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# The Interaction between Styrene–Butadiene Rubber and Carbon Black on Heating

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There is still a considerable degree of uncertainty concerning the molecular structure of rubber containing a finely divided filler and its relation to the enhancement of physical properties usually designated by the term "reinforcement." It is generally believed, however, that there is some associative process whereby the polymer molecules become more or less permanently attached to the filler particles, though the precise nature of the attachment is still open to debate. If there is a relation between the nature or extent of this interaction and the degree of reinforcement, it is of interest to determine at which stage of the compounding procedure it occurs. Evidence for reaction during milling is found in the insolubility, in normal rubber solvents of stock taken from the mill, a phenomenon usually referred to as the formation of carbon gel or bound rubber.[1] The definitive work of Watson on the formation of carbon gel under controlled conditions indicates that formation of bound rubber can arise from the reaction of polymer radicals produced by shear with the filler particles which act as radical acceptors.[2,3] After milling, a rubber compound is normally subjected to heat and pressure in a molding press, but the possibility of further reaction under these conditions does not appear to have been fully explored. Of course, in the presence of compounding ingredients, the interaction between polymer and filler, as normally detected and measured by swelling in solvent, will be masked by the effect of the vulcanization process. However, an approach to the problem can be made by studying simpler mixtures from which the compounding ingredients have been omitted. This approach has been adopted in the present investigation, which has been concerned with the behavior on heating of dispersions of carbon black in styrene-butadiene rubber (SBR).

In such highly viscous systems the mobility of the polymeric free radicals produced by milling may be reduced to such an extent that they can persist for appreciable periods of time at room temperature after the milling process. Heating to curing temperature (150°C.) will serve to increase the mobility of the radicals and hence to promote further reaction, leading to an increased extent of association between polymer and filler above that found on milling alone. Furthermore, at the curing temperature, decomposition of active groups in the system, such as hydroperoxide, can also yield free radicals, which may further contribute to the polymer–filler interaction. The results of the investigation can be interpreted in terms of this hypothesis.

## EXPERIMENTAL MATERIALS AND METHODS

### Materials

The sample of SBR (Plioflex 1502) was obtained through the courtesy of the Goodyear Tire and Rubber Company. It contained 1.25% of a Wing-Stay S, stabilizer (antioxidant), an alkylated phenol which normally was removed by acetone extraction for 24 hr. before use. The rubber was then wholly soluble in benzene (except for a surface layer which was removed and discarded), and this solvent had an intrinsic viscosity of 2.4 at 30°C.

Philblack O, an H.A.F. carbon black, was obtained from the Phillips Petroleum Company and was used as received.

Thiophenol was of normal laboratory grade and was not further purified before use. Analytical grade benzene was used for all swelling measurements.

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## Preparation of Dispersions of Carbon Black in Rubber

The ball-milling and freeze-drying procedure of Watson was adopted.[3] Twenty grams of SBR were dissolved in 400 ml. of benzene in a ball mill of 1 qt. (950 ml.) capacity and 10 g. of carbon black added. The mill was about half-filled with $^3/_4$-in. pebbles and rotated at 120 rpm for 16 hr. The solution containing the filler was then separated and freeze-dried over 48 hr. to give the final solid dispersion.

## Milling

A conventional rubber mill was used, with 6 in. diam., water-cooled rolls revolving at 24 rpm (front) and 33.6 rpm (back). With the nip adjusted to 0.005 in., one-gram samples of the dispersion were dropped through the rolls, with an interval of about 3 sec. between successive passes to avoid excessive heat buildup in the sample.

## Heating

The samples were heated in conventional molding presses, both for convenience and also to duplicate the type of treatment to which compounded samples were normally subjected. It was also considered that better heat transfer could be obtained by pressing out the samples into thin sheets at the reaction temperature. Two presses were used. The first, heated by steam, gave excellent temperature control (±1°C.). The second had electrically heated platens, with rather worse temperature control (±3°C.), but was more convenient for the experiments carried out at different pressures. One-gram samples of the rubber–black mixture were placed between thin ($^1/_{16}$-in.), preheated, galvanized sheets, which were then quickly placed in the press and pressure applied to give a sheet about 0.5 mm. in thickness. The time taken for the insertion or removal of a sample was about 15 sec.

## Measurement of Sol Fraction, Gel Swelling, and Gel Composition

After the milling or heating treatment, the samples were allowed to stand at room temperature for 24 hr. They were then divided into two parts (to give duplicate determinations), and each part was weighed accurately. The samples were immersed in 50 ml. of benzene in a stoppered flask and stored in the dark for six days, during which time they received 30 min. shaking every day in a conventional laboratory shaker. After this period of standing, the supernatant liquid was removed as completely as possible, the swollen gel being centrifuged if necessary. The gel was washed by immersion in 50 ml. of fresh benzene for 30 min., and the wash solvent was removed in like manner. The total volume of the solution and washings was measured, and after centrifuging to remove suspended solid particles, 20-ml. samples were removed. The solid content was obtained from the residue after freeze-drying the solutions over a period of 24 hr. Thus the total sol fraction could be calculated.

The gel fraction was surface-dried as well as possible and transferred to a weighing bottle. The swollen weight was then obtained. After drying to constant weight at 40°C. and $^1/_2$ atm. pressure, the dry weight of the gel was found. A comparison between the original weight of the sample and the sum of the weights of the dry gel and the sol fraction gave an indication of the losses involved in this procedure. In most cases this did not amount to more than 2% of the original weight of the sample.

To obtain the gel composition, a known weight of the dry gel was heated at 450°C. in a slow stream of nitrogen until all the rubber had been depolymerized and volatilized, as judged by the weight constancy of the carbon black residue. A control experiment on a sample of carbon black showed that it contained 0.83% of volatile matter removable under the same conditions. The polymer had an ash content of 0.57% which largely compensated for the volatile content of the carbon black, so that no further correction was made for either of these factors.

## The Representation of Experimental Results

To characterize adequately the extent of the interaction between polymer and filler, two factors must be taken into account: (*1*) the amount of rubber retained in the insoluble gel fraction and (*2*) the degree of swelling of the insolubilized rubber.

The bound rubber content (B.R.C.) is defined as the weight of rubber associated with each gram of carbon black in the gel and is obtained directly from the gel composition. An alternative measure of this quantity, which also takes account of the original composition of the rubber–black mixture, is the bound rubber fraction (B.F.R.), the fraction of the total rubber which is rendered insoluble by association with the filler.

According to the statistical thermodynamic treatment of a swollen elastomer network by Flory and Rehner,[4,5] the degree of swelling is related to the number of effective chains per unit volume. Though their relation is probably not strictly applicable to a sample containing filler particles to which the polymer chains are attached, a similar type of relation might be expected to apply to the swollen rubber matrix, the filler particles being considered inextensible. This assumption has frequently been made for want of any satisfactory alternative,[6-8] and the same procedure will be adopted here. From the known weights of the dry and swollen gel, the weight of benzene imbibed by a unit weight of bound rubber can be calculated, the filler being assumed to be inert. The volume fraction $v_r$ of the swollen rubber matrix can then be inserted into the Flory-Rehner equation to give the apparent number of effective network chains per unit volume of bound polymer. A value of the polymer-solvent interaction parameter $\gamma$ of $0.37 + 0.27v_r$ has been assumed in this calculation.[6] To give a measure of the total extent of the interaction between rubber and filler, the chain density (C.D.) is defined as the number of moles of effective network chains ($\times 10^6$) associated with one gram of filler. However, little reliance is placed on any quantitative interpretation of the data expressed in this way, the figures obtained should be regarded merely as a convenient index of the tightness of the gel and the extent of the polymer-filler interaction. Unfortunately, no distinction can be made between those chains formed by direct attachment of the rubber molecules to the filler particles and those which arise by a crosslinking reaction taking place between the rubber chains already attached to the particles, though it is believed that the latter make only a very small contribution to the total effect.

The results obtained in this work are expressed in terms of the three interaction parameters, the bound rubber content (B.R.C.), in bound rubber fraction (B.R.F.), and the chain density (C.D.).

## EXPERIMENTAL RESULTS

### Interaction between Polymer and Filler on Milling

In confirmation of the results obtained by Watson, it was found that the interaction parameters increased on milling and attained a constant limiting value after about 30 passes through the mill (Table I).

TABLE I
Mixture Composition: S.B.R., 63.3%; Philblack O, 36.7%

| No. of passes | B.R.C. | B.R.F. | C.D. |
|---|---|---|---|
| 0 | 0.204 | 0.118 | 0.54 |
| 1 | 0.326 | 0.189 | 1.4 |
| 5 | 0.531 | 0.307 | 3.0 |
| 15 | 0.769 | 0.445 | 10.4 |
| 30 | 0.963 | 0.557 | 17.2 |
| 100 | 1.013 | 0.586 | 17.2 |

### Interaction between Polymer and Filler on Heating

#### *Unmilled Samples*

On heating unmilled samples of the rubber-filler dispersion at 150°C. in the press, the bound rubber content again rapidly attained a constant value, whereas the chain density continued to increase over the total period of heating (Fig. 1).

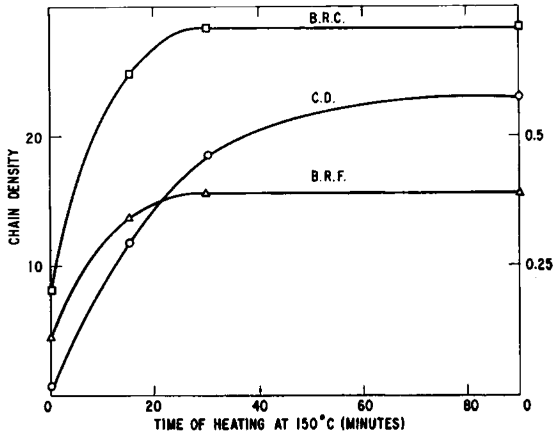

Figure 1.

A maximum experimental time of 90 min. was chosen, since this represents the maximum time expected at this temperature for the vulcanization of normal SBR mixes. These results indicate that heating is about as effective as milling in promoting the reaction between polymer and filler, at least to the extents of milling used in these experiments (100 passes).

#### *Milled Samples*

Milling the samples before the heat treatment gives a considerable increase in the extent of the interaction. The results obtained with samples passed 15 and 100 times through the mill before heating are compared with those obtained from

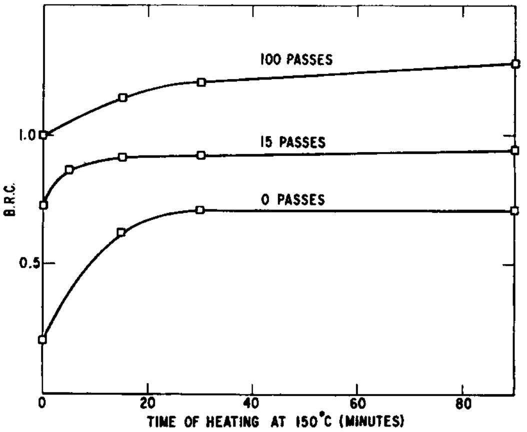

Figure 2.

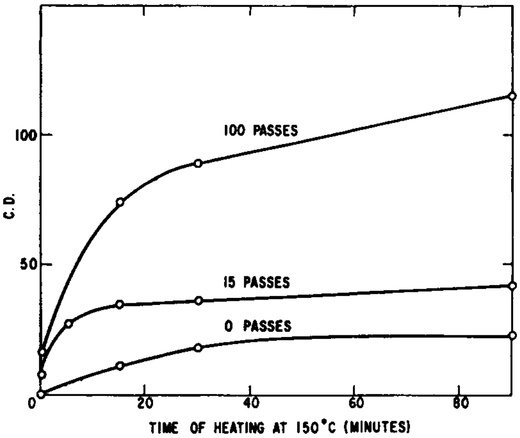

Figure 3.

similar experiments on unmilled samples in Figures 2 and 3.

Since, during the normal curing cycle, rubbers are subjected to pressure and heat simultaneously, it was desirable to determine what effect each has on the extent of the interaction between polymer and filler.

A sample of the rubber-black mixture was passed 15 times through the mill and subjected to various pressures for 30 min. at room temperature (Table II).

TABLE II
Mixture Composition: SBR, 65.7%; Philblack 0, 34.3%

| Pressure, psi | B.R.C. | B.R.F. | C.D. |
|---|---|---|---|
| 0 | 0.788 | 0.412 | 9.6 |
| 1,000 | 0.769 | 0.402 | 10.4 |
| 5,000 | 0.791 | 0.413 | 9.1 |
| 10,000 | 0.726 | 0.379 | 8.7 |
| 20,000 | 0.757 | 0.395 | 9.3 |

A similar sample, subjected to the same milling treatment was heated at 150°C. for 15 min. at various pressures (Table III).

TABLE III
Mixture Composition: SBR, 65.4%; Philblack 0, 34.6%

| Pressure, psi | B.R.C. | B.R.F. | C.D. |
|---|---|---|---|
| 0 | 0.984 | 0.522 | 24.7 |
| 1,000 | 0.970 | 0.514 | 32.1 |
| 3,000 | 0.922 | 0.489 | 27.2 |
| 10,000 | 0.925 | 0.490 | 29.2 |

The interaction between polymer and filler has been studied at four different temperatures, 110, 130, 150, and 170°C., for both unmilled and milled (15 passes) samples. If it is assumed that there is a direct proportionality between the chain density and the number of polymer-filler attachments, an activation energy for the overall process of forming such attachments can be calculated from the initial slopes of the chain density versus time curves at the different temperatures. For unmilled samples this has the value of 18.4 kcal./mole, while for milled samples the activation energy is 9.7 kcal/mole (Fig. 4).

Because of the low activation energy and high initial rates of the interaction for the milled samples, it is possible that some reaction will occur at room temperature after milling. Consequently, the parameters used to define and measure the extent of polymer-filler interaction may depend on the interval which elapses between the milling process and the immersion of the sample in benzene. Such a dependence has been observed. After

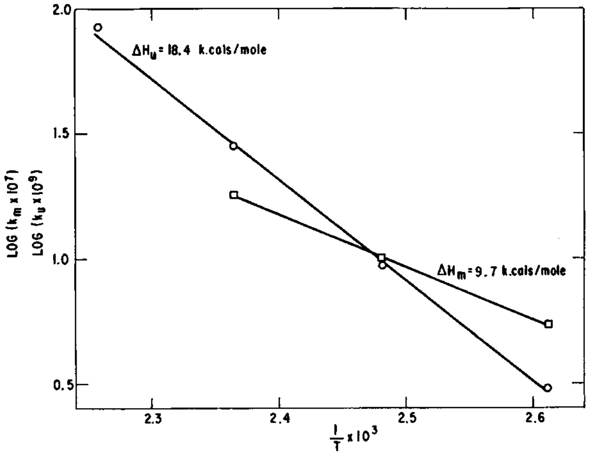

Figure 4.

passing samples 100 times through the mill, they were kept at room temperature in air and *in vacuo* for periods up to 24 hr. before immersion in benzene (Table IV).

TABLE IV
Mixture Composition: SBR, 65.6%; Philblack 0, 34.4%
No. of passes, 100

| Delay interval, hr. | B.R.C. | B.R.F. | C.D. |
|---|---|---|---|
| Stored in Air | | | |
| 0 | 0.405 | 0.212 | 1.5 |
| 1 | 0.652 | 0.342 | 2.5 |
| 3 | 0.950 | 0.498 | 7.5 |
| 8 | 1.008 | 0.526 | 11.1 |
| 24 | 1.040 | 0.545 | 12.2 |
| Stored *in vacuo* | | | |
| 0 | 0.405 | 0.212 | 1.5 |
| 1 | 0.526 | 0.276 | 1.7 |
| 3 | 0.827 | 0.433 | 5.4 |
| 8 | 0.901 | 0.472 | 8.2 |
| 24 | 0.942 | 0.494 | 9.7 |

The difference between the results obtained on storing in air and *in vacuo* is small but consistent and is probably a real effect.

Similar experiments carried out after heating unmilled and milled (15 passes) samples for 15 min. at 140°C. showed that no further reaction occurred on standing for up to 24 hr. (Table V).

TABLE V
Mixture Composition: SBR, 65.4%; Philblack 0, 34.6%

| Delay interval, hr. | B.R.C. | B.R.F. | C.D. |
|---|---|---|---|
| Unmilled sample | | | |
| 0 | 0.643 | 0.341 | 11.5 |
| 0.25 | 0.644 | 0.341 | 10.8 |
| 1 | 0.635 | 0.337 | 11.1 |
| 9 | 0.625 | 0.331 | 11.8 |
| 24 | 0.640 | 0.339 | 11.1 |
| Sample milled 15 passes | | | |
| 0 | 0.877 | 0.465 | 29.0 |
| 0.25 | 0.880 | 0.466 | 26.2 |
| 1 | 0.856 | 0.454 | 29.0 |
| 9 | 0.842 | 0.446 | 24.3 |
| 24 | 0.857 | 0.454 | 25.3 |

To establish if the changes which take place on standing after milling (as shown in Table IV) had any influence on the results of subsequent heat treatment, samples were milled 15 times and then stored in air and *in vacuo* at room temperature for intervals up to 24 hr. before being heated for 30 min. at 150°C. (Table VI).

TABLE VI
Mixture Composition: SBR, 65.6%; Philblack 0, 34.4%

| Delay, hr. | B.R.C. | B.R.F. | C.D. |
|---|---|---|---|
| Stored in air | | | |
| 0 | 0.873 | 0.457 | 26.1 |
| 1 | 0.873 | 0.457 | 28.3 |
| 3 | 0.821 | 0.430 | 22.5 |
| 6 | 0.902 | 0.473 | 30.6 |
| 24 | 0.858 | 0.450 | 26.8 |
| Stored *in vacuo* | | | |
| 0 | 0.873 | 0.457 | 26.1 |
| 1 | 0.828 | 0.434 | 26.3 |
| 3 | 0.827 | 0.433 | 24.5 |
| 6 | 0.861 | 0.451 | 27.4 |
| 24 | 0.869 | 0.455 | 30.1 |

As standard procedure, all samples were kept at room temperature for 24 hr. after milling or heating before immersion in benzene.

Though most of this work has been carried out on mixtures containing about 34% (50 parts) of carbon black, this parameter has been varied, and the results obtained on mixtures containing 20.5% (25 parts), and 42.8% (75 parts) of carbon black are summarized in Tables VII, VIII, and IX, which also include the corresponding results from the usual mixture for comparison. As has been reported previously, the bound rubber content decreased as the loading was increased.[9] However, the increased loading more than compensated for this decrease, so that the bound rubber fraction showed a direct variation with loading (Table VIII).

TABLE VII

| No. of passes | Time of heating, min. | B.R.C. at various carbon black contents | | |
|---|---|---|---|---|
| | | 20.5% | 34.5% | 42.8% |
| 0 | 0 | 0.263 | 0.180 | 0.151 |
| | 15 | 0.853 | 0.564 | 0.488 |
| | 90 | 1.038 | 0.626 | 0.549 |
| 15 | 0 | 0.259 | 0.546 | 0.583 |
| | 15 | 0.940 | 0.807 | 0.797 |
| | 90 | 1.112 | 0.896 | 0.813 |
| 100 | 0 | 0.265 | 0.881 | 0.850 |
| | 15 | 1.280 | 1.153 | 1.154 |
| | 90 | 1.333 | 1.198 | 1.056 |

TABLE VIII

| No. of passes | Time of heating, min. | B.R.F. at various carbon black contents | | |
|---|---|---|---|---|
| | | 20.5% | 34.5% | 42.8% |
| 0 | 0 | 0.068 | 0.095 | 0.113 |
| | 15 | 0.220 | 0.297 | 0.365 |
| | 90 | 0.268 | 0.330 | 0.411 |
| 15 | 0 | 0.067 | 0.288 | 0.436 |
| | 15 | 0.242 | 0.425 | 0.596 |
| | 90 | 0.287 | 0.472 | 0.608 |
| 100 | 0 | 0.068 | 0.464 | 0.636 |
| | 15 | 0.330 | 0.607 | 0.863 |
| | 90 | 0.344 | 0.631 | 0.790 |

TABLE IX

| No. of passes | Time of heating, min. | C.D. at various carbon black contents | | |
|---|---|---|---|---|
| | | 20.5% | 34.5% | 42.8% |
| 0 | 0 | 0.78 | 0.79 | 0.69 |
| | 15 | 2.2 | 9.5 | 16.4 |
| | 90 | 3.3 | 13.1 | 20.9 |
| 15 | 0 | 0.86 | 3.8 | 12.5 |
| | 15 | 3.2 | 26.8 | 76 |
| | 90 | 4.9 | 44.6 | 68 |
| 100 | 0 | 1.9 | 7.4 | 95 |
| | 15 | 5.7 | 98 | 297 |
| | 90 | 9.5 | 127 | 311 |

## Interaction in the Presence of Additives

If, as is believed, the interaction between polymer and filler is due to the presence of free radicals, the addition to the system of specific compounds of known reactivity to free radicals (acceptors) should have predictable effects on the results obtained. Such a compound is thiophenol ($C_6H_5$-SH), and this has been incorporated by swelling into milled and unmilled samples for 24 hr. before heat treatment.

With unmilled samples, all three parameters are reduced by the presence of thiophenol, the magnitude of this effect depending on the concentration of the reagent (Figs. 5 and 6). Thus, when 5% of thiophenol was present, the bound rubber content was reduced by about 34% and the chain density by about 75%. With samples which had been milled 100 times, the effect of the thiophenol was similar (Figs. 7 and 8). Five per cent of thiophenol reduced the bound rubber content by about 23% and the chain density by about 78%. A much more profound effect was found when the radical acceptor was added to the mixture before milling (Figs. 9 and 10). In this case the bound rubber content was reduced by about 60% and the

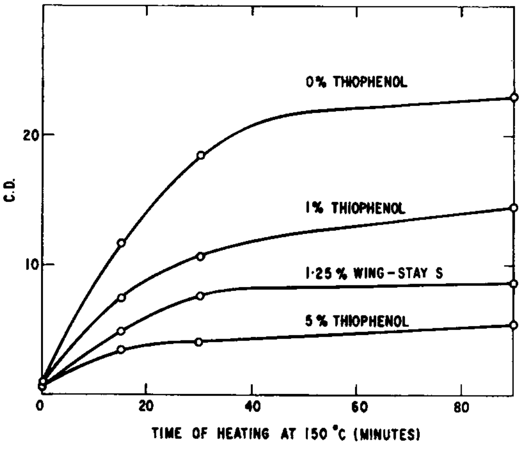

Figure 6.

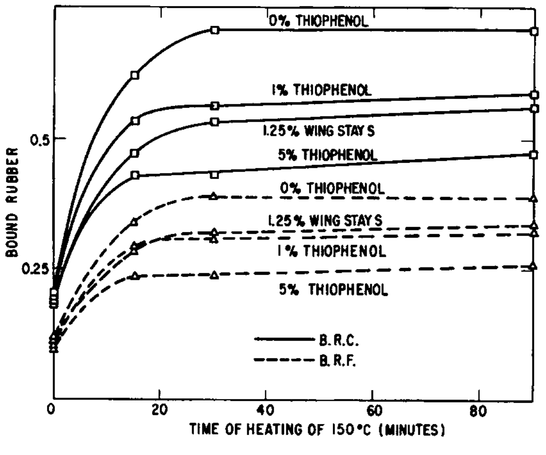

Figure 5.

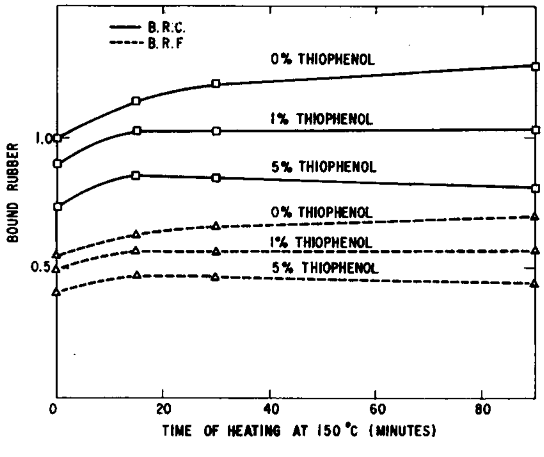

Figure 7.

chain density by about 94%. It appears that the presence of thiophenol during milling eliminates the free radicals which normally persist after this process, and hence the influence of milling on the subsequent heat treatment is largely lost. This may be seen by comparing the results obtained on heating an unmilled sample with thiophenol, with those obtained on heating (at 150°C.) a sample which has been milled with the same amount of thiophenol (Table X).

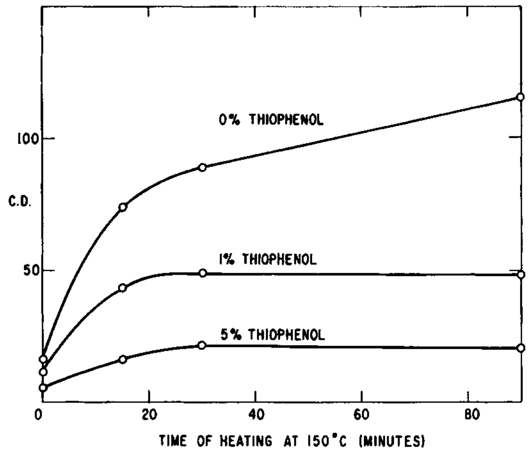

Figure 8.

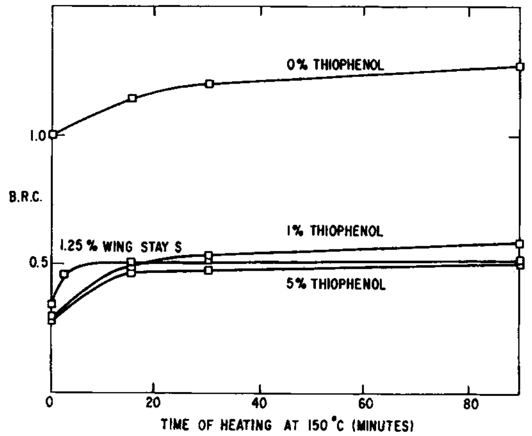

Figure 9.

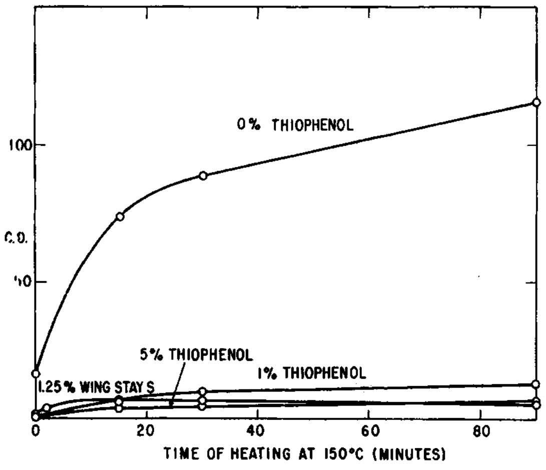

Figure 10.

TABLE X

Mixture Composition: SBR, 64.5%; Philblack 0, 35.4%

| Time of heating, min. | B.R.C. | B.R.F. | C.D. |
|---|---|---|---|
| | Thiophenol content, 1% | | |
| Unmilled sample | | | |
| 0 | 0.186 | 0.102 | 1.0 |
| 15 | 0.535 | 0.293 | 7.5 |
| 30 | 0.562 | 0.308 | 10.7 |
| 90 | 0.589 | 0.323 | 14.5 |
| Milled 100 times | | | |
| 0 | 0.295 | 0.162 | 1.0 |
| 15 | 0.504 | 0.276 | 6.3 |
| 30 | 0.537 | 0.294 | 10.1 |
| 90 | 0.592 | 0.325 | 13.0 |
| | Thiophenol content, 5% | | |
| Unmilled sample | | | |
| 0 | 0.181 | 0.099 | 1.0 |
| 15 | 0.432 | 0.237 | 3.4 |
| 30 | 0.432 | 0.237 | 4.0 |
| 90 | 0.474 | 0.260 | 5.5 |
| Sample milled 100 times | | | |
| 0 | 0.281 | 0.154 | 0.64 |
| 15 | 0.473 | 0.259 | 4.2 |
| 30 | 0.483 | 0.264 | 5.0 |
| 90 | 0.510 | 0.280 | 6.9 |

If no radicals are present after the samples are milled with thiophenol, no change is expected in the interaction parameters when the samples are allowed to stand after milling. This has been shown to be the case (Table XI).

TABLE XI

Mixture Composition: SBR, 65.7%; Philblack 0, 34.3%

| Delay, hr. | B.R.C. | B.R.F. | C.D. |
|---|---|---|---|
| 0 | 0.206 | 0.108 | 1.13 |
| 1 | 0.219 | 0.114 | 0.62 |
| 3 | 0.244 | 0.127 | 0.87 |
| 6 | 0.224 | 0.117 | 0.74 |
| 24 | 0.233 | 0.122 | 0.74 |

## The Role of the Antioxidant as a Radical Acceptor

The SBR as supplied contained a stabilizing antioxidant (Wing-Stay S, alkylated phenol). In most experiments this material was removed by extraction, but it was desirable to determine what effect it had on the polymer–filler interaction. Some experiments were therefore carried out with the unextracted polymer.

### *Interaction on Milling*

When antioxidant was present in the polymer–filler mixture, the extent of interaction on milling was greatly reduced (Table XII).

TABLE XII

| No. of passes | B.R.C. | B.R.F. | C.D. |
|---|---|---|---|
| Extracted sample[a] | | | |
| 0 | 0.18 | 0.095 | 0.79 |
| 15 | 0.546 | 0.288 | 3.76 |
| 100 | 0.881 | 0.464 | 7.37 |
| Unextracted sample[b] | | | |
| 0 | 0.195 | 0.101 | 0.61 |
| 15 | 0.308 | 0.160 | 1.07 |
| 100 | 0.343 | 0.178 | 1.72 |

[a] Mixture composition: SBR, 65.5%; Philblack 0, 34.5%.
[b] Mixture composition: SBR, 65.8%; Philblack 0, 34.2%.

On heating after milling, the values of the interaction parameters for the extracted samples showed a much greater dependence on the extent of milling than those for the unextracted samples, in which the effect of prior milling was largely eliminated (Figs. 11 and 12). Clearly, in this respect, the antioxidant resembles thiophenol in its action. From Figures 5, 6, 9, and 10 it will be observed that in both the unmilled and milled samples the antioxidant has an activity about the same as that of thiophenol at the same concentration level by weight.

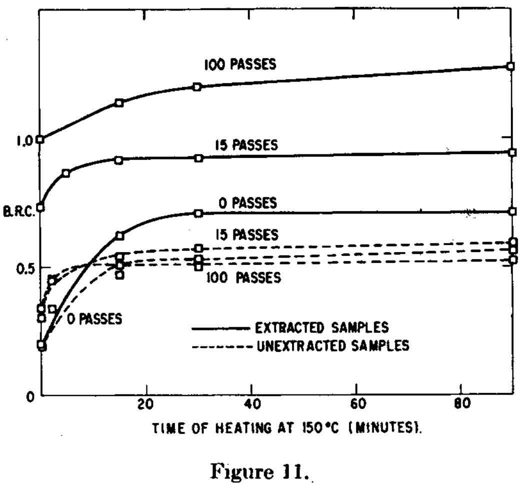

Figure 11.

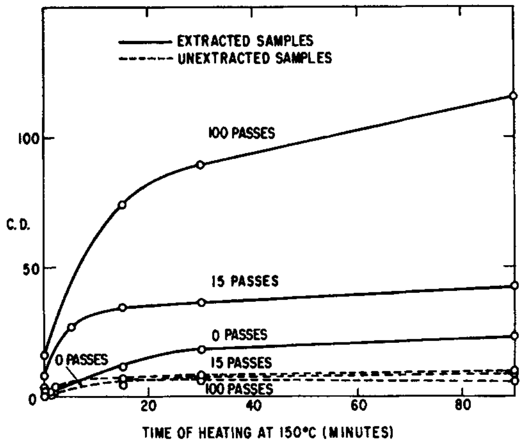

Figure 12.

## DISCUSSION

Many of the features of the interaction between polymer and filler can be explained on the assumption that polymer free radicals can react with active sites on the filler particle surface, thereby forming a bond which is stable to the action of a swelling agent. This mode of reaction must involve three stages: (*1*) generation of polymer free radicals; (*2*) migration of the free radicals to the reactive sites on the filler particles; (*3*) reaction at the particle surface.

The first two stages in this process will depend on the conditions under which the interaction is occurring, whereas the final stage will be essentially independent of the environment. It is therefore convenient to discuss first this reaction between the radicals and the filler. The possibility that free radicals can react with finely divided particles of carbon black has received considerable attention in recent years.[3,10–13] In doing so the carbon black may function as a free-radical itself, or as a radical acceptor in the usual sense of the term; evidence exists for both modes of action.[10] Reactions of either type are characterized by low energies of activation and rapid rates at normal (room) temperatures, and consequently, under the conditions of interaction between polymer and filler which obtain in this work, the overall rate of the process will depend on the rates of the first and second steps and not on that of the final step.

The possibility also exists of mutual termination of the polymer free radicals. This effect will contribute to the interaction provided that at least one of the reacting radicals is already attached to a filler particle. The third alternative fate of the free radicals involves reaction with the polymer chains, a process corresponding to the transfer reaction to polymer in free radical polymerization. The rates of such reactions are many orders of magnitude less than that of a radical-radical termination step, or of a transfer reaction to an efficient transfer agent, or radical acceptor.[14] However, this disparity may be compensated to some extent by the high effective, i.e., available, concentration of the polymer chains, compared with those of the polymer free radicals, or the active sites on the filler surface. If a branching reaction of this type does occur, it will lead to an apparent increase in the polymer-filler interaction, as measured by the interaction parameters.

### Interaction on Milling

In this case, which has been studied in considerable detail by Watson,[3] it is believed that the free radicals are produced by the shearing action of the mill.[15] The concomitant mixing action also helps to bring the reactive radicals into the proximity of the surface of the filler, thereby fulfilling the second of the conditions necessary for interaction. Radical-radical termination reactions, as discussed above, will also presumably occur.

When the milling is stopped, a certain concentration of free radicals will persist, but because of the high bulk viscosity of the medium and the lack of any mixing action the mobility of these radicals will be reduced to such an extent that only a relatively small fraction can migrate to, and react with, the filler particles or other radicals in a reasonable length of time (24 hours) at room temperature. It is believed that it is this reaction which accounts for the increase in the interaction parameters on standing between milling and swelling (Table IV). The possibility of radicals being trapped or frozen in a viscous polymer in this way has often been suggested previously.[16]

### Heating of Milled Samples

It is believed that the main function of heating is to increase the rate of diffusion of the polymer free radicals, so that they can migrate to favorable positions for either radical-radical or radical-filler reactions. The activation energy associated with this process should therefore be that characteristic of a polymer flow or diffusion process, and for GR-S a value of 10.3 kcal./mole has been obtained.[17] The value of 9.7 kcal./mole observed for the activation energy of interaction of milled samples (Fig. 4) is in good agreement with that reported previously for the diffusion process.

A direct indication of the free radical nature of the reaction is found in the influence of thiophenol, a compound of known activity to free radicals, on the extent of interaction on heating after milling. If this compound is added after milling, but before heating, the interaction is reduced to an extent dependent upon the amount of the reagent present (Figs. 7 and 8). On milling, thiophenol reduces the extent of interaction presumably because it competes successfully with the carbon black for the available free radicals.[3] It appears that it also reacts with those free radicals which normally persist after milling and thus eliminates the interaction which usually occurs on standing (Table XI), and reduces that which occurs on heating (Figs. 9 and 10). Thus the effect of milling is almost entirely lost (Table X).

The extent of the reaction which occurs on heating varies directly with the amount of prior milling (Figs. 2 and 3), and hence it may be deduced that the concentration of "frozen radicals" after milling increases with increasing amounts of milling. Since the generation of free radicals on milling is probably due to mechanical shear, it is plausible to assume that the rate of this process is determined primarily by the bulk viscosity of the medium. For the extents of milling used in this investigation, the bulk viscosity of the dispersion increases with milling because of the interaction which occurs under these conditions (Table I), and thus the dependence of the extent of interaction on heating on the amount of prior milling is understandable. The influence of the mixture composition on the interaction (Tables VII, VIII, and IX) can be explained in a similar way.

The radicals produced by shear during milling are presumably alkylic, and hence would be expected to react readily with atmospheric oxygen, though in this respect they appear to be somewhat less reactive than allylic radicals.[3] It is not possible to decide, from the present data, whether the radicals which react with the filler on heating after milling have, at some intermediate stage, reacted with oxygen. Since the results are not influenced significantly by the conditions of storage between milling and heating (Table VI), it is possible that the original and oxidized radicals are closely similar in their reactivity to carbon black, unless, of course, the oxidation is complete before storage starts.

### Heating of Unmilled Samples

While the continued reaction of free radicals produced by milling can account for some of the polymer-filler interaction on subsequent heating, a second factor must also be considered to account for the interaction which occurs on heating unmilled samples (Fig. 1), which presumably do not contain trapped free radicals initially. The general features of this reaction, particularly its sensitivity to free radical acceptors (Figs. 5 and 6), indicates that it also proceeds by a free radical mechanism, but in this case some other mode of generation must be invoked. It is suggested that they arise by the thermal decomposition of reactive groups, rather than by thermal dissociation of primary chemical bonds in the polymer chains. The activation energy of such a decomposition process is high, and it is this step which governs the overall rate of the reaction, rather than the rate of diffusion as in milled samples. The higher activation energy of interaction of unmilled samples (18.4 kcal./mole, Fig. 4) is in accord with this hypothesis. Heating experiments have been performed on polymer–filler dispersions prepared from SBR which had been pre-oxidized by heating for 96 hr. in air at 50°C. before preparation of the dispersion. The results obtained were not significantly different from those using conventional dispersions. More severe oxidizing conditions (96 hr. in air at 80°C.) have a gelled material which was unsuitable for the preparation of the dispersion.

It appears, therefore, that the state of oxidation of the polymer has little influence on the extent of interaction on heating unmilled samples of the dispersion. It is possible that the concentration of chemical groups which decompose to form radicals is not increased by oxidation, or that the reactivity is associated with the filler and not the polymer. In support of the latter viewpoint, it has been noted that on heating unmilled dispersions of polymer and filler, in which the same amounts of different fillers were present, the chain density increased with increasing oxygen content of the filler.[18]

At different extents of loading with the same filler, the chain density increases with loading on heating unmilled samples (Table IX). The weight of polymer per gram of filler in the untreated dispersion decreases as the loading increases. Hence, if the number of free radicals produced on heating is related to the concentration of reactive groups on the polymer, the chain density (which refers to unit weight of filler) should decrease with increased loading. Furthermore, if the interaction was due to the decomposition of reactive groups in the filler, the chain density should be independent of the loading. Thus neither hypothesis is capable of accounting for the results satisfactorily.

### The Influence of Other Radical Acceptors

It is interesting to note that the antioxidant (stabilizer) normally present in SBR is itself a radial acceptor with an efficiency about the same as that of thiophenol (Figs. 5, 6, 9, and 10). The results obtained in experiments on polymer–filler dispersions prepared from the unextracted rubber (Table XI, Figs. 11 and 12) can be explained on the assumption that the stabilizer functions in this way.

### Interaction by Absorption

Unmilled samples show some degree of interaction without heating; interaction which occurs during the preparation of the dispersion. The ball-milling process subjects the polymer molecules to shear, but this much less severe than in cold milling. Thus, ball-milling a 5% solution of natural rubber in benzene for 24 hr. reduces the intrinsic viscosity (in benzene at 25°C.) from 6.0 to 5.8. It is therefore unlikely that free radicals are produced under these conditions, and it is more plausible to assume that in this case the interaction is due to adsorption of the polymer molecules on the filler.[19,20] In support of this view, almost identical results for the interaction parameters are obtained for dispersions prepared from extracted and unextracted rubber, whereas the free radical activity of the antioxidant is clearly indicated from its effect on milling and heating the dispersions.

It is not possible, from the present data, to state unequivocally how much of the interaction between polymer and filler is due to the direct attachment of polymer molecules to the surface of the filler and how much to a branching reaction within the polymer molecules attached to the filler. Energetic considerations, as discussed above, favor the former process. Also, if analogous milling and heating experiments are performed on the polymer without filler, only a negligible amount of gel is formed.

However, it is possible that the conditions under which interaction occurs in the different stages may lead to qualitative, as well as quantitative, differences in the interaction. In samples which have been heated after milling, the total interaction will be made up of the contributions of four different effects.

*1.* Adsorption of the polymer on the filler.[19,20]

*2.* Interaction on milling.[2,3]

*3.* Interaction arising from decomposition of reactive groups on heating.

*4.* Interaction from reaction of free radicals which persist after milling.

Any attempt to relate polymer–filler interaction to reinforcement should take account of all of these contributions to the interaction. Up to the present only the first two of these possibilities have been considered, the second having received much more attention than the first. The present work has shown that heating, which introduces the third and fourth effects, can lead to extents of interaction much greater than those found after milling. Because of the different energy requirements and the environmental factors involved in these processes, the relative contributions to the total interaction may depend somewhat critically on the conditions under which the milling and heating (curing) are carried out, and this in turn may influence the degree of reinforcement. It has been shown that an antioxidant is capable of exercising a pronounced effect on the interaction. It is probable that other compounding ingredients may also have specific effects, not only on the mill but also during the subsequent heating which effects vulcanization.

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## Synopsis

The interaction between a carbon black filler and styrene-butadiene rubber is increased if the material is heated after milling. This effect has been attributed to the polymeric free radicals which are presented after milling but which require a high temperature to increase their mobility to the point where they can react. The extent of interaction increases with time of heating and with the amount of milling before heating. The postulated mechanism is supported by the experimental activation energies and by the predictable influence of free radical scavengers on the system.

## Résumé

L'interaction entre le charbon actif et un caoutchouc à base de styrène-butadiène augmente si les produits sont chauffés après leur broyage. On a attribué cet effet aux radicaux polymériques libres présents après le broyage, mais qui requièrent une température élevée pour accroître leur mobilité au point de pouvoir réagir. Le degré d'interaction augmente en fonction du temps de chauffage et en fonction de la durée broyage avant le chauffage. Le mécanisme proposé est confirmé par les énergies d'activation expérimentales et par l'influence de capteurs des radicaux libres sur le système.

## Zusammenfassung

Die Wechselwirkung zwischen Russ als Füllstoff und einem Styrol-Butadienkautschuk wird erhöht, wenn das Material nach dem Mahlen erhitzt wird. Dieser Effekt wurde auf die Wirkung freier Polymerradikale zurückgeführt, die nach dem Mahlen zwar vorhanden sind, aber eine hohe Temperatur brauchen, damit ihre Beweglichkeit soweit erhöht wird, um eine Reaktion zu ermöglichen. Das Ausmass der Wechselwirkung nimmt mit der Erhitzungsdauer und mit der Stärke des Mahlens vor dem Erhitzen zu. Der aufgestellte Mechanismus wird durch die experimentell ermittelte Aktivierungsenergie und durch den diesem Mechanismus entsprechenden Einfluss von Abfangstoffen für freie Radikale auf das System gestützt.

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