropy effect. In addition, the known decrease in extrudate swell with increasing carbon black level or structure results from local stress release mechanisms involving the rubber–black aggregates and their connective filaments, either through limitation of the elastic energy storage by higher viscous dissipation, or by local microrelaxation processes. In other words, upon flow strain the complex rubber–carbon black morphology organizes itself in what could be called an "elasticity dissipation structure."

AN EXTRACTION KINETIC METHOD FOR BOUND RUBBER ASSESSMENT

At first sight, bound rubber (BdR) is a property that seems easy to measure since it involves treating an uncured sample with the appropriate solvent for a sufficient time, in such a manner that all the extractable chains are dissolved. Then the extracted material is dried and the bound rubber obtained by weighing (see ref. 3 for a detailed description of the standard technique, used by most authors). Practical experience shows, however, that the time for complete extraction of the mobile species can be very long and that, even if an extended extraction period is used, for in-
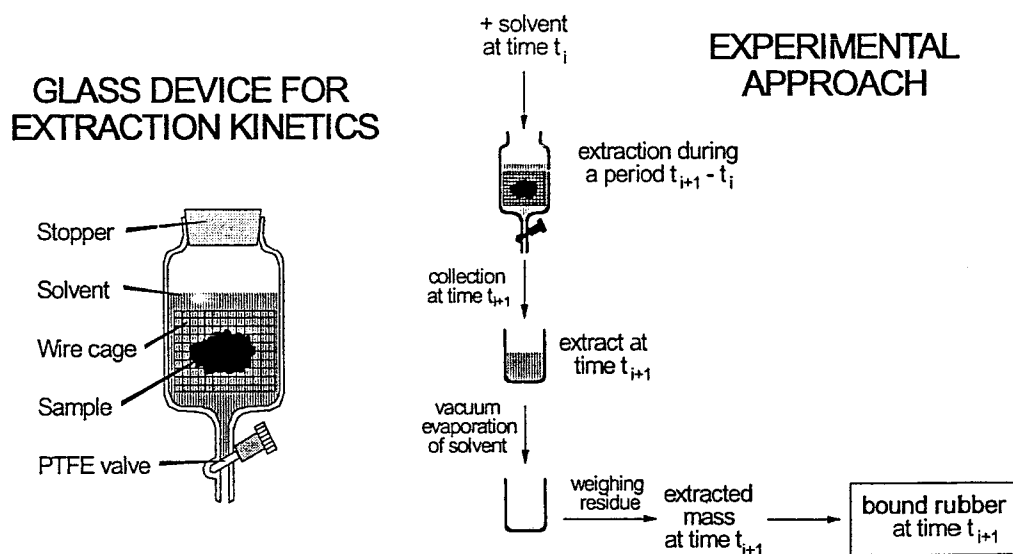
Figure 2   Extraction kinetic method for BdR assessment.

stance 100 h, bound rubber measurement still suffers from a considerable scattering results, as demonstrated by repeating the test. In order to overcome these deficiencies and to obtain additional information, a method was developed that considers the kinetics of the extraction process, and models it in order to derive what can be considered as the absolute BdR content of the tested material (at room temperature).[5]

As shown in Figure 2, a special glass device is used to swell test samples in fixed quantities of the appropriate solvent for well-defined periods. Around 2 g of sample is weighed in a steel wire basket and disposed in the glass vessel with a polytetrafluoroethylene (PTFE) valve at the bottom. A known quantity of solvent is poured into the vessel and left in contact with the rubber sample. After various periods of time, the solvent (which contains some extracted species) is col-

lected through the valve and another portion of pure solvent is poured into the vessel for a further extraction period. The procedure is repeated until complete extraction is achieved. The extracts are collected and evaporated under vacuum to assess the extracted quantity of rubber.

Data are fitted using a simple model based on the assumption that, when an uncured filled compound is treated with a good solvent for the rubber, the soluble polymer is removed at a rate proportional to the amount of extractable rubber remaining in the compound, that is,

$$[\%\mathrm{Extr}]_t = (100 - [\%\mathrm{BdR}]) \times (1 - e^{-bt}) \quad (1)$$

where $[\%\mathrm{Extr}]_t$ is the amount of extracted rubber at time t (in % of the initial gum content), $[\%\mathrm{BdR}]$ the amount of bound rubber, and b a rate constant. When the data are fitted through nonlinear regression, the bound rubber is directly obtained, as shown in Figure 3.

The advantages of the method are that the bound rubber value so derived is absolute since it corresponds to an infinite extraction time, with *de facto* compensation for experimental scatter, and that additional analysis (for instance molecular weight measurements by gel permeation chromatography) can be performed on extracted materials.

The residue can also be recovered, dried under vacuum, and the bound rubber content cross-checked by thermogravimetric analysis.
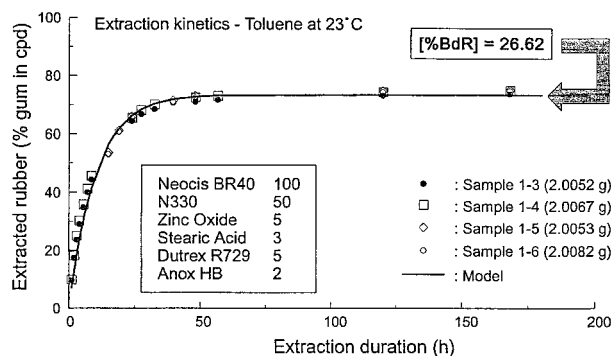

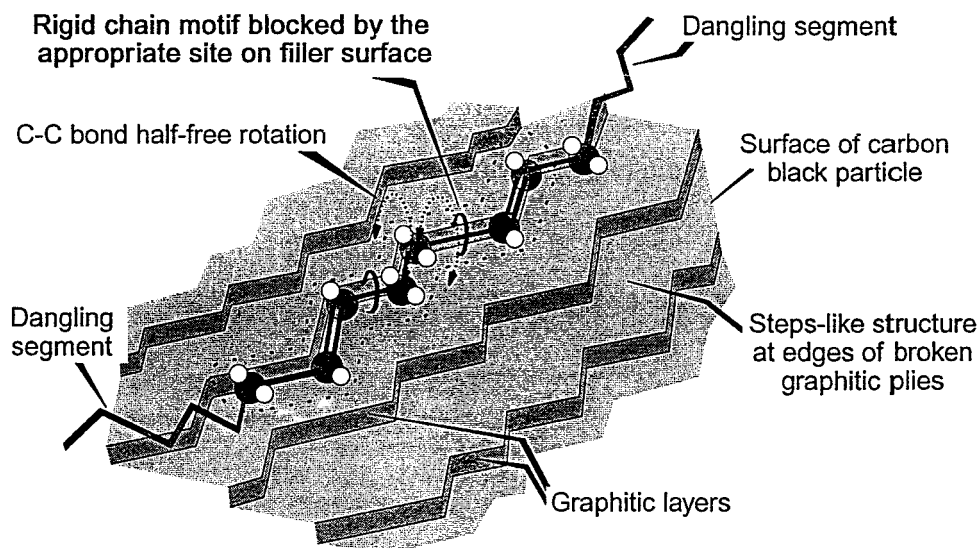**Figure 3**   Extraction kinetics: results on a polybutadiene compound.

Figure 4 Pictorial view of rubber–carbon black interaction.

A MOLECULAR MODEL FOR THE ORIGIN OF BOUND RUBBER

A theory for bound rubber was developed by Meissner in 1974 that treats the effect as a random adsorption of structural units of polymer on "reactive sites" assumed to exist on the filler surface.[9] In this model, the size of the adsorbed polymer segment is fixed and identified with the structural unit of the polymer, but no hypothesis is drawn as to the chemical or physical nature of the reactive sites, while filler particles are considered to act as polyfunctional crosslinking agents. The filler is characterized by its specific surface area, and the (mean) area of one active site on the filler particle is a fitting parameter. This theory and its further developments[10–12] explain well certain aspects of bound rubber—namely, that with respect to molecular weight distribution (MWD) of the initial gum rubber, the one of extracted rubber is shifted toward the lower molecular weight. In other words, bound rubber is made up of the largest rubber chains, an aspect of Meissner's theory that is substantiated by published data.[5,12,13] However, this theory does not explain why BdR at equal level of the same filler depends on the chemical nature of the elastomer[3] and does not meet the observed effect of storage time on bound rubber.[3,5]

A model for bound rubber in the polysiloxane–silica system has been proposed by Cohen-Addad.[14,15] In such systems, the rubber–filler interaction is clearly of a chemical nature and reactive sits well defined (silanol groups). The site area is thus no longer an unknown and can be considered as the surface (on the filler particle) associated with one hydrogen bond. The model predicts that BdR increases with the square root of the number-average molecular weight of the initial gum polymer. With more common rubber–filler systems—for instance, carbon black filled diene elastomers—one can hardly consider a chemical interaction because, as demonstrated by Wang et al.,[16] BdR tends to zero when the extraction process is performed at high temperature (i.e., >80°C).

By considering that carbon black–rubber interactions are of a physical nature and result from topological constraints exerted by the filler surface on the appropriate elastomer motif, we developed a model assigning a clear molecular origin to bound rubber.[17] As pictorially illustrated in Figure 4, for a strong rubber–filler interaction to occur, the surface topology of a carbon black particle must encounter the appropriate conformation of a chain segment. Once a suitable motif has conformed itself with respect to the corresponding site on the carbon black surface, the interaction can be destroyed only if strains are exerted on the dangling segment, with the right force, in the right direction. By extending somewhat Cohen-Addads' views, we derived the following mathematical expression for the model, in order to incorporate as well the effect of storage on bound rubber, by considering that initially adsorbed short chains are progressively replaced by longer ones during the storage maturation process, i.e.,
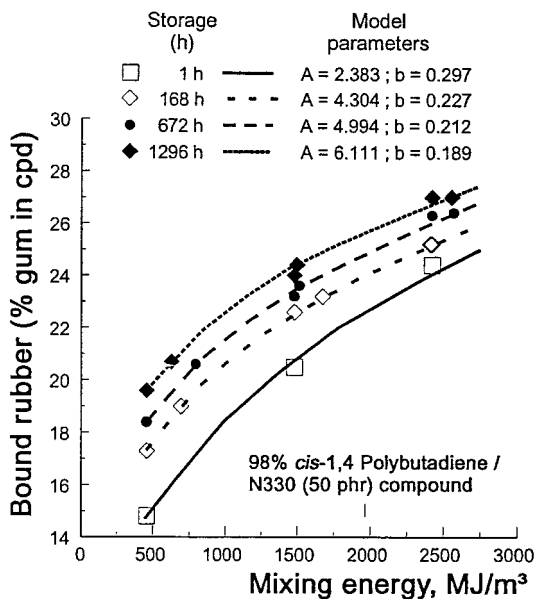
Figure 5 Effect of mixing energy and storage on bound rubber level.

$$\text{BdR}(t) = \left[\frac{\sqrt{M_0}}{A_0} \frac{cS_P}{N_{AV}} \right]$$
$$\times \sqrt{\bar{M}_n(0) + [\bar{M}_n(\infty) - \bar{M}_n(0)](1 - e^{-\beta t})} \quad (2)$$

where M_0 is the weight of one skeletal bound, A_0 the average area of one interaction site (nm^2), c the filler concentration (g/g of gum polymer), S_p the specific surface area of filler (m^2/g), N_{Av} the Avogadro number (6.023×10^{23}) $\bar{M}_n(0)$, and $\bar{M}_n(\infty)$ the number average molecular weight (g/mol) of bound rubber before and after infinitely long storage period of rubber compound respectively, β a kinetic parameter, and t the storage time.

This model can be used to explain the effect of the chemical nature of the elastomer on bound rubber. For instance, at equal loading of the same black, bound rubber is higher for natural rubber than for high cis-polybutadiene, and ethylene–propylene rubber always exhibits the lowest bound rubber level.[3] It is not the unsaturation per se that is the important parameter in bound rubber level but rather the limit in flexibility of the main chain imparted by double bonds. A reasonable estimation can therefore be offered for the surface area of one interaction site. For a diene elastomer (i.e., natural rubber, polybutadiene, styrene–butadiene rubber (SBR), . . .), A_0 would correspond to the half-lateral surface of at least two structural units of the polymer (for instance,
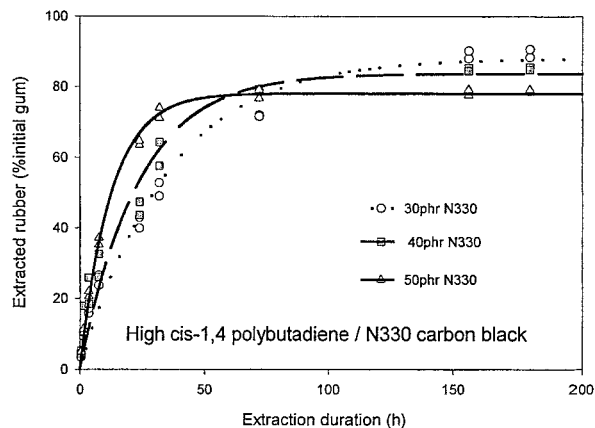

Figure 6 Bound rubber in polybutadiene compounds.

2×0.327 nm^2 for polyisoprene and polybutadiene). With high cis-1,4-polybutadiene compounds, the best fit of eq. (2) to experimental data was obtained when considering A_0 equals to 2.4 times the half-lateral surface of the C$_4$H$_8$ unit, quite a satisfactory result with respect to average molecular weights assumed.

VARIOUS EXPERIMENTAL ASPECTS OF BOUND RUBBER

Bound Rubber and Mixing Energy

When preparing a filled compound in the mixer, it is obvious that interactions begin to occur as soon as the rubber and the filler are in contact, but like many physicochemical processes, one would not expect this interaction to be instantaneous but to exhibit a kinetic character. In other words, how bound rubber is formed during the early stage of mixing is thus expected to be one of the most critical aspect of compounding, likely to be reflected by the rheological properties of the material.

It has been known for a long time that the amount of bound rubber is dependent on the extent of mixing. For instance, Cotten[18,19] reported that, in oil-extended SBR and polybutadiene com-

Table I Bound Rubber Data on High cis-1,4-Polybutadiene Compounds

N330 (phr)	BdR (%)	b	R^2
30	11.9	0.0287	0.9743
40	16.3	0.0431	0.9553
50	22.0	0.0825	0.9969
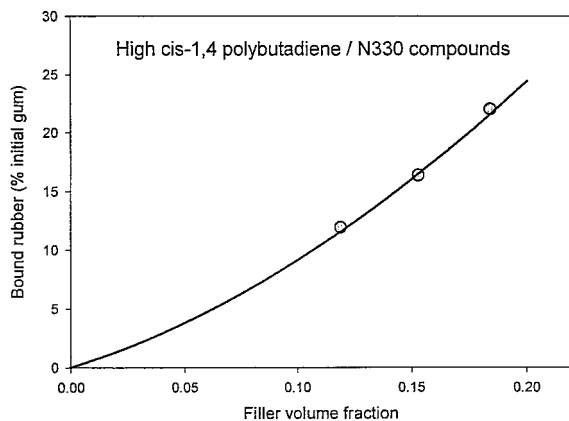
Figure 7 Bound rubber versus carbon black volume fraction.

Figure 8 Mobile rubber extraction rate parameter.

pounds with N339 carbon black (50 phr), bound rubber content increased with mixing time until a plateau value was reached. We made similar observations when preparing SBR 1500/N330 compounds,[20] and further concluded that quite high levels of specific mixing energy (above 1500 MJ/m³) are needed to achieve optimum rubber–filler interaction.

We investigated in details this aspect by preparing a model* polybutadiene–carbon black formulation in a Banbury internal mixer in such a manner that compounds received different levels of mixing energy. Then they were stored under argon at room temperature and the bound rubber variation upon storage was evaluated. Remilling experiments were also performed and the bound rubber subsequently evaluated.

Results of the study of this series of samples, with various mixing energy levels and storage period, demonstrate that, at equal storage time, there is a sample scaling law between the overall mixing energy and the bound rubber, i.e.,

$$[\%\mathrm{BdR}] = Q \times (E_{\mathrm{mix}} + E_{\mathrm{remill}})^c \qquad (3)$$

where E_{mix} is the mixing energy received by the compound in the internal mixer, E_{remill} the energy of remilling, and Q and c parameters that depend on the formulation. Since rheological properties of filled compound are dependent on the mixing energy level, there is thus a clear link between bound rubber content and flow properties. (See Fig. 5.)

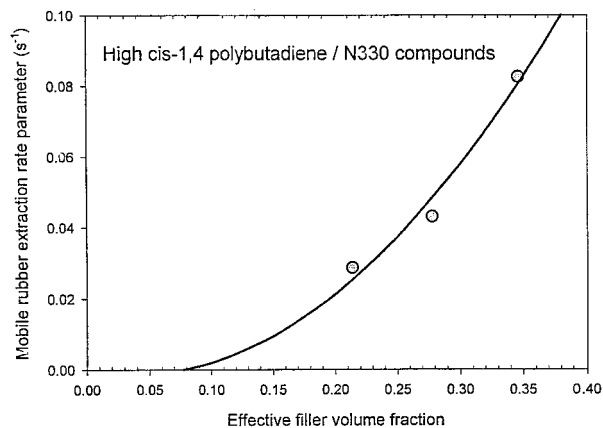
* Only the filler and the elastomer.

Bound Rubber and Filler Level

High *cis*-1,4-polybutadiene compounds with different levels of N330 carbon black and the usual ingredients (but no curatives).[†] were prepared in a Banbury mixer in such a way that a specific mixing energy level of around 1200 MJ/m³ was achieved. Samples were stored for one year in plastic bags, at room temperature, in darkness, then tested for bound rubber content.

Figure 6 shows results of the extraction kinetic experiment, from which bound rubber contents and rate parameter *b* were obtained, as shown in Table I. As expected the higher the filler level, the higher the bound rubber content. The effect is not linear, however, and it is interesting to treat it with a quadratic equation, with respect to the well-known Guth, Gold, and Simha relation-

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[†] Neocis BR40: 100; N330: 30, 40, or 50; ZnO: 5; oil: 5; stearic acid: 3; trimethylquinolein (polymerized): 2; *M*-isopropyl-*N′*-phenyl-*p*-phenylene diamin: 1.
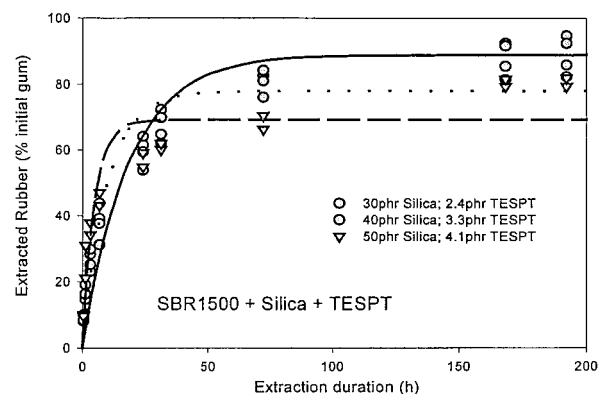

Figure 9 Bound rubber in silica-filled SBR compounds.

Table II   Bound Rubber Data on Silica-Filled SBR Compounds

| Silica (phr) | Silane (phr) | Extraction Kinetic Method | | | Dry Residue BdR (%) |
		BdR (%)	b	R^2	
30	2.4	11.1	0.054	0.943	11.0
40	3.3	22.1	0.103	0.943	19.2
50	4.1	30.9	0.210	0.858	29.0

Figure 10   Bound rubber in silica with silane compounds.

ship.[21,22] As shown in Figure 7, a perfect fit of the experimental data is obtained with the following equation:

$$[\%\text{BdR}] = A \times 2.5 \times \Phi_B + B \times 14.1 \times \Phi_B^2 \quad (4)$$

where Φ_B is the volume fraction[‡] of the filler, A and B fitting parameters equal respectively to 24 and 22. In agreement with a proposal by White and Crownder,[23] A and B are parameters that account for asymmetry of filler particles.
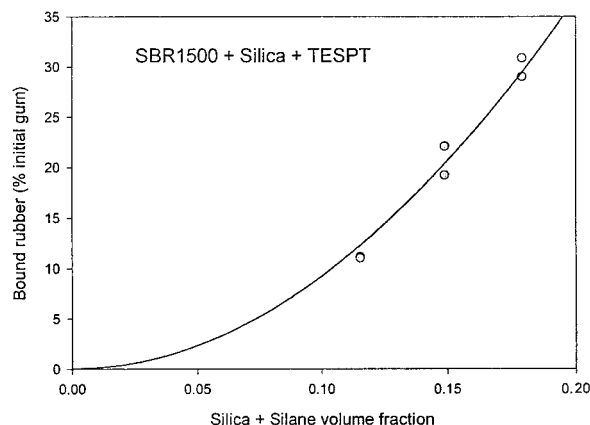
In addition to bound rubber for an infinite extraction time, the extraction kinetic method provides also a "rate parameter" b that reflects how the compound swells and how the mobile rubber species are extracted. A number of complex physicochemical effects are involved in this process, whose detailed discussion is outside the scope of this report. The data above show that the higher the filler level, the higher the parameter b and hence the faster the extraction process.

With respect to the model depicted in Figure 1 for carbon black filled compounds, it is clear that the variation of the rate parameter b must be considered with respect to the effective filler volume fraction Φ_{Eff}, that is the volume fraction of the filler Φ_B plus the volume fraction of bound rubber Φ_{BR}. The latter is easily calculated according to

$$\Phi_{BR} = \frac{[\%\text{BdR}]\rho_{\text{cpd}}}{\rho_{\text{cpd}}W_{\text{cpd}}} \quad (5)$$

where [%BdR] is the bound rubber content (in % weight of the gum content of the formulation), ρ_{cpd} and ρ_{gum} the specific gravity of the compound and

the gum rubber respectively, and W_{cpd} the overall phr of the compound. Figure 8 shows that when one uses a quadratic equation to best fit b vs Φ_{Eff}, the rate parameter vanishes for $\Phi_{\text{Eff}} \cong 0.070$, a value that would correspond to a carbon black content equal to 19 phr (including some bound rubber). At this level, the filler particles are so distant and no coherent gel can be obtained. It is worth noting that compounds with (N330) black level below 20 phr do not exhibit any of the rheological characteristics commonly found in highly filled systems—namely, the disappearance of the Newtonian plateau on the viscosity function, or the significant reduction in extrudate swell with increasing filler level.

[‡] In calculating the filler volume fraction, the following specific gravities (g/cm^3) were used for compounding ingredients: NeoCis BR40: 0.90; N330: 1.80; ZnO: 5.57; stearic acid: 0.92; oil: 0.98; Permamax: 1.08; IPPD: 1.17.
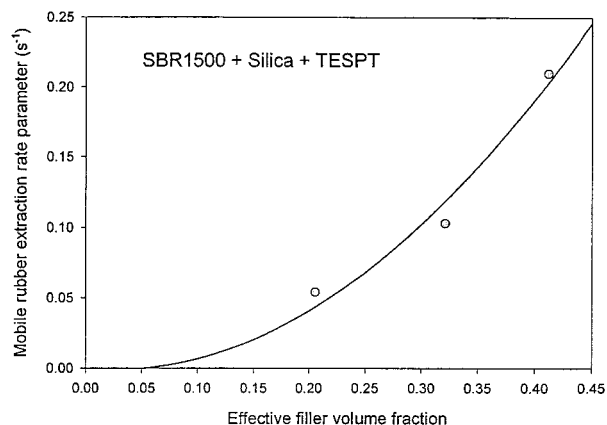

Figure 11   Extraction rate parameter in silica compounds.

Table III Bound Rubber and Mooney Viscometer Data on Polybutadiene, EPDM, and NBR Compounds
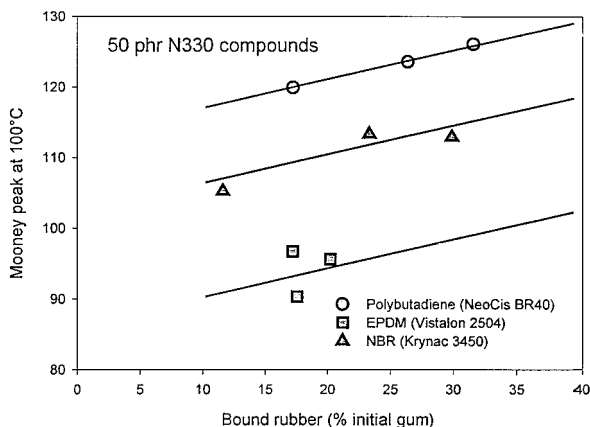
Storage (Day)	Polybutadiene Compound Mooney at 100°C Peak	ML	Bound Rubber	EPDM Compound Mooney at 100°C Peak	ML	Bound Rubber	NBR Compound Mooney at 100°C Peak	ML	Bound Rubber
0.1	111.2	74.9		91.1	59.5		99.5	60.1	
1	119.9	76.5	17.2	90.3	59.6	17.6	105.2	63.5	11.6
15	123.6	81.0	26.4	96.7	61.7	17.2	112.9	66.4	29.8
29	126.1	80.8	31.5	95.6	61.5	20.2	113.3	66.8	23.3

Bound Rubber in Silica-Filled Compounds

SBR 1500 compounds[§] with different levels of silica and the appropriate content of silane were tested for bound rubber using the extraction kinetic method (Fig. 9). While extracted solutions were slightly troublesome, a coherent gel was always obtained, thus indicating that the soft three-dimensional model is also valid for silica-filled compounds, at least when the rubber–filler promoting action of silane has been well conducted during mixing. Despite a larger scatter at the end of the extraction process (when weighing errors are maximum with respect to minute quantities of extracted species in solution), the extraction kinetic fitting gave results in line with measurements made in dried residues, as shown in Table II.

Bound rubber is found to depend on silica level according to eq. (4), provided that one takes into account the volume fraction of the silane, i.e.,

$$[\%BdR] = A \times 2.5 \times \Phi_{\text{si+sil}} + B \times 14.1 \times \Phi_{\text{Si+Sil}}^2$$

$$(6)$$

Accordingly, the curve in Figure 10 is drawn using $A = 0.1$ and $B = 65$. The good fit obtained confirms that the silane covers the silica particles well and bound rubber occurs because of chemical bonding.

As shown in Figure 11, the extraction rate parameter b for mobile species depends on the effective filler volume fraction according to a quadratic equation. The effective filler volume fraction is calculated by considering the silica, the silane and the measured bound rubber. The rate parameter vanishes for $\Phi E_{\text{ff}} \cong 0.050$, a fraction that would correspond to around 15 phr of silica and 1.23 phr of silane. At those levels of filler and promoting agent, no coherent gel would be possible (and therefore our extraction kinetic method would not be applicable).

[§] Prepared and kindly supplied by DEGUSSA; bis(3-triethoxysilylpropyl)tetrasulfane (TESPT) was used in proportion with silica level, in the ratio 8.2 phr TESPT ($\rho = 1.095$ g/cm^3) for 100 phr silica ($\rho = 2.2$ g/cm^3).

Figure 12 Mooney peak versus bound rubber.
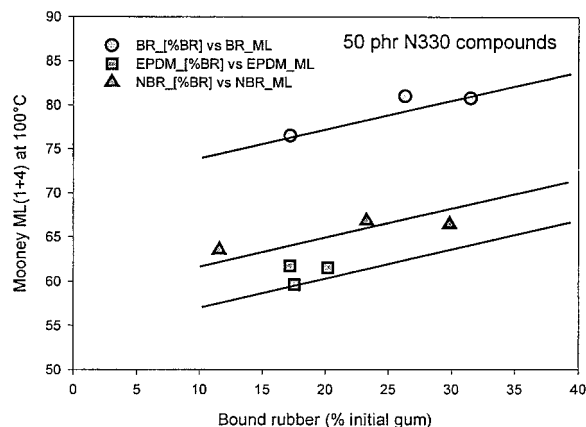
Figure 13 ML(1 + 4) versus bound rubber.

Bound Rubber and Rheological Properties

Three compounds with either high cis-1,4-polybutadiene (NeoCis BR40), or EPDM (Vistalon 2504), or NBR (Krynac 3450) and equal loading (50 phr) of N330 carbon black were prepared in Banbury mixer with the usual compounding ingredients.[#] They were stored at room temperature under plastic cover in darkness and tested at various intervals for Mooney viscosity at 100°C and bound rubber (at room temperature). Bound rubber measurements and Mooney data (in terms of Mooney Peak and ML(1 + 4)) are given in Table III.

Clearly, all data change with storage time and Mooney peaks are more affected than ML (1 + 4). Similar observations were already reported[4] and the higher sensitivity of Mooney peak measurements to storage maturation surely reflects the fact that a change in the soft three-dimensional network (cf. Figure 1) is indeed expected to affect the material response in the earlier times of a strain flow test. It is nevertheless significant that the ML(1 + 4) still varies with storage time, although to a smaller extent. As shown in Figures 12 and 13, with the polybutadiene and nitrile rubber compounds, a linear relationship is seen between bound rubber and rheological properties. The relation is not so clearly established for the EPDM compound despite the straight line that is arbitrarily drawn through the data. Bound rubber is low with ethylene propylene rubber due to the lack of unsaturation in the chain backbone, according to arguments developed above (see A Molecular Model for the Origin of Bound Rubber above). Different scales were used for Mooney Peak and ML(1 + 4) in drawing these figures, and the slopes are consequently different, i.e., the dependence is steeper for Mooney Peak. All these effects are coherent with the model briefly described in A Molecular Model for the Origin of Bound Rubber above.

CONCLUSIONS

There is no doubt anymore that most peculiar rheological properties exhibited by filled rubber compounds find their roots in the complex 3D morphology that results from strong interactions between the surface of filler particles and segments of rubber chains. Bound rubber directly results from such interactions and is likely to be the most sensitive bulk property that can be considered to characterize a filled rubber compound.

Providing our extraction kinetic method is used, an absolute value of bound rubber is obtained at the extraction temperature. There are however important kinetic aspects in the formation of bound rubber and relatively high levels of specific mixing process. After dumping, one needs also a storage period of several weeks (at room temperature) before a stable bound rubber level is reached.

In the case of the carbon black system, such interactions are essentially of physical nature, and a simple model has been proposed that refers to topological constraints between the surface of the filler and appropriate motif of the elastomer chains. The role of the chemical nature of the elastomer in now understood and it is not the unsaturation per se that is the key factor but rather the rigidity it imparts to the segment.

Our experimental data with silica-filled system are still limited in number, but the results in hand show that providing the appropriate interaction chemistry has been achieved during mixing, using the appropriate promoter and the correct mixing procedure, bound rubber is also an important property. The extraction kinetic method gives also good results with silica-filled compounds.

Most observed effects on bound rubber—i.e., storage maturation, mixing energy, chemical nature of the polymer, remilling, etc.—can be modeled through fairly simple mathematical expressions. Any effect that can modify the bound rubber content of a compound will also modify its rheological properties.

REFERENCES

1. Fielding, J. Ind Eng Chem 1937, 29, 880.
2. Dannenberg, E. M. Rubber Chem Technol 1986, 59, 512.
3. Leblanc, J. L.; Hardy, P. Kautsch Gummi Kunstst 1991, 44, 1119.
4. Leblanc, J. L.; Staelraeve, A. J Appl Polym Sci 1994, 53, 1025.
5. Leblanc, J. L.; Stragliati, B. J Appl Polym Sci 1997, 63, 959.
6. Ban, L. L.; Hess, W. M.; Papazian, L. A. Rubber Chem Technol 1974, 47, 858.
7. O'Brien, J.; Cashell, E. M.; Wardell, G. E.; McBrierty, V. J. Macromolecules 1976, 9, 653.
8. Lebranc, J. L. Plast Rubber Comp Proc Appl 1995, 24(5), 241.

[#] That is, ZnO: 5; stearic acid: 3; oil: 5; Antiheat: 3; Antiozonant: 1.

9. Meissner, B. J Appl Polym Sc 1974, 18, 2483 (reprinted in Rubb Chem Technol 1975, 48, 810.
10. Meissner, B. J Appl Polym Sci 1993, 50, 285.
11. Karasek, L.; Meissner, B. J Appl Polym Sci 1994, 52, 1925.
12. Karásek, L.; Meissner, B. J Appl Polym Sci 1998, 69, 95.
13. Kraus, G.; Gruver, J. T. Rubber Chem Technol 1968, 41, 1256.
14. Cohen-Addad, J. P. Polymer 1989, 30, 1820.
15. Cohen-Addad, J. P. Polymer 1992, 33, 2762.
16. Wang, M. J.; Wolff, S.; Tan, E. H. Rubber Chem Technol 1993, 66, 178.
17. Leblanc, J. L. J Appl Polym Sci 1997, 66, 2257.
18. Cotten, G. Rubber Chem Technol 1984, 57, 118.
19. Cotten, G. Plast Rubber Proc Appl 1987, 7(3), 175.
20. Leblanc, J. L.; Evo, C.; Lionnet, R. Kautsch Gummi Kunstst 1994, 41, 401.
21. Guth, E.; Simha, R. Kolloid-Zeitung 1936, 74, 266.
22. Guth, E.; Gold, O. Phys Rev 1938, 53, 332.
23. White, J. L.; Crowder, J. W. J Appl Polym Sci 1972, 16, 473.