Rubber–Filler Interactions: Solution Adsorption Studies

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INTRODUCTION

The addition of certain fillers such as carbon black to rubber greatly improves many of its physical properties. Many of the early workers in the field, such as LeBlanc et al.,[1] noticed that the rubber was so tightly held by the black that milled samples containing more than a certain percentage of black would not disperse in benzene no matter how long the sample is left standing. The interactions between the rubber and the black take place at a slow rate, for if the samples are placed in benzene immediately after milling, they will disperse.[2,3] Even extracting the milled samples in Soxhlet extractors using benzene as the solvent does not remove all the rubber from the black.[4] Menadue[5] and others found that this insolubilizing power of the fillers is roughly in agreement with their reinforcing ability.

Studying the solution adsorption of GR-S by the graphitized black Graphon, Kolthoff and co-workers[6,7] found that the low molecular weight fractions are adsorbed first and then gradually replaced by the fractions of higher molecular weight. Golub[8] found that the low molecular weight fractions of GR-S are preferentially adsorbed by Graphon, and Poynton,[9] using a channel ink black as adsorbent, reports the same for natural rubber. When Golub[10] used different blacks, however, there was either no preferential adsorption or preferential adsorption of the high molecular weight material only. It is possible that in all cases the high molecular weights would be preferentially adsorbed, but that the lower molecular weights, being adsorbed faster, are found on the blacks when equilibrium has not been reached. Landler[11] noticed that the lower molecular weight fractions of rubbers are adsorbed first on a chromatographic column. In general, it is reported that the blacks containing the lesser amounts of chemisorbed oxygen (the furnace blacks) adsorb more rubber; and

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that removing the chemisorbed oxygen increases the adsorptive capacities.[3,6]

During milling, a large amount of rubber is irreversibly bound to the black, and only a small amount is physically adsorbed and removable by washing with fresh solvent.[3,12] Electron microscopy showed that, when milled samples were dissolved in benzene, the black had much rubber associated with it, but that the black was comparatively free of rubber after being simply added to a rubber solution.[13] As opposed to solution adsorption of the rubber, bound rubber values obtained during milling are reduced by removing the chemisorbed oxygen from the black.[14,15] In milling, the high molecular weight fractions are preferentially bound.[3,9,12,14]

It was early noticed that heating a rubber–black mix improves the physical properties of the final vulcanizate.[16,17] Gessler[18] found that the bound rubber content increases with continued heat treatment and postulates that heating causes strong carbon–polymer bonds to form. Edwards and Storey[19] also studied bound rubber formation during heat treatment. The more highly unsaturated the rubber, the greater is the effect of heat treatments.[20] Surface oxygen is necessary for heat treatment to be effective,[21] although sulfur, selenium, tellurium, or polynitroso compounds,[22] benzidine, urea, or thiourea[23] may take the place of the oxygen.

The above discussion, and also other work[24] [30] indicate that the carbon–rubber linkages are of two types: one a relatively weak, van der Waals-type attachment, and the other, a strong chemisorptive bond. The van der Waals or physical forces would be influenced by the steric conditions of the fillers[31,32] and by their surface. Much work has been done to increase this physical adsorption by making the fillers more compatible with, or wettable by, the rubber. Hauser[33] has discussed the general problem of organophilic clays. Kambara[34] found that the reinforcing ability of calcium carbonate is

greatly improved by treatment with a cation soap. Presumably, the polar end attaches itself to the filler surface; the nonpolar end, which is compatible with the nonpolar rubber, remains on the outside. Amines and glycols have been reported to have the same effect on other inorganic fillers.[35-38]

It is thus seen that the reinforcing ability of non-black fillers can be improved by making their surface more organophilic. It appears therefore that, where chemisorption does not take place, physical adsorption of the polymer on the filler surface may play a strong part in reinforcement. The nature of this physical adsorption has not been thoroughly investigated, and the purpose of this work is to study the solution adsorption of rubbers on fillers, to determine whether this adsorption is physical or chemical, to determine the effects of polymer molecular weights and unsaturation on this adsorption, and to try to work with such a system that extrapolation to rubber-black mixes in the absence of the solvent may be possible.

Choice of the Polymer and the Solvent

The most convenient elastomers to work with are the butyl rubbers and polyisobutylenes, as they are the least subject to oxidative degradation, and large relative variations in unsaturation can be obtained with but small absolute changes in the structure of the polymer. Benzene was chosen as the solvent because the so-called theta temperature of this system (the temperature at which the preference of the polymer segments for other polymer segments is nearly the same as for solvent molecules[39] and the polymer in solution behaves most closely to the bulk polymer), occurs[40] at 24°C. With other solvents, the theta temperature is either far from room temperature, or the viscosity-molecular weight relationships are not known.

EXPERIMENTAL

Materials

The butyl rubber used in this work was GR-I-25 obtained from the Reconstruction Finance Corporation, Office of Synthetic Rubber. This polyisobutylene–isoprene copolymer has about 3 wt.-% of its weight derived from the isoprene, and contains about 0.15% N-phenyl-2-naphthylamine as a stabilizer.[41] The polyisobutylenes used were Vistanex LM-H, B-60, B-100, and B-140, obtained from the Enjay Company, Inc., and also two experimental polymers, B-260 and B-150, which were

provided by the Standard Oil Development Company. The B-150 was specially prepared without a stabilizer, and was used to show that the stabilizer has no effect on the adsorption. The other polymers, with the exception of the low molecular weight LM-H, which also was not stabilized, contain about 0.1% of a stabilizer.[42]

The main filler used in this study was Cabot's Vulcan R (Vulcan 3, a high abrasion furnace black, in the unpelletized form). Also used were Cabot's Vulcan 3, Spheron 6 (a medium processing channel black), Elf 1 (an unpelletized channel ink black), and Columbia Chemical's Hi-Sil, a precipitated, hydrated silica. Mallinckrodt's reagent-grade benzene was the solvent. The materials were not dried before using.

Masterbatch Solutions

Three to four liters of masterbatch solutions of up to 2% concentration of the polymers were prepared in brown glass jars. In the preparation of these masterbatches, the higher molecular weight polymers were partially degraded. Once prepared, however, the solutions were stable; no changes in viscosity or concentration occurred on standing. The solutions were kept at or above 25°C. in order to prevent precipitation of the higher molecular weight fractions (24°C., the theta temperature, is the critical miscibility temperature for polymer of infinite molecular weight). The masterbatches used are listed in Table I.

TABLE I
Masterbatch Solutions

Master-batch	Polymer	Solvent	Polymer concn., g./100 ml.	Molecular weight[a]
MB 1	B-140	Benzene	0.758	1,050,000
MB 2a	B-140	Toluene	0.596	1,740,000[b]
MB 2b	B-140	Cyclohexane	0.762	—
MB 4	LM-H	Benzene	0.961	76,000
MB 5	B-150	Benzene	0.331	1,780,000[c]
MB 7	B-260	Benzene	0.486	3,270,000
MB 9	LM-H	Benzene	1.87	77,000
MB 10	B-100	Benzene	0.985	970,000
MB 11	B-100	Benzene	0.335	1,100,000
MB 12	B-100	Benzene	0.890	1,160,000
MB 14	B-260	Benzene	0.514	1,970,000
MB 15	GR-I-25	Benzene	1.029	278,000
MB 16	LM-H	Benzene	1.86	76,000

[a] Molecular weights determined from viscosities in benzene at 25°C. unless otherwise specified.

[b] Molecular weights determined in toluene at 30°C.

[c] Molecular weights determined in benzene at 30°C.

Adsorption

Masterbatch solution (100 or 200-ml. portions) was pipetted into 4- or 8-oz. narrow mouthed bottles into which from $1/4$ to 22 g. of the carbon black had already been introduced. When solutions more dilute than the masterbatch were desired, benzene was added to the bottles first. The bottles were then tied to the spokes of a wheel on a horizontal axis in a water thermostat maintained at 25.0°C., and the wheel was rotated at approximately 35 rpm. The high molecular weight B-260, reached equilibrium in about 9 hr., at which time no changes in concentration and viscosity took place on additional shaking. For the lower molecular weight polymers, 3 hr. was sufficient. After shaking, the bottles were allowed to rest in the water bath to allow the black to partially settle. The length of this resting time had no effect on the adsorption. The bottles were placed in a centrifuge kept at or above 25°C. (to prevent precipitation of the high molecular weights), and after centrifuging, the clear supernatant liquid was decanted off. No noticeable polymer sedimentation occurred during centrifuging, for the viscosities of the solutions at the tops and bottoms of the bottles were identical. Concentration and viscosity determinations were run on the supernatant liquid containing the unadsorbed polymer.

No degradation occurred in this procedure when pure masterbatch solution was agitated and centrifuged, and no changes occurred in the adsorption runs when agitation was continued for longer than normal periods of time. To show that true equilibrium had been reached, the method of approach to equilibrium was varied, and no changes in adsorption occurred. Thus it made no difference whether all the black was added at once or part was added in the middle of the run, whether all solution was added at the beginning of the run or part in the middle, or whether the solution was diluted before the run was begun, or some solvent was added in the middle of the run. Runs made at 25°C. with reagitation at 30°C., where less adsorption occurs, show that some of the polymer adsorbed at the lower temperature has come off the surface of the black.

Concentration Determinations

Concentrations measured were made gravimetrically, by evaporating off the solvent from known volumes of solution. The freeze-drying technique of Lewis and Mayo[43] was used, whereby the solvent is sublimed off from the frozen solution, and a porous structure is left behind from which the remaining solvent is quickly removed under vacuum at room temperature. The soft, low molecular weight LM-H did not attain this porous structure; instead, a film of polymer was left behind, which required over a month to reach constant weight.

Molecular Weight Determinations

Molecular weights were calculated by use of the relationship of Fox and Flory[44] that holds at 25°C.:

$$[\eta] = 8.3 \times 10^{-4} \bar{M}_v^{0.83} \qquad (1)$$

where $\bar{M}_v$ is the viscosity-average molecular weight, $[\eta]$ is the intrinsic viscosity (here taken as $[\eta] = (\ln n_r)/c$ at a relative viscosity n_r of 1.2), dl./g., n_r is the viscosity of the solution divided by the viscosity of the pure benzene, and c is the solution concentration in grams per 100 ml.

Rehner and Gray[45] state that unpublished data of Flory shows that this equation holds for butyl rubber as well as for polyisobutylene. Viscosities were measured in a series 50 Fenske viscometer at 25°C. with an efflux time for the pure benzene of about 190 sec. No kinetic energy corrections were made.

RESULTS AND DISCUSSION

Unless otherwise specified, the adsorbent is Vulcan R. It was found that the high molecular weights are preferentially adsorbed to a marked degree: the molecular weights of the unadsorbed polymer decreased rapidly with adsorption, as shown in Figures 1-4. The viscosity-average molecular weight $\bar{M}_v$ of the unadsorbed polymer divided by the initial viscosity-average molecular weight $\bar{M}_{v0}$ is plotted as a function of the fraction of polymer adsorbed. Raising the temperature to 75°C. did not affect this preferential adsorption. That the high molecular weight fractions are preferentially adsorbed was also shown when polymers of average molecular weight higher than that of the original material was washed or extracted off the black with cyclohexane (a better solvent than benzene) or benzene at temperatures above 25°C.

Although no molecular weight distribution curves were available for the polymers used here, it is possible to compare these experimental curves with the limiting curve for polymers with the most probable distribution:[39]

$$w_x = xp^{x-1}(1 - p)^2 \qquad (2)$$

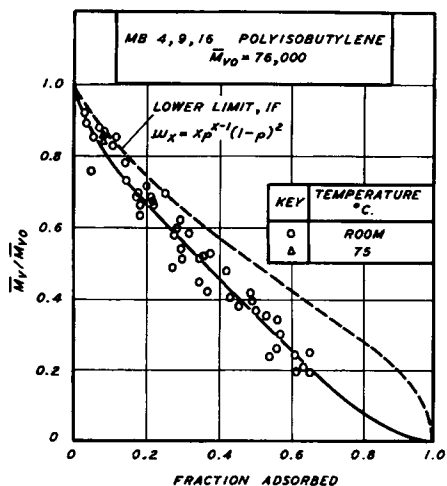Fig. 1. Molecular weight of unadsorbed polymer vs. fraction adsorbed.

Fig. 3. Molecular weight of unadsorbed polymer vs. fraction adsorbed.

where w_x is the weight fraction of polymer of degree of polymerization x, and p is a constant just under unity.

The viscosity-average molecular weight, found from the relation

$$[\eta] = K\bar{M}_v{}^a \qquad (3)$$

is related to the distribution function given in eq. (2) by:[46]

$$\bar{M}_v = \left[\sum_1^\infty w_x M_x \Big/ \sum_1^\infty w_x\right]^{1/a} \qquad (4)$$

where M_x, the molecular weight of polymer of degree of polymerization x, is equal to the product of the monomer molecular weight M_0 and the degree of polymerization x.
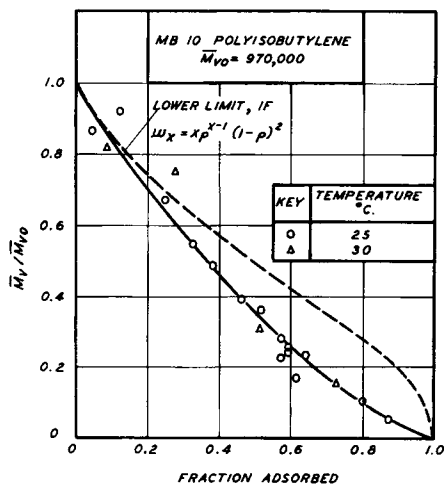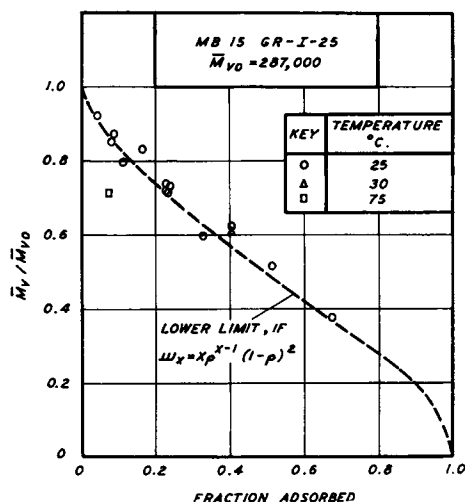
The limiting form of the curve of molecular weight versus fraction adsorbed occurs when all the material of one molecular weight is adsorbed before any of the next lower weight. If all polymer with a degree of polymerization greater than a critical degree of polymerization x_c is adsorbed, eq. (4) can be written

$$\bar{M}_v{}^a = M_0{}^a \sum_1^{x_c} x^{1+a} p^{x-1} (1-p)^2 \Big/ \sum_1^{x_c} x p^{x-1}(1-p)^2 \qquad (5)$$

The upper summation can be summed exactly only for $a = 1$, at which value the viscosity-average and weight-average molecular weights are identical. When $a \neq 1$, certain approximations must be

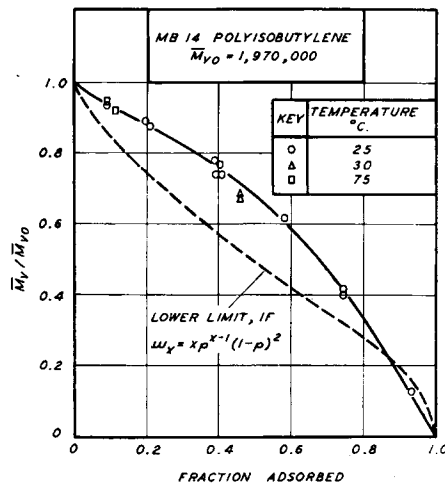Fig. 2. Molecular weight of unadsorbed polymer vs. fraction adsorbed.

Fig. 4. Molecular weight of unadsorbed polymer vs. fraction adsorbed.

made. First, the summations are replaced by integrations, and the lower indices are changed from one to zero (when $x = 0$, $w_x = 0$, and when $x = 1$, $w_x = (1 - p)^2$, which is very small). As p is very near unity (it will be shown that in our case it is always above 0.9986, its value for the low molecular weight LM-H), p^{x-1} is replaced by p_x. Also q is defined by

$$p \equiv e^{-q} \qquad (6)$$

so that $(1 - p)$ is very nearly equal to q; thus eq. (5) becomes

$$\bar{M}_v{}^a = \frac{M_0{}^a \int_0^{qx_c} (qx)^{1+a} e^{-qx} d(qx)}{q^a \int_0^{qx_c} (qx) e^{-qx} d(qx)} \qquad (7)$$

which yields, on integration,

$$\bar{M}_v{}^a = [M_0{}^a \Gamma_{qx_c} (2 + a)]/[q^a \Gamma_{qx_c} (2)] \qquad (8)$$

where Γ_{qx_c} is the incomplete gamma function to q_{xc}. When x_c becomes infinite, eq. (8) defines $\bar{M}_{v_0}$, the initial viscosity-average molecular weight. $\bar{M}_v / \bar{M}_v$ therefore is equal to

$$\bar{M}_v / \bar{M}_{v_0} = [\Gamma_{qx_c} (2 + a) \Gamma_\infty (2)$$
$$\div \Gamma_\infty (2 + a) \Gamma_{qx_c} (2)]^{1/a} \qquad (9)$$

The weight fraction adsorbed, A is given by

$$A = 1 - \sum_1^{x_c} w_x \qquad (10)$$

and becomes, when the above derivation is followed,

$$A = 1 - \Gamma_{qx_c} (2) \qquad (11)$$

Thus eqs. (9) and (11) give the limiting form for the curve of $\bar{M}_v / \bar{M}_{v_0}$ versus A. It should be noted that this curve is independent of the molecular weight of the initial polymer (expressed as p or q), as the parameter qx_c is the only variable, and causes both A and $\bar{M}_v / \bar{M}_{v_0}$ to vary from zero to one. The curve is a function only of the constant a, and for viscosities determined in benzene at 25°C., a is 0.53.[44] The curves of $\bar{M}_v / \bar{M}_{v_0}$ versus A, found by use of tabulated values of the incomplete gamma function,[47] are plotted alongside the experimental data in Figures 1–4.

These curves show that for the low molecular weight LM-H (Fig. 1) and for the polyisobutylene in MB10 (Fig. 2), more low molecular weight polymer is present than given by eq. (2), the most probable distribution. The experimental curve for the butyl rubber (Fig. 3) is identical with the limiting curve, showing that if all the high molecular weight polymer is adsorbed first, then the butyl

rubber has the most probable distribution. By the same reasoning, the polymer in MB14 (Fig. 4) appears to have more high molecular weight material than would be indicated by the most probable distribution. These curves also suggest that it is highly probable that the black does indeed adsorb essentially all of one molecular weight fraction before adsorbing the next lower fraction. As most of this work was carried out near the theta temperature of this rubber–benzene system, it can be expected that this strong preferential adsorption of the higher molecular weights by the black will also take place in the bulk rubber.

Calculated Molecular Weight Distribution Curves

If all the material at one molecular weight is adsorbed before that of the next lower weight, then from the experimental data discussed above, molecular weight distribution curves can be calculated. First the average molecular weight of the increments adsorbed by the addition of a small amount of black is found as a funtion of the fraction already adsorbed. Then, assuming that all the higher molecular weight material is adsorbed first, the distribution curve is easily built up.

Then, eq. (4), which relates the viscosity-average molecular weight to the distribution function, may be written as

$$\bar{M}_v{}^a = \sum_x W_x M_x{}^a / W \qquad (12)$$

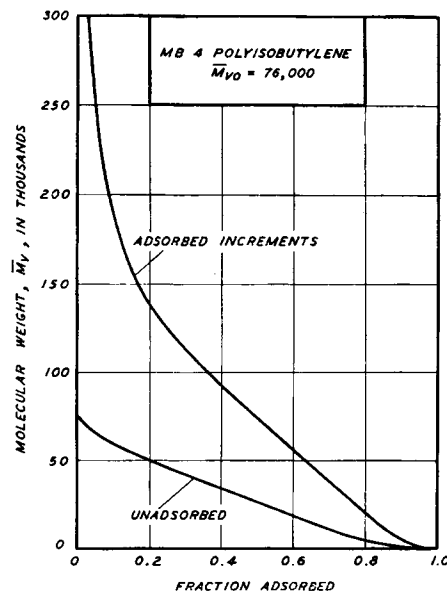where W_x is the total weight of x-mer present in

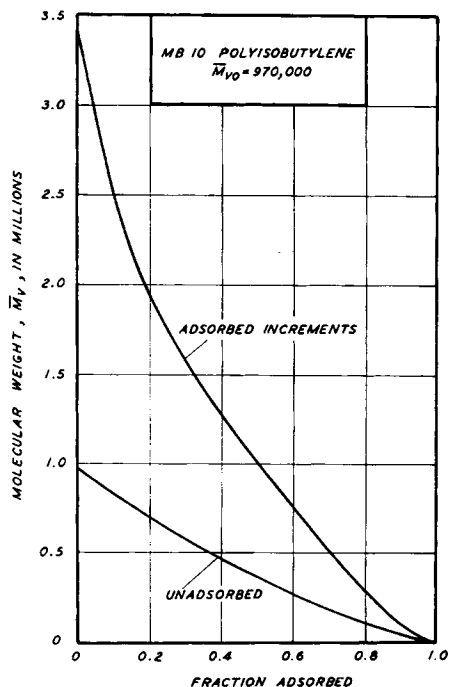Fig. 5. Molecular weight of polymer incrementally adsorbed.

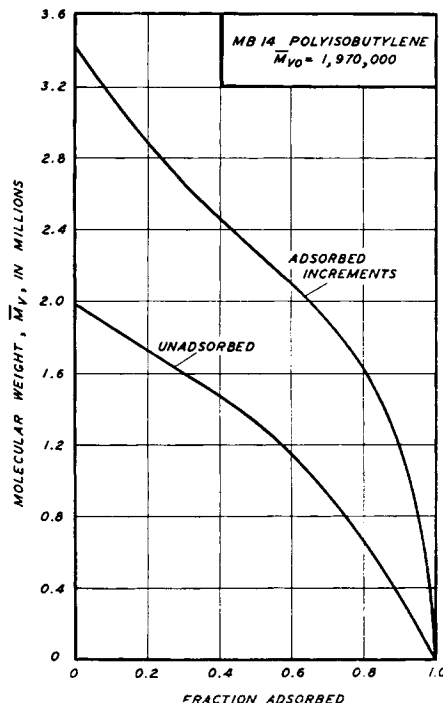Fig. 6. Molecular weight of polymer incrementally adsorbed.

Fig. 7. Molecular weight of polymer incrementally adsorbed.

solution, and W is the total weight of unadsorbed polymer.

Differentiating with respect to W to find the changes when a small amount of polymer is removed, we have

$$d\bar{M}_v{}^a/dW = (1/W)\ (d \sum_x W_x M_x{}^a/dW)$$
$$- (\sum_x W_x M_x{}^a/W^2) \quad (13)$$

Introducing eq. (12) and rearranging, we obtain

$$W(d\bar{M}_v{}^a)/dW) + \bar{M}_v{}^a = \sum_x M_x{}^a\ (dW_x/dW) \quad (14)$$

The term on the right-hand side is the viscosity-average molecular weight of the small amount dW of adsorbed material raised to the ath power, or $\bar{M}_{v_a}{}^a$. If there were originally present W_0 grams of polymer,

$$W = W_0(1 - A) \quad (15)$$

and

$$dW = -W_0 dA \quad (16)$$

and therefore

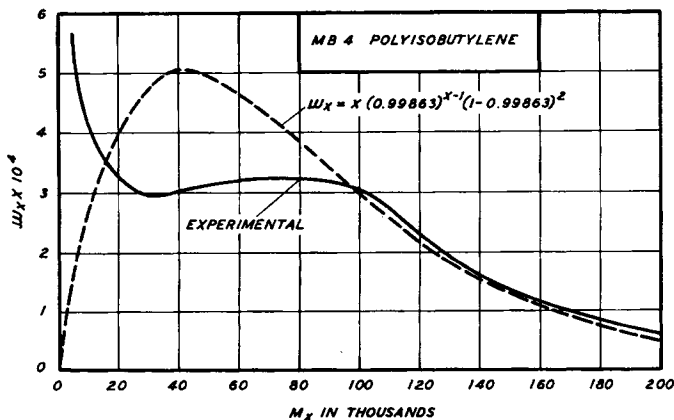$$\bar{M}_{v_a}{}^a = \bar{M}_v{}^a - (1 - A)(d\bar{M}_v{}^a/dA) \quad (17)$$

Fig. 8. Molecular weight distribution (w_x is the weight fraction of polymer of molecular weight M_x).
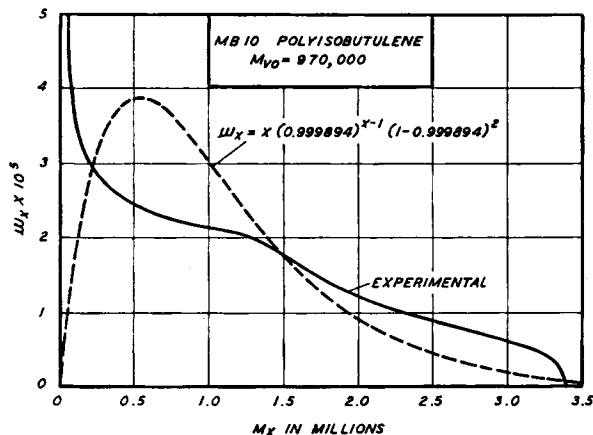
Fig. 9. Molecular weight distribution (w_x is the weight fraction of polymer of molecular weight M_x).

The viscosity-average molecular weight of the polymer incrementally adsorbed, found from eq. (17), is shown in Figures 5–7. It was not calculated in the case of the butyl rubber, for from Figure 3 it is known that the butyl rubber would follow the most probable distribution curve.

The assumption now made is that all the higher molecular weight materials are adsorbed first. The true distribution curves are then easily found from these curves, and are plotted in Figures 8–10. The sharp cutoff at high molecular weights of MB14 shown in Figure 10 is caused by the degradation by mechanical work of the very high molecular weight species during preparation of the masterbatch, to the extent that the average molecular weight was almost halved (compare MB7 and MB14, Table I). The most probable distribution curves are plotted in these same figures, with the constant p in eq. (2) so chosen that the viscosity-average
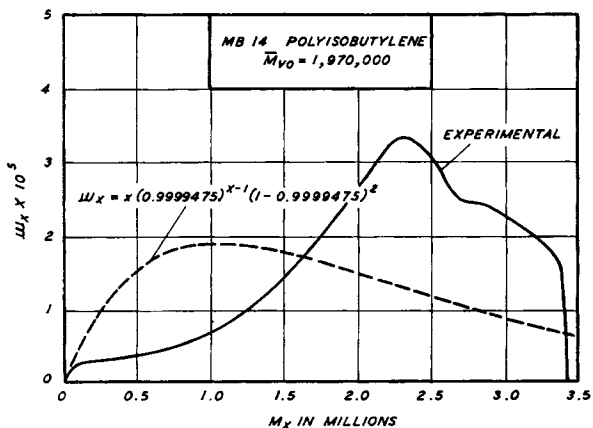
molecular weight would be correct. By substitution of $1 - p$ for q in eq. (8) and use of the value 56.1 for the monomer molecular weight M_0, and since, for the polymer as a whole, $qx_c = \infty$, we obtain for p

$$p = 1 - (104/\bar{M}_{v_0}) \qquad (18)$$

Adsorption Curves

Adsorption curves for the GR-I-25 and the B-260 in MB14 are shown in Figures 11 and 12. It is
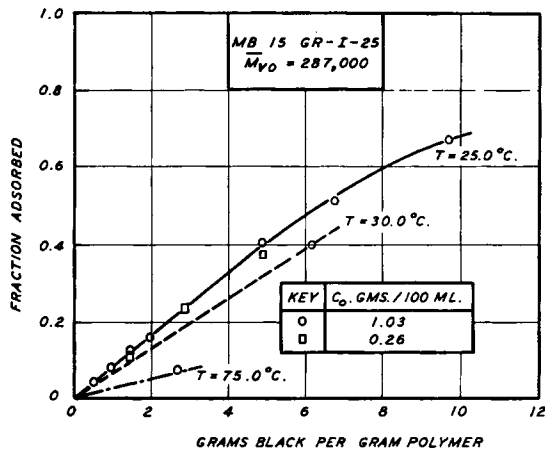
Fig. 11. Fraction adsorbed vs. amount of black.

seen that initially the fraction adsorbed is essentially proportional to the amount of black present, but tends to level off as more black is added. The data of Figure 11 are replotted in Figure 13 as B, the grams adsorbed per gram of black, versus the final concentration. This curve should not be confused with a normal adsorption isotherm, for here a heterogeneous polymer is being adsorbed, and, as shown above, the molecular weight of the unad-

Fig. 10. Molecular weight distribution (w_x is the weight fraction of polymer of molecular weight M_x).

Fig. 12. Fraction adsorbed vs. amount of black.

Fig. 13. Adsorption isotherm.

Fig. 15. Effect of molecular weight on adsorption at 25.0°C.

sorbed polymer changes during adsorption, so that different species are adsorbed throughout the run. A true adsorption isotherm could be drawn only if the same polymer were being considere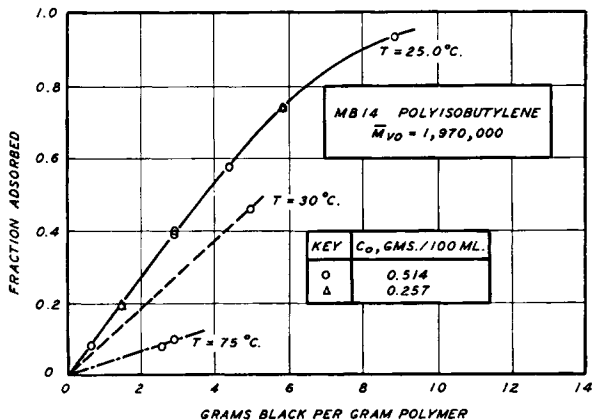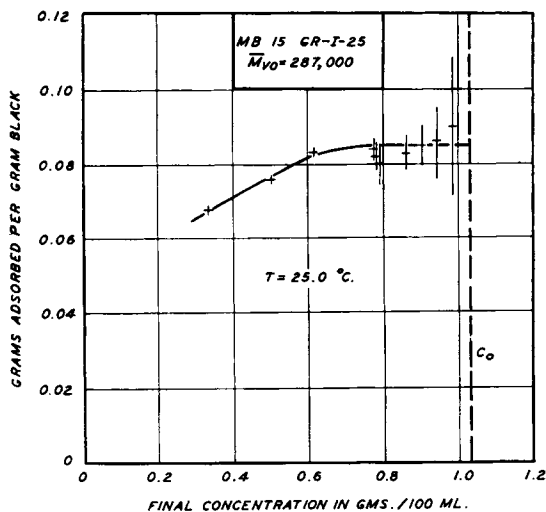d throughout. For example, if different initial concentrations were used, the adsorptions should be compared when the same fraction had been adsorbed. For the LM-H in MB16 an isotherm has been constructed for the case when 20% has been adsorbed, with the unadsorbed polymer having a molecular weight of 49,000. Both Langmuir and Freundlich isotherms were fitted to the four points obtained, as shown in Figure 14.
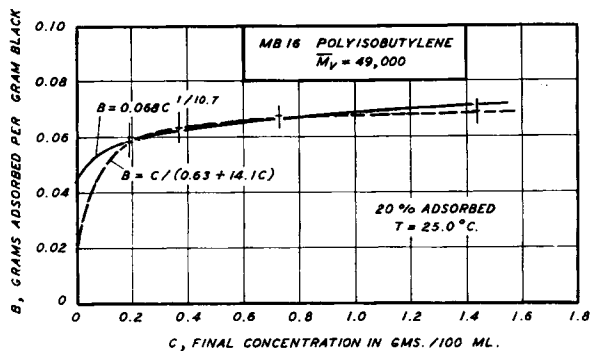
Fig. 14. Adsorption isotherm.

Effect of Molecular Weight

The effect of molecular weight on adsorption is shown in Figure 15. It is seen that the adsorption on a weight basis increases with molecular weight, but that the molecular weight has but a small effect above about 500,000. As the polymers studied here have a wide molecular weight distribution, the curve

in Figure 15 is just indicative, and cannot be used to predict exactly the adsorption of polymers with different distributions.

In the adsorption curves (Figs. 11 and 12), it was seen that the fraction adsorbed varied linearly with the amount of black added up to about four parts of black per initial weight polymer. Because the higher molecular weights are preferentially adsorbed, the molecular weight of the unadsorbed polymer decreases as more black is added. Therefore, if much more high molecular weight polymer is adsorbed than low molecular weight polymer, the adsorption curves should be immediately concave downward, and not linear.

Effect of Temperature

In several runs in which the temperature was increased to 30 and 75°C. the adsorption decreased,

Fig. 16. Effect of temperature of adsorption.

TABLE II
Effect of Concentration on Adsorption on Vulcan R Black at 25.0°C.

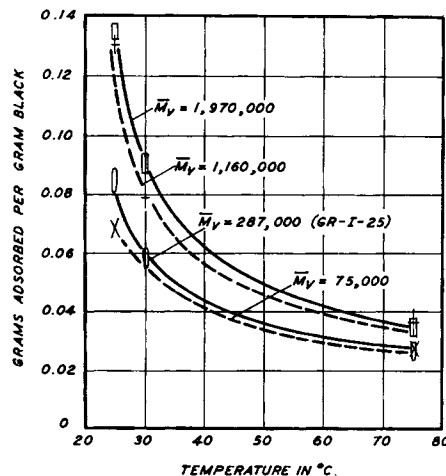| Masterbatch	Run	Initial polymer concn., g./100 ml.	Amt. black, g./g. polymer	Polymer adsorbed, g./g. black	$\bar{M}_v$ of remaining polymer
MB12	—	0.889	—	—	1,160,000 ± 4%
	1	0.889	1.70	0.125 ± 0.005	840,000 ± 4%
	2	0.444	1.70	0.133 ± 0.005	900,000 ± 4%
	3	0.222	1.70	0.130 ± 0.005	800,000 ± 6%
	4	0.889	3.43	0.127 ± 0.002	535,000 ± 5%
	5	0.444	3.43	0.125 ± 0.002	532,000 ± 5%
	6	0.222	3.43	0.120 ± 0.004	580,000 ± 6%
	7	0.889	5.67	0.115 ± 0.001	275,000 ± 6%
	8	0.444	5.67	0.112 ± 0.001	283,000 ± 7%
	9	0.222	5.67	0.110 ± 0.001	300,000 ± 11%
MB14	—	0.514	—	—	1,980,000 ± 5%
	9	0.514	1.46	0.134 ± 0.010	1,760,000 ± 5%
	10	0.257	1.46	0.137 ± 0.006	1,750,000 ± 6%
	12	0.514	5.82	0.127 ± 0.003	790,000 ± 11%
	13	0.257	5.82	0.127 ± 0.002	830,000 ± 13%
MB15	—	1.029	—	—	287,000 ± 4%
	9	1.029	1.46	0.085 ± 0.006	246,000 ± 4%
	10	0.257	1.46	0.077 ± 0.007	230,000 ± 5%
	5	1.029	2.91	0.084 ± 0.003	215,000 ± 4%
	6	0.257	2.91	0.081 ± 0.002	205,000 ± 6%
	12	1.029	4.87	0.083 ± 0.002	184,000 ± 3%
	13	0.257	4.87	0.076 ± 0.001	172,000 ± 9%
MB16	—	1.862	—	—	74,000 ± 5%
	1	1.862	3.23	0.069 ± 0.005	49,200 ± 4%
	2	0.931	3.23	0.067 ± 0.005	49,000 ± 4%
	3	0.466	3.23	0.063 ± 0.006	48,800 ± 8%
	4	0.233	3.23	0.058 ± 0.007	48,900 ± 12%

as shown in Figure 16. It is seen that the higher molecular weight polymers are more affected by temperature changes than are the lower molecular weight polymers. This is probably so because the critical miscibility temperature where precipitation occurs is higher for the larger molecules; thus the adsorption values for the higher molecular weights have to rise faster as the temperature is lowered than do those for the lower molecular weights.

Effect of Solution Concentration

The effect of the initial polymer concentration c_0 in solution on the adsorption is given for several sets of runs in Table II, and is partially indicated in Figures 11, 12, and 14. With the higher molecular weight polymer in MB14, there appears to be no effect at all, while for the lower molecular weight polymers the adsorption per unit weight of black increases with concentration. If decreasing the concentration reduces the adsorption per unit weight of black, then the adsorption curves should be concave downward from the origin, for the poly-mer concentration decreases as more polymer is adsorbed. This is not the case with the higher molecular weight polymers for which, within the experimental error, the fraction adsorbed is initially proportional to the amount of black. With the low molecular weight polymer, there could be a slight downward curvature from the origin.

In order to determine whether the apparent lack of effect of concentration extends down into the very low concentration regions, an attempt was made to wash or extract the adsorbed polymer off the black. In each washing run, the black was reagitated several times with fresh benzene. From Table III, it appears that very little polymer was washed off by the benzene in Runs 10-33 and 10-34, where the initial molecular weight was 970,000, for the amount remaining on the black is still high. On the other hand, in Runs 9-21 and 9-23 with the low molecular weight LM-H, a small amount is washed off as the solution concentration drops to about 0.06 g./100 ml. Amounts remaining after these runs and their corresponding comparison Runs 9-22 and 9-24

TABLE III
Removal of Polymer Adsorbed on Vulcan R by Washing with 100 ml. Benzene at 25.0°C.

Master-batch	Run	Initial polymer[a] concn., g./100 ml.	Black, g./g. polymer	Washing No.	Wt. Polymer removed in washing,[b] g.	Polymer remaining on black, g./g. black	$\bar{M}_{v_0}$
MB10	—	1.129	—	—	—	—	970,000
	33	1.129	3.18	1	0.547	0.162	
				2	0.082	0.139	
				3	0.031	0.131	
				4	0.014	0.127	
	34	1.129	6.14	1	0.250	0.126	
				2	0.082	0.115	
				3	0.036	0.109	
				4	0.021	0.107	
MB9	—	1.886	—	—	—	—	77,000
	21	1.886	5.25	1	0.863	0.103	
				2	0.291	0.074	
				3	0.123	0.062	
				4	0.056	0.055	
	23	1.886	2.88	1	1.208	0.125	
				2	0.268	0.076	
				3	0.080	0.061	
				4	0.029	0.057	
	22[c]	1.886	5.25	—	—	0.064 ± 0.003	
	24[c]	1.886	2.88	—	—	0.071 ± 0.006	

[a] This is also the total weight of polymer, as 100 ml. of solution were used.
[b] This is also the concentration, as the solutions were diluted to 100 ml.
[c] Comparison runs.

TABLE IV
Removal of Polymer Adsorbed on Vulcan R by Extractions with Benzene at 25.0°C.[a]

Masterbatch	Run	Black concn., g./g. polymer	Extraction No.	Time, days	Polymer extracted, g.	Polymer on black, %	Polymer on black, g./g. black	Polymer concn., g./100 ml.	$\bar{M}_v$
MB16	—	—	—	—	—	—	—	0.928	74,000
	13	3.35	1	27	0.443	4.5	0.0135 ± 0.005	0.212	
			2	9	0.015	1.3	0.004 ± 0.005	0.009	
MB15	—	—	—	—	—	—	—	1.031	293,000
	27	3.03	1	27	0.448	13.0	0.043 ± 0.005	0.167	
			2	9	0.008	11.4	0.038 ± 0.005	0.005	
MB12	—	—	—	—	—	—	—	0.898	1,160,000
	19	3.40	1	27	0.346	22.9	0.068 ± 0.005	0.149	
			2	9	0.009	20.9	0.062 ± 0.005	0.006	
MB14	—	—	—	—	—	—	—	0.521	1,950,000
	26	3.14	1	27	0.195	25.0	0.080 ± 0.005	0.101	
			2	9	0.005	23.1	0.073 ± 0.005	0.005	

[a] Fritted glass thimbles in extraction apparatus; 50 ml. of masterbatch solutions used.

were 0.064 and 0.055 g./g. black and 0.071 and 0.057 g./g. black, respectively.

Soxhlet extractors, jacketed with water at 25°C. and operated under a vacuum such that the condensate temperature also was 25°C., were used in the extraction runs. In order to prevent bypassing of the black by the solvent, fritted glass thimbles, extended to increase the hydrostatic head, were used. Cellite 503, a coarse filter aid, was laid down on the fritted glass, and more Cellite was mixed with the black (before agitation) to increase the flow rate of benzene through the thimble. Cellite

TABLE V
Adsorption by Other Fillers and from Other Solvents at 25.0°C.

Filler	Masterbatch	Run	Initial Polymer Concn., g./100 ml.	Amt. filler, g./g. polymer	Polymer adsorbed, g./g. filler	$\ln \eta_r$ Initial	$\ln \eta_r$ Final
Hi-Sil	MB 4	HS-4	0.939	4.44	—	0.311 ± 2%	0.311 ± 2%
	MB 14	HS-3	0.514	5.11	—	0.954 ± 2%	0.970 ± 2%
	MB 15	HS-1	1.029	4.44	—	0.670 ± 2%	0.699 ± 2%
Cellite 503	MB 16	12[b]	0.928	11.0	—	0.293 ± 2%	0.297 ± 2%
	MB 12	18[b]	0.898	12.4	—	1.225 ± 1.5%	1.232 ± 1.5%
	MB 14	25[b]	0.521	21.9	—	0.932 ± 2%	0.942 ± 2%
	MB 15	26[b]	1.031	10.7	—	0.675 ± 1.5%	0.673 ± 1.5%
Spheron 6	MB 16	10	0.918	2.94	0.005 ± 0.007	0.296 ± 2%	0.285 ± 1%
	MB 12	16	0.891	2.82	0.004 ± 0.004	1.216 ± 1.5%	1.197 ± 1.2%
	MB 14	23	0.517	2.82	0.005 + 0.004	0.934 ± 2%	0.918 ± 2.5%
	MB 15	24	1.029	2.64	0.007 ± 0.004	0.666 ± 1.5%	0.654 ± 1.5%
Elf 1	MB 16	11	0.928	1.78	(−0.003 ± 0.0012)	0.293 ± 2%	0.298 ± 2%
	MB 12	17	0.898	1.84	(−0.017 ± 0.006)	1.225 ± 1.5%	1.263 ± 1.5%
	MB 14	24	0.521	1.68	(−0.008 + 0.007)	0.932 ± 2%	0.937 ± 2%
	MB 15	25	1.031	1.48	(−0.014 ± 0.007)	0.675 ± 1.5%	0.677 ± 1.5%
	MB 1	3[a,b]	0.758	5.3	(−0.005 ± 0.004)	—	—
Vulcan 3	MB 1	1[a,b]	0.758	5.3	0.095 ± 0.003	—	—
	MB 1	5[a,b]	0.758	5.2	0.100 ± 0.003	—	—
	MB 1	6[a,b]	0.758	5.3	0.111 ± 0.003	—	—
Vulcan 3	MB 2a[c]	1[a,b]	0.596	6.4	0.000 ± 0.002	—	—
	MB 2a[c]	4[a,b]	0.596	6.8	0.006 ± 0.003	—	—
	MB 2a[c]	5[a,b]	0.596	7.4	0.005 ± 0.002	—	—
Elf 1	MB 2a[c]	2[a,b]	0.596	6.7	(−0.010 ± 0.003)	—	—
Vulcan 3	MB 2b[d]	1[a,b]	0.762	5.7	0.026 ± 0.003	—	—

[a] Agitated in high-speed shaker at room temperature.
[b] Only 50 ml. solutions used rather than 100 ml.
[c] Toluene is the solvent.
[d] Cyclohexane is the solvent.

does not adsorb any polymer, as shown in Table V. After extracting for one month's time, almost all of the low molecular weight polyisobutylene was removed, but increasing amounts of the higher molecular weight polymers remained (Table IV). Extracting for another week removed a little more polymer, indicating that the adsorption equilibrium is concentration sensitive, but that the adsorption isotherm, plotted as grams adsorbed per gram of black versus concentration, rises very rapidly for the higher molecular weight polymers and then levels off. From these extraction runs, it appears that the adsorption of polyisobutylene and butyl rubber is essentially physical in nature.

Effect of Unsaturation

In every effect investigated, such as those of molecular weight (Fig. 15), temperature (Fig. 16), and concentration (Table II), and also in the extraction runs (Table IV), behavior of the butyl rubber was appropriate for its molecular weight,

indicating that unsaturation of this type and magnitude has no effect. The unsaturation of this GR-I-25 is reported as 1.88 mole-% or 1.88 double bonds per 100 polyisobutylene and isoprene units.[2c] Rough ozonalyses in our work indicated an unsaturation of about 1.5 mole-% for the butyl rubber and about 0.3 mole-% for the Vistanex B-100. Rehner[48] previously reported unsaturation values of 0.07 mole-% for polyisobutylenes fractionated to remove the low molecular weight ends. This indicates either that the value found here is high, or, most likely, that the low molecular weight fractions have most of the unsaturation. In any case, it is seen that a change in unsaturation of several hundred per cent does not affect the adsorption.

Effect of Type of Black

The adsorption by the channel blacks Elf 1 and Spheron 6 is negligible (see Table V), while the furnace blacks Vulcan 3 and Vulcan R adsorb appreciable quantities of polymer. The poor adsorp-

tion by the MPC black Spheron 6 cannot be attributed to its being in pelletized form, for the channel black Elf 1 was not pelletized and still showed no adsorption, and the pelletized Vulcan 3 adsorbed about as much polymer as Vulcan R, its unpelletized form. As these channel blacks have larger surface areas than Vulcan R or Vulcan 3,[49] the differences in adsorptive capacities must be attributed to the surface characteristics.

The furnace blacks contain much less chemisorbed oxygen than do the channel blacks. The organic, low polarity polyisobutylene and butyl rubber undoubtedly prefer the less polar furnace blacks to the more polar, more highly oxygenated channel blacks. The water adsorbed on these fillers undoubtedly increases the polarity differences, for dried channel black will adsorb butyl rubber.[50] As mentioned in the Introduction, other investigators[3,6] had previously found that as the chemisorbed oxygen was removed from the surface of the blacks, solution adsorption of GR-S increased. It should be noted here that neither the polar inorganic filler Hi-Sil nor the polar filler aid Cellite 503 adsorb any polymer (Table V).

Effect of the Solvent

The adsorption of the B-140 by Vulcan 3 from toluene solution was very much less than that from benzene solution, and that from cyclohexane solution was almost negligible (Table V). That more is adsorbed from the poorer solvent (here benzene is the poorest solvent, cyclohexane being the best of the three) was noticed by Kolthoff and Gutmacher[6] in their work with GR-S. It is not surprising, for in a better solvent the attractions for the polymer by the solvent molecules is greater than a poor solvent, and so the attraction by the adsorbent is effectively reduced.

Effect of Banbury Mixing

In order to determine how the filler behaves when mixed into the rubber rather than being added to a rubber solution, samples of rubber-filler mixes prepared on a laboratory Size B Banbury mixer were allowed to rest several weeks at room temperature and then portions were dispersed in 100 ml. of benzene to give approximately 1% solutions. The polymers used here were GR-I-25 and Vistanex B-60, and the fillers, about 40 parts per 100 parts rubber, were Hi-Sil, Vulcan 3, and Spheron 6. The samples were treated as previously described, but the black did not settle even after five days standing. Centrifuging did not clear the solution, although some black did settle from the polyisobutylene solutions. The blacks were finally filtered out under pressure, but filtrate from the GR-I-25–Spheron 6 mix could not be cleared of all the black, even with several passes through the filter.

Table VI, summarizing the mixing studies, shows that the HAF black Vulcan 3 adsorbs about as much polymer as it does when added to a polymer solution (see also Table II, which lists the adsorption by Vulcan R, the fluffy form of Vulcan 3). The adsorption by the inorganic Hi-Sil is greater during mixing than during ordinary solution work, where no adsorption was detected. However, the precision of these results is low, and allowance must be made for the large errors. The channel

TABLE VI
Adsorption in Banbury-Mixed Samples[a]

| Filler | Polymer | Filler, g./g. polymer | Mixing history[b] | | | Polymer concn., (g./100 ml.) | | Polymer absorbed, g./g. filler | $\bar{M}_v$ of unadsorbed polymer |
			Break-down time, min.	Mixing time, min.	Max. temp., °F.	Initial[c]	Final		
Hi-Sil	GR-I-25	0.419	0	45	315	1.028	0.997	0.072 ± 0.023	200,000
Hi-Sil	B-60	0.424	20	75	—	1.023	1.003	0.048 ± 0.023	92,000
Vulcan 3	GR-I-25	0.402	0	30	292	1.031	0.996	0.084 ± 0.023	220,000
Vulcan 3	B-60	0.403	20	75	347	1.031	0.999	0.077 ± 0.023	260,000
Spheron 6	GR-I-25	0.407	0	30	308	1.025	0.868	0.376 ± 0.023	185,000
Spheron 6	B-60	0.402	20	75	354	1.029	0.958	0.169 ± 0.023	390,000
—	GR-I-25	0	10	0	191	—	—	—	289,000[b]
—	B-60	0	20	0	322	—	—	—	536,000[b]

[a] Batches (1400 g.) mixed in Banbury mixer; samples dispersed in benzene by shaking 18 hr. at 25.0°C.

[b] Results of Davies (ref. 53).

[c] All polymer assumed to be completely dissolved.

black Spheron 6, which adsorbed very little polymer when added to polymer solutions, adsorbed a great deal of polymer during mixing, and the adsorption of the unsaturated GR-I-25 was about twice as high as that of the Vistanex B-60.

The high adsorption on the Spheron 6 is probably due to chemical bonding between the oxygenated surface of the channel black and the unsaturated bonds of the polymer, as discussed earlier in the Introduction. The high temperatures (here about 300°F.) developed during mixing are probably necessary for this reaction to take place. Adsorption on the furnace black is not appreciably affected by mixing, because there is very little oxygen on the surface of this black. The greater adsorption of the butyl rubber on Spheron 6 is due to the higher unsaturation of the butyl rubber. The polyisobutylene, however, apparently has enough unsaturation to also bond chemically to this black.

The molecular weights of the unadsorbed polymer are not very significant, as degradation takes place during mixing, and probably takes place to different degrees with the different polymers. The low molecular weight of the B-60 after adsorption by the Hi-Sil may be due to degradation by exposure to light, as this sample, after shaking, was kept partly out of the water bath before separation of the filler, while the others were kept submerged.

It may be concluded that mixing has no apparent effect on the physical adsorption of the rubber on the fillers. It is apparently only in chemisorption that mixing (and the high temperatures generated during mixing) plays an important role.

Thickness of the Adsorbed Polymer Layer

If the carbon black particles are assumed to be well dispersed, so that all the surface is exposed to the polymer, and if the density ρ of the adsorbed polymer is assumed equal to its bulk density, then the thickness h of the adsorbed layer can be easily calculated. The bulk density of polyisobutylene

TABLE VII
Thickness of Adsorbed Polymer Layers

Polymer	Master-batch	$\bar{M}_{v_0}$	Polymer adsorbed, g./g. black	Thickness of adsorbed layer, A.
LM-H	MB9	77,000	0.069	10
GR-I-25	MB15	287,000	0.083	12
B-100	MB12	1,160,000	0.130	18
B-260	MB14	1,970,000	0.136	19

and butyl rubber is 0.91 g./cm.³, and the surface area S of Vulcan R black is 71 m.²/g. by iodine adsorption measurements.[51] The thickness of the adsorbed layers would then be up to 19 A., as shown in Table VII. The listed values are probably minimum thicknesses because of the likelihood of incomplete dispersion of the black aggregates, and because the density of the adsorbed polymer is probably less than its bulk density, for it is believed that segments of the adsorbed molecules extend into solution. As the total width of a polyisobutylene molecule is about 6 A., the adsorbed layer is thicker than the width of one molecule.

In the two mixing studies on the MPC black, the adsorbed layers are much thicker than those on the HAF black. The Spheron 6 has a surface area of about 106 m.²/g.

For the B-60, with 0.17 g./g. black, the thickness is 18 A., and for the GR-I-25, with 0.38 g. adsorbed/g. of black, the thickness is 39 A. For comparison, the thickness of the adsorbed GR-S layer on black in xylene solutions has been estimated by Amborski and Goldfinger[52] as 150–200 A. GR-S is more highly unsaturated than butyl rubber, however, and so more chemical adsorption could have taken place.

Physical Tests

In a related study Davies[53] obtained creep curves on unvulcanized rubber–filler mixes, and from the data on creep at 10 min., constructed a series of pseudo-strain curves. These curves provide some useful information on rubber-filler interactions and so will be discussed in some detail.

The rubbers used were GR-I-25 and Vistanex B-60, and the fillers were Vulcan 3, Spheron 6, and Hi-Sil. The fillers were mixed into the polymer in a Banbury at low speed. The Vistanex B-60, being of higher molecular weight than the butyl rubber (536,000 as opposed to 287,000), was given 20 min. of premastication before the filler was added. One kilogram of polymer was used with about 400 g. of filler, the actual weight of filler added being found from the weight of the polymer before and after the filler was added. The mixing history is given in Table VI. Next, 100-g. samples were then banded on a standard 6 × 12-in. laboratory mill, and molded for 10 min. at 250°F. under 500 psi pressure. Tensile specimens were cut with the grain by use of a 1-in. wide die and creep curves were run at 72°F. under low loads (less than 10 psi), a cathetometer being used to measure the separation of the inch marks. From these creep
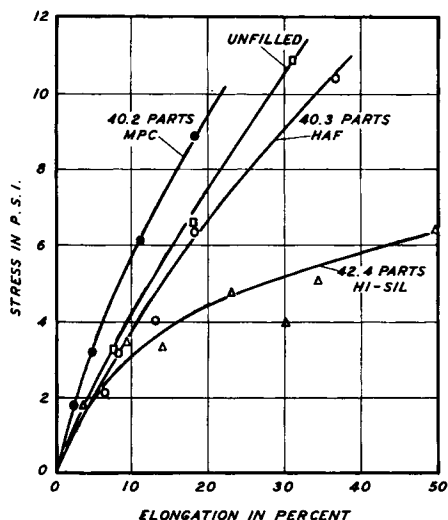
Fig. 17. Pseudo stress–strain curves (after 10 min.) for poly-
isobutylene (Vistanex B-60).

curves, plots of stress versus strain after 10 min.
creep were prepared as shown in Figures 17 and 18.

These pseudo-stress–strain curves show firstly
that mixes with the MPC black Spheron 6 are
stiffer than mixes with approximately equal load-
ings of the HAF black Vulcan 3. By electron
microscope measurements, the surface area of
Spheron 6 is 106 m.^{2}/g., while that of the Vulcan 3
is 89 m.^{2}/g., and the Vulcan 3 has a higher struc-
ture than the Spheron 6.[49] As the high structure is
associated with a high modulus, the stiffness of the
Spheron 6-loaded stocks should be attributed to
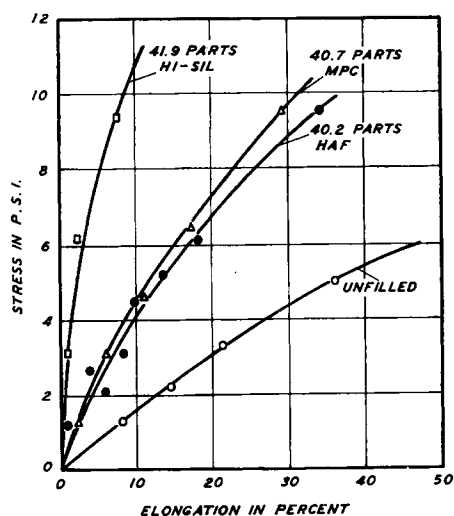either its higher surface area or higher surface oxy-

Fig. 18. Pseudo stress–strain curves (after 10 min.) for butyl
rubber (GR-I-25).

gen content. Zapp and Guth[54] have shown that
the increase in the internal energy contributions of
rubber to stress or modulus, as compared to the
pure gum vulcanizate, correlated well with the total
surface of the black added to the rubber, when both
channel and furnace blacks were used. (The en-
tropy contributions were a function of the volume
of black added only.) However, Gessler and
Ford[18] showed that the sulfur used for vulcaniza-
tion can take the place of oxygen on the surface of
the black. Therefore in an unvulcanized rubber–
black mix, not only the surface area but also the
surface complexes may play a part in the stiffness
of the batch at a given loading.

Comparisons between the polyisobutylene sam-
ples and the butyl samples are difficult to make, due
to the different molecular weights of the two ma-
terials. It is interesting to note, however, that the
modulus of the softer butyl rubber is increased by
the addition of the blacks, while the modulus
of the stiffer polyisobutylene is increased by
Spheron 6 and reduced by Vulcan 3. Now the
stiffness of these unvulcanized materials is due to
their viscosity, and this, in turn, depends on the
secondary valence forces between the particles.
In the lower molecular weight butyl rubber, the
main effect is most likely due to the hydrodynamic
action of the black particles, i.e., the polymer does
not flow at the surface of the particles. With the
longer polyisobutylene molecules, the reduction
in the intermolecular attractive forces due to in-
creased separation of the polymer molecules by the
black particles may more than offset the normal
stiffening action. As the cohesive forces are more or
less directly proportional to the molecular weight
of the polymer, this separating action would be
more important with the higher molecular weight
polymers.

The surface area effect of the blacks on the
modulus may be due to surface adsorption of the
polymer, thereby increasing the effective volume of
the black and its hydrodynamic action.

The greater increase in the stiffness of the butyl
rubber by Hi-Sil as compared to the blacks is
probably due to its irregular shape. As shown by
Guth,[55] irregularly shaped particles cause a larger
increase in stiffness than do spherical particles.
On the other hand, the modulus of the Hi-Sil loaded
polyisobutylene stock is lower than that of the black
loaded stocks. One possible explanation is that in
this particular case the polymer was greatly de-
graded in the mill, but this is not too likely. It is
more probable that in the polyisobutylene, the Hi-

Sil reduces the secondary valence forces, as mentioned above, but that there is flow of polymer on the surface of the filler due to nonwetting of the surface by the polymer. Butyl rubber has unsaturated groups and is therefore slightly more polar than polyisobutylene. Accordingly, butyl rubber would more likely wet the highly polar silica. This wetting could not be too great, however, or the polyisobutylene would be at least partly stiffened by the Hi-Sil. There is other evidence for the poor wetting of Hi-Sil by butyl rubber; Smith[56] reports that butyl rubber accepts only a very low loading of Hi-Sil, compared to other fillers.

CONCLUSIONS

1. For the equilibrium adsorption of polyisobutylene and butyl rubber from benzene solution by a high abrasion furnace black, the adsorption is essentially physical in nature. The high molecular weight species are preferentially adsorbed to such an extent that apparently reliable molecular weight distribution curves can be obtained from these simple equilibrium adsorption measurements. The adsorption decreases with temperature and, on a weight basis, increases with the molecular weight of the polymer. However, at high molecular weights, above about 500,000, the effect of molecular weight is small. Variation of solution concentration in the range 0.25–1% has essentially no effect on the adsorption of the higher molecular weight (above 1,000,000) polymers. On the other hand, increasing the solution concentrations increases the adsorption of the lower molecular weight materials. Also, unsaturation of the polymer up to 1.88 mole-% has no noticeable effect on the adsorption.

2. Equilibrium adsorption by the more polar, oxygenated, undried channel blacks or the highly polar, inorganic Hi-Sil is negligible.

3. The behavior of the polymers in benzene solutions as studied here should be similar to their behavior in the bulk rubber at the same temperature, for the temperature used (25°C.) is near the so-called theta temperature (24°C.) at which the polymer in solution and in the bulk form should act in nearly the same manner.

4. Adsorption from good solvents (cyclohexane, toluene) is less than from poor solvents (benzene).

5. Adsorption values for the furnace black and the Hi-Sil after Banbury mixing and subsequent dissolution in benzene are approximately the same as during solution adsorption. For the medium processing channel black, however, adsorption

values are much higher, especially with the more unsaturated butyl rubber as opposed to the almost saturated polyisobutylene. This indicates that chemical adsorption has taken place between the unsaturated rubber molecule and the surface of the MPC black.

6. Stiffening of a polymer by a filler is dependent on its surface area or surface condition, in addition to its volume.

7. A high molecular weight polymer can be softened by the introduction of a filler. It appears that the increased separation of the molecules reduces the intermolecular forces of attraction, and this reduction may more than counteract the normal stiffening action of the filler.

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Synopsis

To help explain the mechanism of rubber reinforcement, studies of equilibrium adsorption from benzene solution of several polyisobutylenes and of a butyl rubber onto a high abrasive furnace black and other fillers were made. The adsorption is essentially physical in nature. On a weight basis, it decreases with increasing temperature in the range 25–75° C., is unaffected by unsaturation of the polymer, and increases with concentration in the range 0.25–1% for the lower molecular weight polymers and with increasing molecular weight (but above about 500,000 the effect is small). Adsorption of the higher molecular weight polymers is unaffected by concentration. Adsorption by the more polar, oxygenated channel blacks or by the highly polar, inorganic Hi-Sil is negligible. The higher molecular weight species are preferentially adsorbed to such an extent that apparently reliable molecular weight distribution curves can be obtained from these simple equilibrium experiments. Milling studies show that a high molecular weight polymer can be softened by a filler.

Résumé

En vue d'expliquer le mécanisme de renforcement du caoutchouc des études de l'équilibre d'absorption ont été faites sur plusieurs polyisobutènes et un caoutchouc butylique en solution benzénique à l'égard d'un noir à abrasion élevée et à l'égard d'autres charges. L'absorption est essentiellement de nature physique et, sur un base pondérale, décroît par augmentation de température (dans le domaine 25–75°C), croît avec le poids moléculaire (l'effet est cependant minime au delà de 500.000), n'est pas affectée par l'insaturation du polymère, et croît en fonction de la concentration dans le domaine de 0.25 à 1% pour les polymères de plus bas poids moléculaire. L'adsorption par les polymères de plus haut poids moléculaire n'est pas affectée par la concentration. L'adsorption par les noirs plus fortement polaires et oxygénés ou par les Hi-Sil inorganiques fortement polaires est négligeable. Les espèces de poids moléculaire plus élevé sont adsorbées préférentiellement de sorte que l'on peut obtenir des courbes de distribution de poids moléculaires apparemment reproducibles aux dépens de ces expériences d'équilibre. Des études de mouture montrent également qu'un polymère de poids moléculaire élevé peut être plastifié par un additif.

Zusammenfassung

Zur Aufklärung des Mechanismus der Kautschukver-stärkung wurde eine Untersuchung des Adsorptionsgleich-gewichtes mehrerer Polyisobutylene und eines Butyl-kautschuks aus Benzollösung an einen Hochabriebs-Ofenruss und andere Füllstoffe durchgeführt. Die Adsorption ist im wesentlichen physikalischer Natur und, auf eine Gewichts-basis bezogen, nimmt sie mit steigender Temperatur (im Bereich von 25–75°C) ab, mit dem Molekulargewicht zu (jedoch ist der Effekt über etwa 500,000 klein), ist unab-hängig vom Doppelbindungsgehalt des Polymeren und nimmt bei den niedrigermolekularen Polymeren im Bereich von 0,25 bis 1% mit der Konzentration zu. Auf die Adsorp-tion der höhermolekularen Polymeren hat die Konzentration keinen Einfluss. Adsorption durch die stärker polaren, sauerstoffhältigen "channel"-Russe oder durch das hoch-polare, anorganische Hi-Sil ist vernachlässigbar. Die höhermolekularen Molekelarten werden in einem solchem Ausmass bevorzugt adsorbiert, dass es möglich ist, aus diesen einfachen Gleichgewichtsversuchen offenbar verlässliche Molekulargewichts-Verteilungskurven zu erhalten. Mah-lungsversuche zeigen, dass eine Erweichung eines Polymeren von hohem Molekulargewicht durch einen Füllstoff möglich ist.