Bound Rubber Theory and Experiment

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SYNOPSIS

Adsorption of polymer on filler from bulk is known to result in a partial loss of polymer solubility ("bound rubber"). The existing theories of this phenomenon were critically examined, and the random adsorption model suggested by the author was found to provide the most complete explanation of available experimental data. Theory based on this model and containing one adjustable parameter (filler surface area per adsorption site) correctly predicts the change of molar mass distribution with adsorption on filler and satisfactorily describes the experimental dependence of fraction B of the filler-bound polymer on filler concentration and surface area and on $\bar{M}_w$ of the polymer, in both narrow and very broad molar mass distributions. No distinct effect on B of a moderate degree of branching of EPM, EPDM chains could be detected. It is concluded that the modification of the random adsorption model suggested by Shiga is not warranted, neither theoretically nor experimentally. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Generally, the incorporation of carbon black and other reinforcing fillers into (originally soluble) rubbery polymers results in a partial loss of polymer solubility. A certain fraction B of the polymer, usually denoted as bound rubber, obviously becomes strongly adsorbed on the surface of filler particles and the polymer-filler attachments involved are able to resist the desorptive action of the solvent. In the moderately low filler concentration range the filler bound polymer molecules together with the filler particles present there develop a three-dimensional gel-like structure called carbon gel or polymer-filler gel.

The relationship of bound rubber to rubber reinforcement was recognized quite early, and dozens of papers have been devoted to the study of this effect and of the bound rubber structure. Reviews on the subject have been published by a number of authors, most recently, by Dannenberg.[1] Quantitative treatments of the phenomenon of filler-induced insolubilization of polymers have also been reported.[2-8] Some aspects of the problem have been dealt with, but controversial points still exist. It is

the purpose of the present paper to critically review the existing theories of bound rubber and the results of their experimental tests, with the aim to arrive at a unified and more satisfactory quantitative description of the bound rubber effect.

REVIEW OF THE EXISTING BOUND RUBBER THEORIES

Kraus and Gruver

The first theoretical treatment of bound rubber was attempted by Villars.[2] His theory treats bound rubber as a gel of filler particles, the bonding material of which consists of longer polymer molecules. However, it was shown by Kraus and Gruver[3] that the Villars theory was unable to give a satisfactory description of their own data. Kraus and Gruver[3] themselves studied the dependence of filler-adsorbed polymer fraction on the molar mass M of narrow-distribution rubbers (BR, SBR) and used the empirical power law function, eq. (1) to describe their data:

$$B_K = KM^n. \tag{1}$$

Here, B_{KG} is the fraction of filler-bound polymer in the Kraus–Gruver theory (denoted by A in their pa-

per) and K and n are empirical parameters. The data were adequately described with $n = 0.5$. According to Kraus and Gruver, in a polydisperse polymer each polymer fraction may be assumed to contribute to bound rubber in proportion to its mass fraction $w(M)dM$ and to M^n:

$$B_{\mathrm{KG}} = \int_o^\infty KM^n w(M) \, dM. \qquad (2)$$

The molar mass distribution $w_U(M)$ of the free (filler-unbound) polymer (denoted as $w_f(M)$ in the original paper[3]) is then given by the equation

$$w_U(M) = (1 - B_{\mathrm{KG}})^{-1}(1 - KM^n)w(M). \qquad (3)$$

Kraus and Gruver tested eq. (3) and with $n = 0.5$ they found a good agreement between the predicted distributions of free rubber and those determined experimentally by the GPC method.

At this point it should be noted that the range of applicability of the empirical eq. (1) is in fact limited by the requirement that KM^n [$= (M/M_k)^n$] must not exceed unity. The parameter M_k ($= K^{-1/n}$) is the upper limit of M for which eq. (1) may be applied, and it is perhaps in line with Kraus and Gruver to assume that macromolecules larger than M_k will be completely adsorbed. With this additional assumption the Kraus and Gruver theory is reformulated as follows:

$$\text{for} \quad M \le M_k: \quad B_{\mathrm{KG}} = (M/M_k)^n \qquad (4a)$$

$$\text{for} \quad M > M_k: \quad B_{\mathrm{KG}} = 1 \qquad (4b)$$

$$B_{\mathrm{KG}} = \int_o^{M_k} \left(\frac{M}{M_k}\right)^n w(M) \, dM + \int_{M_k}^\infty w(M) \, dM \qquad (5)$$

$$\text{for} \quad M \le M_k: \quad w_U(M)$$
$$= (1 - B_{\mathrm{KG}})^{-1}(1 - (M/M_k)^n)w(M) \qquad (6a)$$

$$\text{for} \quad M > M_k: \quad w_U(M) = 0 \qquad (6b)$$

The Kraus and Gruver theory does not predict how K, n should depend on filler concentration c and on the filler specific surface area P. The value of M_k may be expected to decrease with increasing c, P, and the degree of polymer–filler interaction. If $n = 0.5$, then M_k is high. If, however, $n \ge 1$ (and the values of c, P are not too low), M_k may well lie within the usual range of molar masses present in polydisperse commercial polymers. This is illustrated by Figure 1, where the dependence of B_{KG} on M is plotted for three values of n.
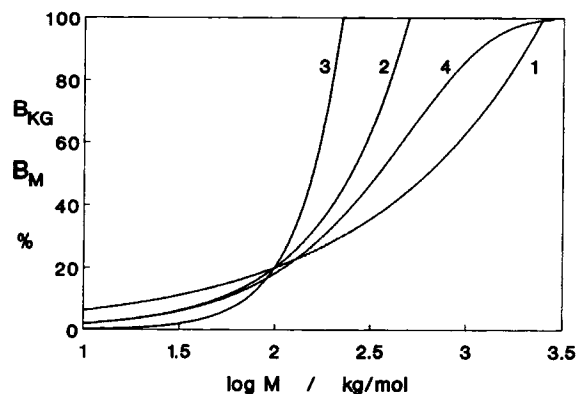

Figure 1 The B_{KG} and B_M vs. M dependence. B_{KG} calculated from eqs. (4a) and (4b). Curves: 1, $n = 0.5$; 2, $n = 1$; 3, $n = 2$; values of M_k chosen to give $B_{\mathrm{KG}} = 0.2$ for $M = 100$ kg/mol. B_M calculated from eq. (10), the same initial slope as in curve 2.

Pliskin and Tokita

For a soluble (gel-free) polymer the Pliskin and Tokita[4] equation for bound rubber may be derived by using simple arguments: Product of the filler concentration c (mass of filler/mass of polymer) and of the specific surface area P of the filler (filler surface area/mass of filler) gives the polymer–filler contact area per unit mass of polymer, AC. The mean thickness ΔR_o of the filler-bound polymer layer multiplied by AC gives the volume VB of filler-bound polymer per unit mass of polymer: $VB = \Delta R_o AC$ (layer thickness × layer area/mass of polymer). Mass of the filler-bound polymer per unit mass of total (initially gel-free) polymer is then given by

$$B_{\mathrm{PT}} = \rho_P \Delta R_o c P \qquad (7)$$

where B_{PT} is the fraction of filler-bound polymer in the Pliskin–Tokita theory and ρ_P is the polymer density. Pliskin and Tokita tested their equation experimentally, using an assumption (for which the theory does not give any proof) that ΔR_o is independent of c and, for fillers with the same surface activity, independent of P. If so, then B_{PT} should increase linearly with c, P. The Pliskin–Tokita theory does not consider the effect of M of the polymer.

Equation (7) has been used in the literature to calculate, from the experimental values of B, c, P, ρ_P, the mean thickness ΔR_o ($= B/\rho_P c P$) of the bound rubber layer. This value has often been taken as a characteristic of the degree of polymer–filler interaction. Values of the order of several nanometers were obtained for ΔR_o from the adsorption of hydrocarbon rubbers on furnace blacks.[4]

Meissner

The Meissner theory[5] treats the effect of bound rubber as random adsorption of structural units of polymer chains on reactive sites assumed to exist on the surface of filler particles. Because of the working method used, it may be called a statistical theory of filler-bound polymer. In this theory, the bound rubber fraction B_M is calculated as

$$B_M = 1 - \sum_{y=1}^{\infty} w_y (1 - q)^y. \qquad (8)$$

Here, y is the number of structural units per chain, w_y is the mass fraction of y-mer chains in the original distribution, q is the fraction of filler adsorbed structural units:

$$q = cPM_o/A_oN_A \qquad (9)$$

N_A is the Avogadro constant, M_o is the molar mass of the polymer structural unit and A_o is the filler surface area per one reactive site; A_o is the only adjustable parameter of the theory and is a characteristic of the degree of polymer–filler interaction. The size of the structural unit is considered to be small. The theory assumes that each structural unit has the same probability of reacting with reactive sites on the filler surface; polymer unit and filler reactive site are able to react only once; q is small. For a continuous distribution $w(y)$ eq. (9) may be changed to:

$$B_M = 1 - \int_o w(y) e^{-qy} \, dy. \qquad (10)$$

The chain-length distribution $w_{y,U}$ [or, $w_U(y)$] of the free (filler-unbound) polymer is given by the equations:

$$w_{y,U} = (1 - B_M)^{-1} w_y (1 - q)^y \qquad (11)$$

$$w_U(y) = (1 - B_M)^{-1} w(y) e^{-qy}, \qquad (12)$$

B_M being defined by eqs. (8) and (10). From eqs. (11) and (12) the molar mass averages (e.g., the mass-average $\bar{M}_{w,U}$) of the filler-unbound polymer can be calculated. Preferential adsorption of longer chains is predicted, in conformity with experimental observations.

Equations (8), (10), (11), and (12) may be solved numerically if the molar mass distribution of the original polymer is known. Such calculation was done[5] using the Kraus and Gruver data.[3] The mea-

sure of agreement between experimental and calculated molar mass distributions of free (filler-unbound) polymer was found to be satisfactory. The calculated A_o values ($50 - 120$ nm^2 for furnace blacks in BR, SBR,[5] NR,[6] and 10–100 nm^2 for surface-modified silica in MVQ[6]) are reasonable. The dependence of B on c, P was also satisfactorily predicted.[5]

The substitution of the Schulz–Zimm distribution into eq. (10), gives[5]

$$B_M = 1 - \frac{1}{(1 + \epsilon\gamma)^1} \qquad (13)$$

where $\epsilon = (1 - \bar{M}_n/\bar{M}_w)$ is the dispersion parameter of the original distribution and γ is the adsorption index, that is, the number of adsorbed structural units per mass-average original macromolecule:

$$\gamma = q\bar{M}_w/M_o = cP\bar{M}_w/A_oN_A. \qquad (14)$$

In a monodisperse polymer:

$$B_M = 1 - \exp(-\gamma) \qquad (15)$$

in a random distribution:

$$B_M = 1 - \frac{1}{(1 + \gamma/2)^2} \qquad (16)$$

in the Schulz–Zimm distribution with infinite $\bar{M}_w/\bar{M}_n$:

$$B_M = \gamma/(1 + \gamma). \qquad (17)$$

These equations may be used to describe experimental data also in a case where the effect on B of only one variable is known. For instance, from eq. (16) the dependence of B on c may be written with an adjustable parameter c_M as

$$B_M = 1 - \frac{1}{(1 + c/c_M)^2}.$$

The statistical theory of bound rubber predicts[5] that in the random distribution the mass average molar mass, $\bar{M}_{w,U}$ of the filler-unbound polymer should decrease with B in the following way:

$$\bar{M}_{w,U}/\bar{M}_w = (1 - B_M)^{1/2}, \qquad (18)$$

whereas in the Schulz–Zimm distribution with an infinite value of $\bar{M}_w/\bar{M}_n$ we have

$$\bar{M}_{w,U}/\bar{M}_w = 1 - B_M. \tag{19}$$

The statistical theory of bound rubber predicts— unlike the Pliskin–Tokita theory—a nonlinear dependence of B_M on c, P. At a constant degree of polymer–filler interaction A_o the predicted value of $B_M/\rho_P cP$ is not constant but increases with $\bar{M}_w$. At a given $\bar{M}_w$ it depends also on details of the molar mass distribution of the polymer. In a given distribution $B_M/\rho_P cP$ decreases with increasing c and/ or P.

The B_M vs. γ dependence is predicted to be more curved with increasing width of the molar mass distribution of the polymer. This effect is pronounced in the Wesslau logarithmic normal distribution (Fig. 2). In the Schulz–Zimm distribution it is much less significant and for high $\bar{M}_w/\bar{M}_n$ values a limiting B_M given by eq. (17) is approached.

The mass-average molar mass values $\bar{M}_{w,U}$ of the filler unbound polymer have also been calculated; their relative values $\bar{M}_{w,U}/\bar{M}_w$ are plotted vs. B_M in Figure 3. With increasing polydispersity they decrease steadily in the Wesslau distribution whereas in broad Schulz–Zimm distributions they approach a straight line with a negative unit slope given by eq. (19).

Cotten

Cotten[7] performed GPC measurements similar to those of Kraus and Gruver using black compounds
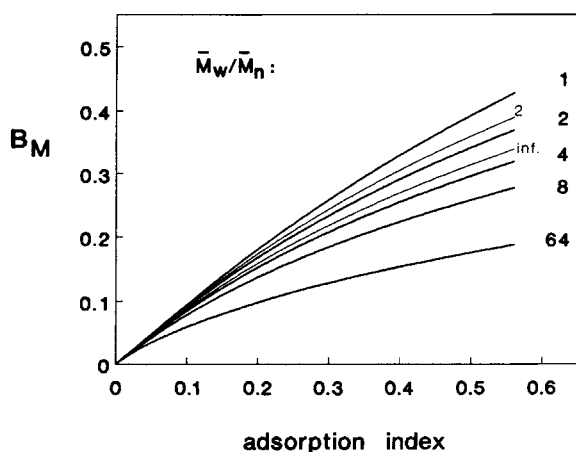
Figure 2 The B_M vs. γ dependence calculated from the statistical theory for the Wesslau distribution, eq. (10) (thick lines) and for the Schulz–Zimm distribution, eq. (13) (thin lines). $\bar{M}_w/\bar{M}_n$ values are indicated on the curves.
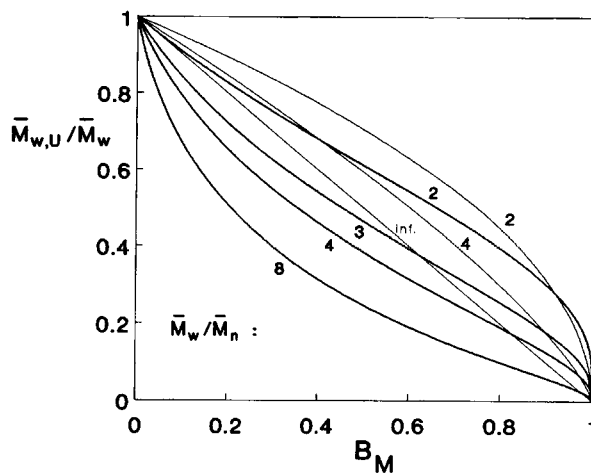
Figure 3 The $\bar{M}_{w,U}/\bar{M}_w$ vs. B_M dependence calculated from the statistical theory for the Wesslau distribution, eq. (12), (thick lines) and for the Schulz–Zimm distribution, eqs. (18) and (19) (thin lines). $\bar{M}_w/\bar{M}_n$ values indicated on the curves.

of SBR. He compared his data with the Kraus–Gruver eqs. (2) and (3) and came to a conclusion that a satisfactory description of the decrease in the viscosity average molar mass $\bar{M}_{v,U}$ of free rubber with increasing B, requires a higher value of the exponent n ($n = 1$) than that found by Kraus and Gruver ($n = 0.5$). He argues that $n = 1$ corresponds to the result of the Meissner theory: since q is small, $(1 - q)^y \simeq (1 - qy)$, and with this approximation the Meissner eqs. (8) and (10) should, in Cottens' opinion, reduce to the Kraus and Gruver eq. (2) with $n = 1$:

$$B_M \simeq 1 - \int_0^\infty w(y)(1 - qy)\, dy$$

$$= \int_0^\infty KMw(M)\, dM \tag{20}$$

where $K \simeq q/M_o$. However, as can be seen in Figure 4, the measure of agreement between the experimental molar mass distribution of the free (filler-unbound) polymer and the molar mass distribution calculated from the original distribution using the Kraus and Gruver eq. (2) with $n = 1$ can hardly be regarded as satisfactory. The experiment strongly deviates from the theoretical prediction in the range of both medium and high M. The value of M_k obtained (240 kg/mol) lies within the range of M contained in the distribution and the experiment does not conform to the expectation that all macromolecules larger than M_k should be attached to the filler.
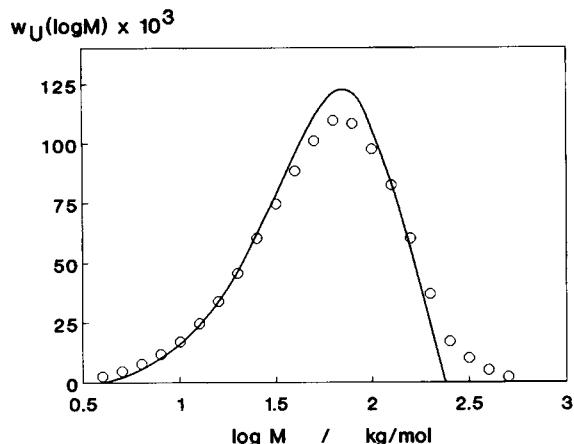
Figure 4 Molar mass distribution of free (filler-unbound) polymer, SBR/N-347 black. Points: experimental, Cotten.[7] Curve: calculated[7] from the Kraus and Gruver theory[3] for $n = 1$.

Second, $(1 - qy)$ is not a satisfactory approximation to the function $(1 - q)^y$. This can be readily calculated and is illustrated by Figure 1, where the result of the statistical theory for a monodisperse polymer is compared with the Kraus and Gruver curve for $n = 1$. For values of B higher than, say, 15%, approximation (20) becomes increasingly inaccurate, and in no case can the result of the statistical theory be satisfactorily approximated by the relation $B_M \simeq KM$.

Shiga

Shiga[8] has proposed that for branched polymer chains the concept of molar mass contained in the Meissner theory should be altered to molecular size: the molar mass M_{br} of the branched polymer should be reduced to that of the linear polymer, M_l, (using the mean square radii of gyration). Furthermore, according to Shiga, the Meissner theory should be modified to express a severer dependence of the bound rubber on molar mass than anticipated by the original theory. Instead of the Cotten value of $n = 1$, Shiga uses $n = 2$. From the Kraus and Gruver eq. (2) he then obtains:

$$B_{Sh} = \int_o^\infty KM_l^2 w(M_l)\, dM_l \qquad (21)$$

and arrives at

$$B_{Sh} = K\bar{M}_{l,z}\bar{M}_{l,w} \qquad (22)$$

where B_{Sh} is the bound rubber fraction according to the Shiga concept, the subscripts z, w denote the z-average and mass-average of the reduced molar mass M_l. Shiga[8] presents a plot to show that his bound rubber data obtained on linear and branched EPM and EPDM conform to eq. (22).

It is difficult to see why the mechanism of adsorption considered by the statistical theory should be substantially altered by a moderate degree of branching of polymer chains. One must admit, of course, that branched polymer units (and perhaps units adjacent to the branch) might differ from nonbranched units in their mobility and possibly in their adsorption capacity. However, with the fraction of branched units remaining small (the molar mass per branch does not decrease below ca. 30 kg/mol in Shiga EPDM samples[9]) the behavior of a large majority of units may be expected to remain unchanged, and the amount of bound rubber to be still determined by the same factors as in linear polymers. Second, Shiga does not give direct experimental evidence for his statement that $n = 2$. The only direct experimental determination of the exponent n (based on B vs. M measurements on narrow distribution polymers) published so far is that of Kraus and Gruver; they showed that n is beyond a doubt smaller than unity. The Cotten value of $n = 1$ is based on indirect evidence. Third, in view of what has been said above, the Shiga eq. (21) should be written in the form

$$B_{Sh} = \int_o^{M_k} (M_l/M_k)^2 w(M_l)\, dM_l + \int_{M_k} w(M_l)\, dM_l.$$

This relation does **not** lead to eq. (22) used by Shiga to describe his data. Thus, the theoretical basis of eq. (22) does not seem to be sufficiently sound.

EXPERIMENTAL TESTING OF THE THEORIES

B vs. $(cP\bar{M}_w)$

Kraus and Gruver[3] prepared three series of carbon black compounds based on narrow distribution polybutadienes. One of the three variables c, P, $\bar{M}_w$ was varied in each of the series while the other two were kept constant and were known. The compounds were prepared under the same conditions (avoiding degradation) and the data are thus well-suited for an experimental test of the statistical theory prediction according to which, in polymers having the same type of molar mass distribution and with fillers showing the same degree of surface activity, the

bound rubber fraction should be a unique function of the product $(cP\bar{M}_w)$ [eqs. (14–16)]. This prediction is tested in Figure 5. The numerical values of B, c, P, and $\bar{M}_w$ were obtained (with some inaccuracy) from the Kraus and Gruver figures 4 and 5 and used to calculate $(cP\bar{M}_w)$. In the molar mass series the last point deviated strongly from the correlation and was left out; on the other hand, the molar mass data on SBR taken from Kraus and Gruver figure 6 were included. The concentration series seems to be slightly shifted to lower B values but, on the whole, the correlation seems satisfactory. Theoretical curves calculated for uniform chains and for the Wesslau distribution with $\bar{M}_w/\bar{M}_n = 1.4$ are fitted to the data using the same value of $A_o = 112$ nm². It represents an averaged characteristic of the degree of polymer–filler interaction for all the as-mixed compounds of BR (and SBR) differing in $\bar{M}_w$ (50–410 kg/mol, with $\bar{M}_w/\bar{M}_n$ ranging between 1.2 and 1.44) and containing different amounts of furnace blacks (0–100 phr) having a specific surface area between 30 and 140 m²/g.

The Pliskin and Tokita equation has also been compared with this set of data. A straight line going through the origin was fitted to the B vs. (cP) dependence of the c and P series and from its slope the value of $\Delta R_o = 2.6 \pm 0.4$ nm was obtained. In the M-series the value of (cP) is constant but B is not and, as a result, the calculated ΔR_o values differ widely, ranging from 1 to 4.8 nm. This demonstrates the principal limitation of the Pliskin and Tokita equation that does not take into account the properties of the polymer (its MMD) and, as a result, the values of ΔR_o calculated from experimental
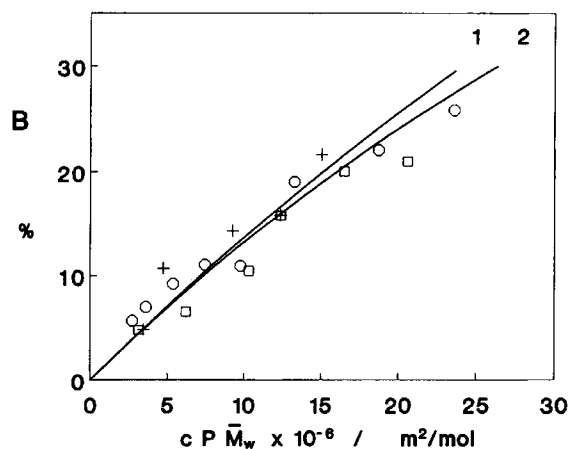

Figure 5 The dependence of B on $(cP\bar{M}_w)$. Points: Kraus and Gruver,[3] variable: M, circles; c, squares; P, crosses. Curves: B_M calculated from the statistical theory: 1, uniform chains; 2, Wesslau distribution, $\bar{M}_w = 1.4$
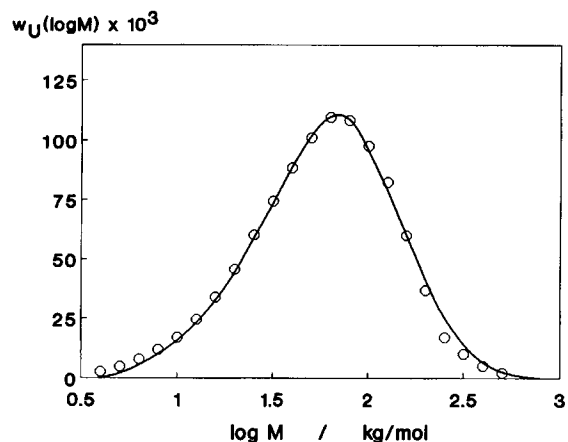

Figure 6 Data of Figure 4 (points) compared with the statistical theory eq. (12) (curve), $B = 0.503$, $M_m = 155.3$ kg/mol.

measurements can only be used to compare systems based on polymers with similar molar mass average and distribution.

Molar Mass Distribution of Filler-Unbound SBR

The Cotten distribution data shown in Figure 4 are compared with the statistical theory in Figure 6. The measure of agreement between the experimental and calculated distributions may be regarded as very good. The relevant eq. (12) has been used here in the form

$$w_U(\log M) = (1 - B_M)^{-1}w(\log M)\exp(-M/M_m)$$

$w(\log M)$ is the distribution of uncompounded polymer for which we used the GPC data obtained on masticated polymer. An assumption that on mastication of gum polymer a similar degree of polymer degradation occurs as in the compounding step in the Banbury mixer is probably only approximate. For the adjustable parameter M_m the value of 155.3 kg/mol was found to satisfy the condition $\Sigma w(\log M)\exp(-M/M_m) = 1 - B_M$, where B_M is given by the experimental value of B (=0.503). The compound contained 50 phr of N-347 black, $c = 0.5$, $P \simeq 92$ m²/g. Since $\bar{M}_w/M_m = cP\bar{M}_w/A_oN_A$, one obtains $A_o = cPM_m/N_A = 12$ nm². This rather low value of A_o indicates a high degree of polymer–black interaction in this compound that contains an unusually high amount of bound rubber.

$\bar{M}_{v,U}$ vs. B Correlation

From the knowledge of the molar mass distribution of the uncompounded (gum) SBR 1500 and using
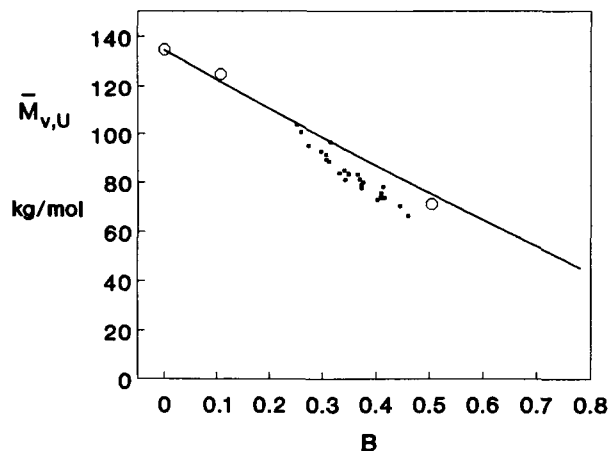
Figure 7 Experimental dependence of $\bar{M}_{v,U}$ on B (SBR 1500/N-347 black, Cotten[7]) compared with the statistical theory curve calculated from the MMD of masticated polymer [eq. (12)]. Exponent of the Mark–Houwink equation, $a = 0.715$.

the Kraus and Gruver equations, Cotten[7] calculated theoretical curves correlating the viscosity average molar mass $\bar{M}_{v,U}$ of filler-unbound polymer with the fraction of filler-bound polymer B. He found his experimental points to lie between the curves for $n = 1$ and $n = 2$ and ascribed the deviation from the curve for $n = 1$ to a small amount of polymer degradation.

An analogous calculation based on the statistical theory has been done in this study using the Cotten molar mass distribution data obtained on Banbury masticated SBR 1500. The calculated $\bar{M}_{v,U}$ vs. B correlation curve is shown in Figure 7. The Cotten data on two compounds given in his figures 4 and 5 are compared with our calculated values in Table I and plotted in Fig. 7 (circles). The differences between the experimental and calculated values of $\bar{M}_{v,U}$ appear to be insignificant. With further data (taken from Cotten table 1, compounds prepared in the

Banbury mixer; plotted as small squares in our Fig. 7) there is some downward deviation. However, if one takes into account that this type of plot is highly sensitive to the exact shape of MMD in the range of very high M and that the high shear conditions prevailing during the mixing step and resulting in an unknown degree of polymer degradation might not be exactly imitated by gum rubber mastication, a comparison of the statistical theory with the experiment shown in Figure 7 may probably still be regarded as a satisfactory agreement.

Adsorption on Filler of Branched Polymer Chains

The Shiga B values[8] obtained with compounds of gel-free branched broad distribution EPM and EPDM (samples Nos. 3, 7, 12–14) are plotted versus $\bar{M}_w$ in Figure 8. With use of the statistical theory eq. (8), the theoretical B_M vs. $\bar{M}_w$ curve 3 was calculated for an artificially constructed broad molar mass distribution with dispersion parameters imitating those of the EPDM sample No. 12. The curve was fitted to the five experimental points using the value of 3100 kg/mol for the adjustable parameter M_m. A good description of the data was obtained. The scatter of experimental points around the curve is of the same magnitude as that of the Kraus and Gruver data around curves 1 and 2. The Shiga com-
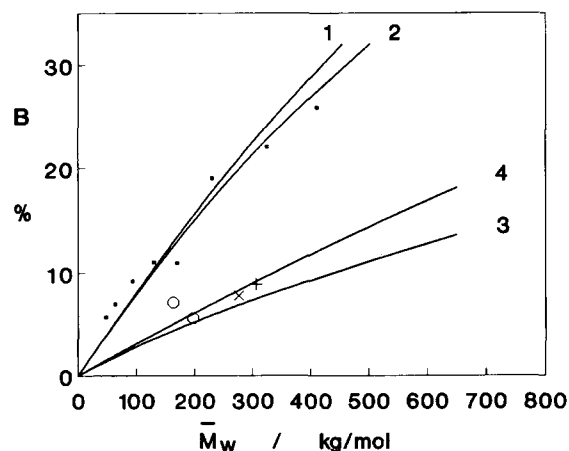
Table I   Experimental and Calculated Values of $\bar{M}_{v,U}$

	B (%)	Experimental $(\bar{M}_{v,U})$	Calculated (kg/mol)
N-347 black	50.3	71.0	75.4
Graphitized N-347 black	10.6	124.7	121.9
Gum polymer (masticated)	0	134.6	

Calculation from eq. (12).
Data Cotten,[7] SBR 1500/N-347 black.

Figure 8 Experimental dependence B vs. $\bar{M}_w$: crosses apply to broad-distribution branched EPDM (Shiga,[8] samples No. 7, 12–14) and irradiated EPM (No. 3); circles apply to linear EPM (Nos. 1 and 2). Curve 3: B_M calculated for a broad MMD using eq. (10); curve 4: B_M calculated for random distribution, the same M_m as for curve 3. For the sake of comparison the Kraus and Gruver data[3] on narrow-distribution BR, SBR are shown (small squares) together with the statistical theory curves: 1, uniform chains, 2, Wesslau distribution, $\bar{M}_w/\bar{M}_n = 1.4$.

pounds contained 80 phr of FEF black ($c = 0.8$, $P = 44$ m^2/g) and in the calculation of A_o the possible effect of the presence of processing oil (80 phr) on B was not considered. A rather large value of $A_o = 180$ nm^2 was obtained that indicates a smaller EPM, EPDM/furnace black interaction than that observed in as-mixed compounds of BR, SBR. Adsorption of oil on the carbon black surface, if it did occur, may have resulted in a decreased polymer-filler contact area, and thus, in a lower A_o value. However, information on this effect is lacking.

In Figure 8 the Shiga B values obtained on two samples of linear EPM with MMD close to random distribution (Nos. 1, 2, circles) are also plotted. The theoretical curve 4 was calculated for the random distribution using the same value of the adjustable parameter M_m as that used above for curve 3. The description of all data by statistical theory curves may be regarded as satisfactory.

Branched broad distribution EPDM samples Nos. 4 and 6 are not completely soluble and, therefore, their behavior cannot be predicted by the random adsorption model. One can only speculate that B values of gel-containing polymers are somewhat higher than those of gel-free polymers with comparable values of $\bar{M}_w$. This has indeed been observed (not shown here), with the difference amounting to 2.4 and 3.8%.

From the above discussion it can be concluded that the statistical theory of bound rubber in its original unmodified form gives a satisfactory description (with the same A_o value) of experimental data obtained on both narrow distribution linear EPM polymers and broad distribution branched EPM, EPDM polymers.

CONCLUSION

A critical examination of the existing theories of the adsorption of polymer on filler from bulk leads to a conclusion that the most complete explanation of available experimental data is offered by the random adsorption model suggested by the author. The theory based on it correctly predicts a change of MMD of the polymer with its adsorption on filler and satisfactorily describes the experimental dependence of B on c, P, and $\bar{M}_w$, in both narrow and very broad molar mass distributions. An analysis of experimental data did not reveal any distinct effect of a moderate degree of branching of EPM, EPDM chains on B. It is concluded that the Shiga modification of the random adsorption model is not warranted, neither theoretically nor experimentally. The degree of interaction between furnace black and EPM, EPDM polymer chains, as measured by the value of the adjustable parameter A_o, does not seem to depend on the presence of termonomer and on the degree of polydispersity of the polymer.

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