

## Theory of Bound Rubber

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### Synopsis

A theory of bound rubber formation has been developed which treats the effect as random adsorption of structural units of polymer on reactive sites which are assumed to exist on the surface of filler particles. Equations are derived for the fraction of bound rubber and for the molecular weight distribution of free (unbound) rubber. The theory contains only one adjustable parameter, the filler surface area per reactive site,  $A_0$ . It is shown for the case of the Schulz distribution that the amount of bound rubber depends but slightly on the dispersion parameter of the polymer and is determined essentially by the adsorption index  $\bar{M}_w cP/A_0N_A$ , where  $c$  is the filler concentration,  $P$  is its specific surface area, and  $N_A$  is the Avogadro number. All of the experimentally observed features of the bound rubber effect, including preferential adsorption of large molecules, are correctly predicted, the quantitative agreement of the theoretical equations with available experimental data being satisfactory. This supports the underlying assumption that the processes involved in the polymer-filler interaction may be approximated by a random-process model.

### INTRODUCTION

Partial insolubilization of polymer due to adsorption of macromolecules on carbon black and other reinforcing fillers from bulk is commonly known under the name bound rubber. The phenomenon of bound rubber has been extensively studied experimentally, and there are several reviews on this subject.<sup>1-4</sup> On the other hand, a satisfactory theoretical treatment of the effect is still lacking. Some time ago, a theory was developed by Villars<sup>5</sup> which treats bound rubber as a gel of filler particles, the bonding material of which consists of the longer polymer molecules. Recently, Kraus and Gruver<sup>6</sup> have tested this theory and found that it is impossible to satisfy the theoretical equations with their set of experimental data. They conclude that assumptions underlying the Villars theory do not represent the physical situation with sufficient accuracy for quantitative treatment.

From results on narrow-distribution polybutadienes, Kraus and Gruver<sup>6</sup> found a dependence of bound rubber on the square root of molecular weight and used this observation to calculate the molecular weight distribution of free (unbound) rubber. The predicted distributions of the free rubber were in good agreement with the observed distributions determined by the gel permeation chromatography.

In the present paper, a theory of bound rubber is developed which treats the effect as random adsorption of structural units of polymer on reactive sites which are assumed to exist on the filler surface. Equations are derived for the amount of bound rubber and for the molecular weight distribution of free rubber. Available experimental data are used to test the theory.

Bound rubber is commonly referred to as "carbon gel" whenever a coherent network of polymer and carbon black filler is formed. Conditions under which filler-bound polymer develops a three-dimensional gel-like structure will be examined theoretically in a next paper.

### BOUND RUBBER

The main features of bound rubber formation are assumed to be described by the following model.

1. Reactive sites exist on the filler particle surface. Each reactive site forms one bond with one structural unit of polymer.

2. The adsorption of macromolecules on the filler surface proceeds through random adsorption of their structural units on reactive sites on the filler surface whereby bonds are formed which are sufficiently permanent to resist the swelling action of the solvent.

3. Each structural unit has the same probability of reaction with reactive sites on filler surface. One unit may form only one bond to filler surface.

4. The fraction  $q$  of structural units which bear a bond to filler surface (i.e., the fraction of adsorbed units) is small.

Some of these assumptions are similar to those of Villars. There is one important difference. In the Villars theory, segments of polymer chains are adsorbed by the filler, the magnitude of the segment being an adjustable parameter. In the present theory, the magnitude of the segment is fixed and known; the segment is identified with a structural unit. The only adjustable parameter is  $A_0$  defined below.

The following symbols are used throughout the text:

$y$	number of structural units in a polymer chain
$w_y$	weight fraction of $y$ -mer polymer chains in the original molecular weight distribution of the polymer; for high molecular weight polymers, $w_y$ is replaced by $w(y) dy$ , the weight fraction of polymer having values of $y$ between $y$ and $y + dy$
$M_0$	molecular weight of structural unit
$\bar{y}_w, \bar{y}_n, \bar{M}_w, \bar{M}_n$	usual meaning
$c$	filler concentration (g/g of polymer)
$P$	specific surface area of filler (per unit weight)
$A_0$	surface area of filler per one reactive site
$1/A_0$	specific reactivity of the filler surface (number of reactive sites per unit surface area of filler)

$\frac{cP}{A_0 N_A}$  number of moles of reactive sites per unit weight of polymer, (number of moles of adsorbed structural units per unit weight of polymer), where  $N_A = 6.023 \times 10^{23}$  is the Avogadro number

$\frac{M_0 cP}{A_0 N_A} = q$  fraction of adsorbed structural units

$\frac{\bar{M}_w cP}{A_0 N_A} = \gamma$  "adsorption index," number of adsorbed structural units per primary weight average macromolecule, where  $\gamma = q\bar{y}_w$

$B$  bound rubber (or, bound polymer), the weight fraction of polymer adsorbed and insolubilized by the filler

$U$  free (unbound) polymer,  $U = 1 - B$

The calculation of  $U$  is done in the following way. The probability that a structural unit (selected at random) does not bear any bond to filler surface is  $(1 - q)$ . The probability that a  $y$ -mer macromolecule is not bound to filler is  $(1 - q)^y$ . The amount of free (unbound)  $y$ -mer chains is  $w_y (1 - q)^y$ , and the weight fraction of free polymer is obtained by summation.

$$U = \sum_{y=1}^{\infty} w_y (1 - q)^y \quad (1)$$

$$U = \int_0^{\infty} w(y) e^{-ay} dy \quad (2)$$

This general equation may now be solved for special distributions. For instance, in case of the Schulz distribution,

$$w(y) dy = \frac{b^{a+1}}{\Gamma(a+1)} y^a e^{-by} dy \quad (3)$$

where

$$b = \frac{a}{\bar{y}_n} = \frac{a+1}{\bar{y}_w}$$

eq. (2) changes to

$$\gamma \equiv \frac{\bar{M}_w cP}{A_0 N_A} = \frac{1}{\epsilon} \frac{1 - U^\epsilon}{U^\epsilon} \quad (4)$$

where

$$\epsilon = 1 - \frac{\bar{y}_n}{\bar{y}_w}$$

For monodisperse polymer chains ( $\epsilon = 0$ ) and for the random distribution ( $\epsilon = 1/2$ ), eq. (4) gives

$$\text{Monodisperse polymer} \quad \gamma = -\ln U \quad (5a)$$

$$\text{Random distribution} \quad \gamma = 2 \frac{1 - U^{1/2}}{U^{1/2}} \quad (5b)$$

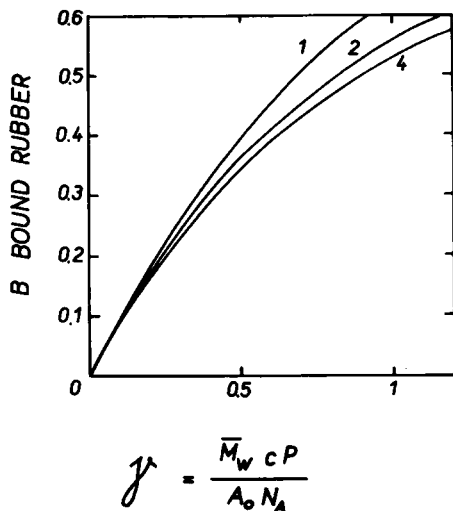


Fig. 1. Bound rubber as function of adsorption index for the Schulz distribution, according to eq. (4). Figures on curves indicate the dispersion parameter  $\bar{M}_w/\bar{M}_n$ .

The dependence of  $B$  on  $\gamma$  for Schulz-type polymers with three different values of the dispersion parameter is illustrated by Figure 1.

### MOLECULAR WEIGHT DISTRIBUTION OF FREE RUBBER

As shown above, the amount of free  $y$ -mer macromolecules is given by  $w_y (1 - q)^y$ . Normalization yields the weight fraction  $w_{y,U}$  of  $y$ -mer macromolecules in free rubber:

$$w_{y,U} = \frac{1}{U} w_y (1 - q)^y \quad (6)$$

where  $U$  is given by eq. (1). For high molecular weight polymers, the distribution  $w_U(y)dy$  of the free rubber is given by

$$w_U(y)dy = \frac{1}{U} w(y) e^{-ay} dy \quad (7)$$

$U$  being defined by eq. (2).

In the Schulz distribution, the weight and number-average values of  $y$  (denoted by  $\bar{y}_{w,U}$ ,  $\bar{y}_{n,U}$ ) of the free rubber are given by the following expressions:

$$\frac{\bar{y}_{w,U}}{\bar{y}_w} = U^\epsilon \quad \frac{\bar{y}_{n,U}}{\bar{y}_n} = U^\epsilon \quad (8)$$

### COMPARISON WITH EXPERIMENT

#### Dependence of $B$ on $c$

For an experimental test of the predicted dependence of  $B$  on  $c$ , our unpublished results have been used. They were obtained on the natural

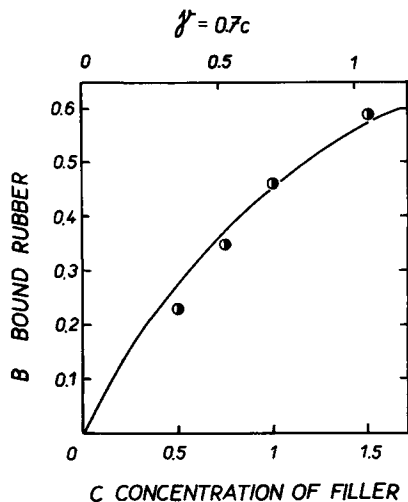


Fig. 2. Bound rubber as function of filler concentration. Points: experimental, natural rubber-HAF black system. Curve: theoretical, eq. (5b).

rubber-HAF black system. The molecular weight distribution of the rubber sample used (limiting viscosity number 1.96 dl/g in toluene at 25°C) was close to the random distribution.<sup>7</sup> The rubber-black compounds were heated for 1 hr at 145°C in the press before the bound rubber determination was done. The experimentally obtained dependence of  $B$  on  $c$  is compared with eq. (5b) in Figure 2. Best fit to data is obtained with use of the value  $\gamma/c = 0.7$ . Together with values of the remaining parameters ( $\bar{M}_w = 2.6 \times 10^5$ ,  $P = 85 \text{ m}^2/\text{g}$ ), this leads to

$$A_0 = 5.2 \times 10^3 \text{ \AA}^2 \quad \frac{10^4}{A_0} = 1.9 \text{ \AA}^{-2}.$$

#### Dependence of $B$ on $P$

An experimental dependence of  $B$  on  $P$  found for SBR 1500 containing various blacks at concentration  $c = 0.5$  (quoted by Kraus<sup>3</sup>) is compared with eq. (5b) in Figure 3. In the absence of more detailed information, the molecular weight distribution of the SBR sample is assumed to be close to the random one. Best fit of eq. (5b) to experiment is obtained using  $P/\gamma = 400 \text{ m}^2/\text{g}$ . Taking a reasonable value for  $\bar{M}_w$  ( $= 2.5 \times 10^5$ ), we get an estimate of  $A_0$ :

$$A_0 = 8.3 \times 10^3 \text{ \AA}^2 \quad \frac{10^4}{A_0} = 1.2 \text{ \AA}^{-2}.$$

#### Dependence of $B$ on $\bar{M}_w$

The Kraus and Gruver data<sup>6</sup> obtained on narrow distribution polybutadienes and SBR copolymers containing ISAF black ( $c = 0.5$ ) are plotted in

Figure 4. Bound rubber determination was done after the stocks were allowed to rest 24 hr at room temperature. The experimental dependence is compared with eq. (5a) and (5b), best fit being obtained with use of  $\bar{M}_w/\gamma = 12.5 \times 10^5$ . Taking  $P = 115 \text{ m}^2/\text{g}$ , we calculate  $A_0 = 12 \times 10^3 \text{ \AA}^2$ . After

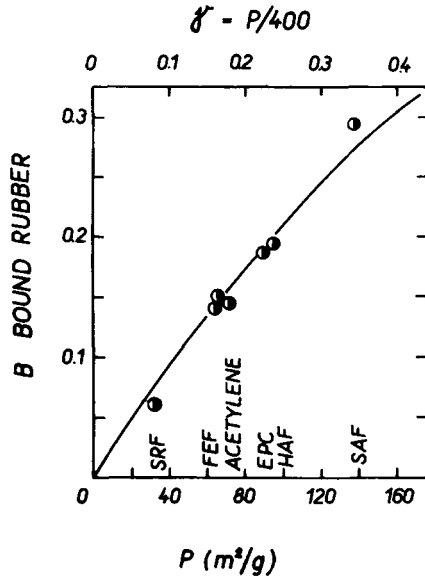


Fig. 3. Bound rubber as function of specific surface area of filler. Points: experimental,<sup>3</sup> for SBR 1500 in presence of 50 phr black. Curve: theoretical, eq. (5b).

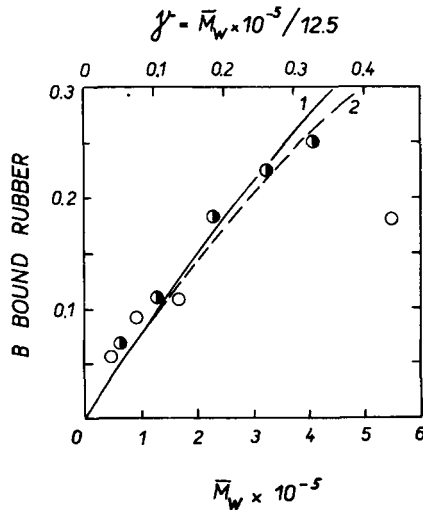


Fig. 4. Bound rubber as function of  $\bar{M}_w$  for narrow distribution polymers in presence of 50 phr ISAF black. Open circles: experimental,<sup>6</sup> polybutadienes. Full circles: experimental,<sup>6</sup> SBR compounds as mixed. Curve 1: theoretical, eq. (5a), for  $\bar{M}_w/\bar{M}_n = 1$ . Curve 2: eq. (5b), for  $\bar{M}_w/\bar{M}_n = 2$ .

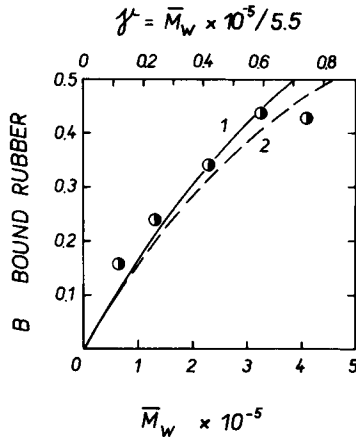


Fig. 5. Bound rubber as function of  $\bar{M}_w$ . Points: experimental,<sup>6</sup> for narrow distribution SBR-50 phr ISAF compounds, heat treated. Curve 1: theoretical, eq. (5a). Curve 2: eq. (5b).

heating the SBR-ISAF black compounds for 20 hr at 90°C, the amount of bound rubber has increased (Fig. 5). This results in a lower value of  $A_0$ :

$$A_0 = 5.2 \times 10^3 \text{ \AA}^2 \quad \frac{10^4}{A_0} = 1.9 \text{ \AA}^{-2}.$$

It is interesting to note that the specific surface reactivity  $1/A_0$  of furnace blacks found for the heat-treated SBR-ISAF system is comparable with that found above for the heat-treated natural rubber-HAF black system.

**Molecular Weight Distribution of Free Rubber**

In Figures 6 and 7, some of the Kraus and Gruver molecular weight distribution data obtained on SBR with use of the gel permeation chromatog-

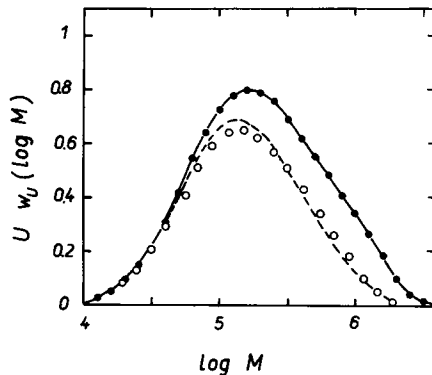


Fig. 6. Distribution of molecular weight for emulsion SBR.<sup>6</sup> Full circles: experimental distribution of the primary polymer (from GPC). Open circles: experimental distribution of free rubber in presence of 50 phr ISAF black (from GPC). Dashed line: theoretical, according to eq. (7),  $U = 0.748$ ,  $q/M_0 = 1.04 \times 10^{-6}$ .

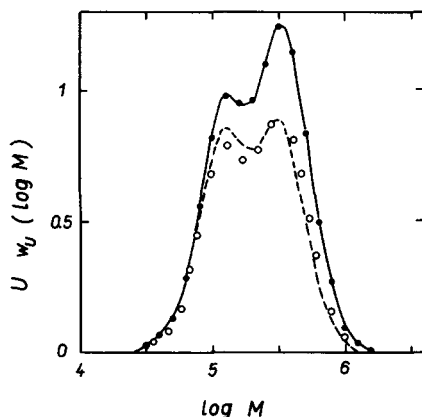


Fig. 7. Distribution of molecular weight for polymer  $T$ .<sup>6</sup> Full circles: experimental distribution of the primary polymer (from GPC). Open circles: experimental distribution of free rubber in presence of 50 phr ISAF black (from GPC). Dashed line: theoretical, according to eq. (7),  $U = 0.75$ ,  $q/M_0 = 1.07 \times 10^{-6}$ .

raphy technique<sup>6</sup> is reproduced. These data are used here to test the theoretical eq. (7).

Figure 6 shows the distribution of molecular weight of free rubber  $w_U(\log M)$  for an emulsion SBR in the presence of 50 phr ISAF black. It is plotted as  $U w_U(\log M)$  versus  $\log M$ . In the same picture, the primary molecular weight distribution of the polymer  $w(\log M)$  is also shown. Starting with the primary distribution data taken from Figure 6 and using the experimental value of bound rubber ( $B = 0.252$ ), we have calculated the value of  $q/M_0 = 1.04 \times 10^{-6}$  by numerical solution of eq. (2). Using the latter value, the molecular weight distribution of free rubber was then calculated from eq. (7) and is shown in Figure 6 as a dashed line. Molecular weight averages of the calculated distribution of free rubber,  $\bar{M}_{w,U}$  and  $\bar{M}_{n,U}$ , were also calculated. They are sufficiently close to those observed experimentally by Kraus and Gruver, as seen below:

	Experimental, Kraus and Gruver	Calculated
$\bar{M}_{w,U}$	247,000	234,000
$\bar{M}_{n,U}$	93,000	94,000

A similar comparison between the observed and calculated distribution of free rubber is shown in Figure 7 for the Kraus and Gruver polymer  $T$  (SBR-ISAF,  $c = 0.5$ ,  $B = 0.25$ ).

## DISCUSSION

The measure of agreement between the observed and theoretically predicted dependence of  $B$  on  $c$ ,  $P$  may be regarded as very good. The effect of molecular weight on bound rubber seems to be slightly overestimated by the present theory when comparison is made with the Kraus and Gruver re-



sults on polybutadienes (Fig. 4). For SBR, the agreement between theory and experiment is much better (Figs. 4 and 5), and also the calculated distributions of free rubber (Figs. 6 and 7) are seen to represent the observed distributions with a good success. The calculated molecular weight averages of free rubber agree remarkably well with the observed ones.

Reasonable values are obtained for the adjustable parameter  $A_0$ . Approximately one reactive site per  $10^4 \text{ \AA}^2$  of surface area calculated for furnace, channel, and acetylene blacks in NR, BR, SBR seems to be a plausible value. Heat treatment of the compound may increase the filler reactivity twofold. Much higher values of  $1/A_0$  are obtained for the system silicone rubber-Aerosil.<sup>8</sup> Compounds of this type when heat treated develop very high amounts of bound polymer (round 90%), and the estimates of  $10^4/A_0$  as high as  $10\text{--}20 \text{ \AA}^{-2}$  are then obtained.

### CONCLUSIONS

The presented theory of bound rubber which contains one adjustable parameter is shown to describe the available experimental data with sufficient accuracy. This may be taken as a support for the underlying assumption that the processes involved in polymer-filler interaction and leading to bound rubber formation may be satisfactorily approximated by a random-process model.

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