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An Electron Microscopic Reinforcement Criteria for Carbon Black Masterbatches

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Introduction

The adequate dispersion of carbon black in rubber has long been recognized as an important factor in obtaining good physical properties in black rubber masterbatches. At the present time the most widely used methods for the microscopic evaluation of carbon black dispersions in rubber are those described by Sweitzer, Hess, and Callan[1] and Leigh-Dugmore.[2] These methods are based on the fact that in dry mixed masterbatches the major difference between two dissimilar dispersions is likely to be in the size and the number of the agglomerate black particles.[1] With the development of wet masterbatching methods,[3,4] which greatly reduces the size and quantity of carbon black agglomerates, such evaluations prove inadequate.

Preliminary results indicated that simply evaluating the manner in which the carbon black was scattered or dispersed in the polymer matrix could not account for observed changes in physical properties of wet masterbatches. This electron microscopic study was made to establish and define terms relating to the reinforcement of rubber stocks by carbon black at levels below the limits of resolution of the light microscope.

Experimental Procedures

Samples of the masterbatches to be studied were frozen in a Dry Ice-isopropyl alcohol bath and subsequently fractured. Replicas were then made of this freshly fractured surface. Either raw or compounded stocks yielded equivalent results.

The replication procedure employed was a refinement of that used by Andrews and Walsh[5] to produce preshadowed positive carbon replicas. Faxfilm,[6] a cellulose-based tape, was substituted for the gelatin as the intermediate negative replica in this two-stage system. This substitution greatly reduced the time necessary for replication, as gelatin requires enzymatic digestion for complete removal from the positive. Light uranium shadowing was then applied before the deposition of the carbon film. This method permits routinely resolutions of better than 100 A.

Since acetone was used as the softener for the Faxfilm during replication, it was necessary to determine the effect of the acetone on the surface of the masterbatch to be replicated. This was done by using polyvinyl alcohol in water in place of Faxfilm as the intermediate negative. Results were identical for both replicating materials, indicating that the acetone does not soften the surface of the masterbatch sufficiently, if at all, to allow rearrangement of the carbon black particles.

No attempt was made to micrograph the replica statistically, since precise figures for black distribution were not required and would be difficult to obtain at best. The whole surface of the final replica was, however, scanned with the electron microscope, and observations were made relative to the complete surface. The micrographs therefore represent typical areas seen. The final magnifications of the micrographs were kept constant at 20,000 diameters to facilitate interpretation.

Results and Discussion

Results have shown the term "dispersion," when used alone, to be inadequate for correlating the quality of carbon black incorporation with the physical properties of a masterbatch. It has been found that at least three descriptive terms must be employed to evaluate the result of carbon black incorporation and to determine its effect on the physical properties of the vulcanizate. These terms, which we will call "reinforcement criteria," are: dispersion, grinding, and bonding. They are discussed in order of increasing effect on vulcanizate properties.

Dispersion

The term "dispersion" relates to the relative evenness with which the black is spread throughout the rubber matrix. Figure 1 is a micrograph of an HAF (high-abrasive furnace black) masterbatch in which the carbon black is poorly dispersed. In area A the black occurs not as individual particles, but as agglomerates of smaller particles. Area B of the micrograph shows a relatively low concentration of carbon black.

Grinding

Carbon black as it is received consists of aggregates or clusters of colloidally fine particles which must be broken down and dispersed in the rubber. The efficiency of the grinding or breaking down of the aggregates is determined by the size of the black particles after their incorporation in the rubber matrix. Ideally, this disaggregation should be to the point that the fundamental black particle is reached. For example, the mean average particle size for HAF black is approximately 240 A. and, for super abrasive furnace (SAF) black, 170 A.

Figure 2 shows an HAF masterbatch sample in which the grinding has been incomplete, as evidenced by the presence of large black particles. These large particles are aggregates of many fine particles which have never been broken apart. They are, however, so intimately associated that they appear as one unit. This is quite a different condition from the

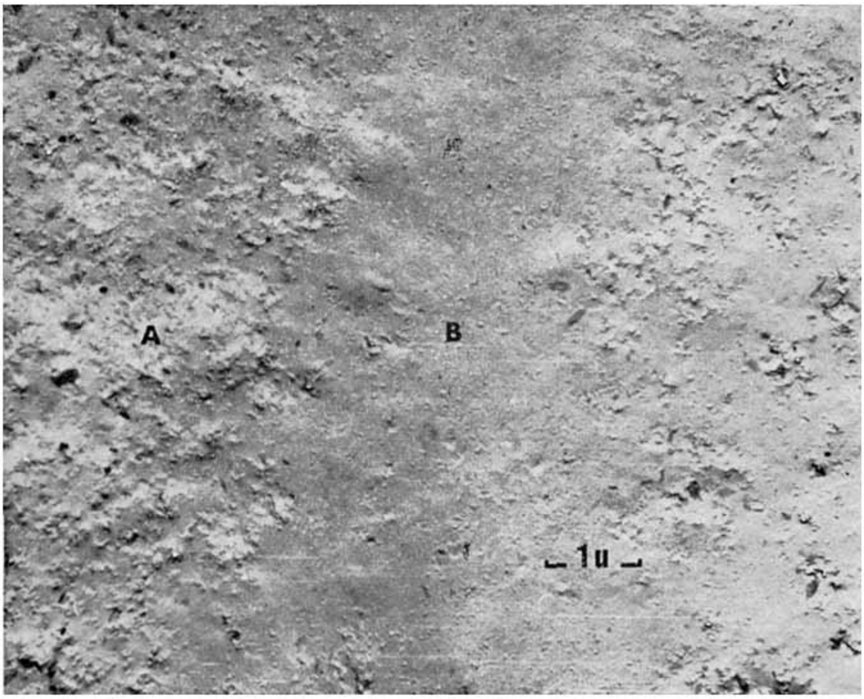

Fig. 1. Poor dispersion.

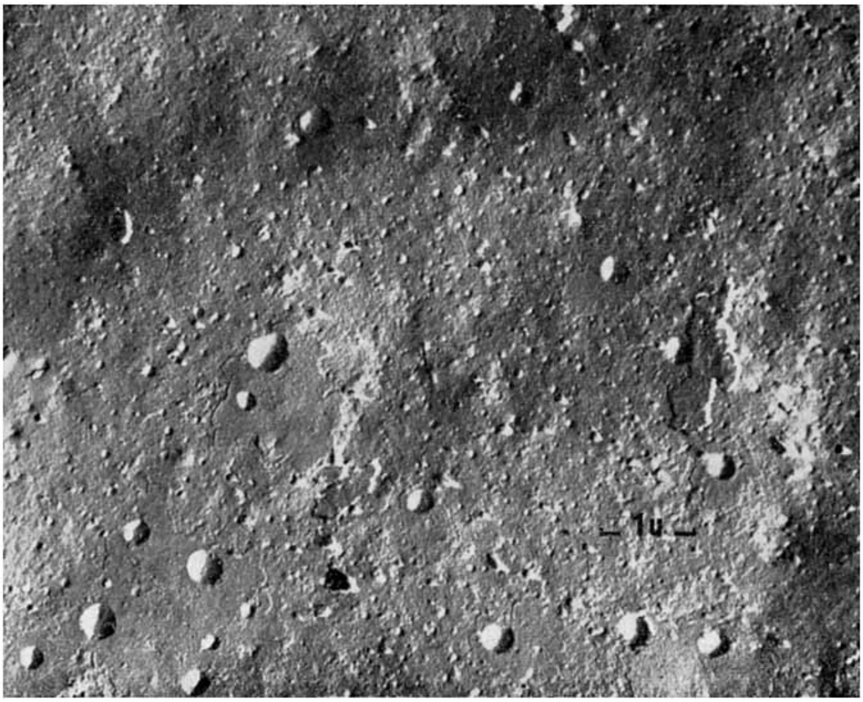

Fig. 2. Poor grinding.

agglomerates seen in Figure 1 which resulted not from poor grinding but poor dispersion. It is this physical difference in appearance of the replicated black particles that allows one to determine whether large clumps of black have resulted from poor grinding or poor dispersion. Light or electron microscopic observations of thin sections of masterbatch cannot distinguish between these two conditions.

Bonding

It has been well established that some sort of carbon gel complex[7] is formed when carbon black is incorporated into rubber. The nature of the bond formed between the carbon black and the surrounding rubber matrix,

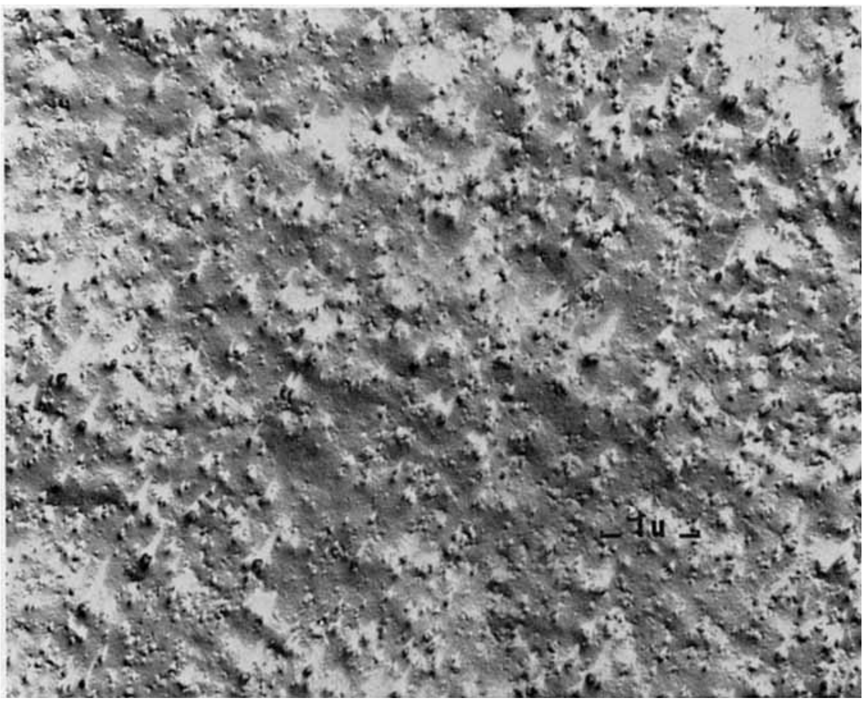

Fig. 3. Poor bonding.

however, is still the subject of speculation. Whether the bonds formed are of a chemical nature or a physical nature is not important here. It is sufficient to agree that some kind of bond exists.

The bond formed between the carbon black and the surrounding rubber appears to have the largest effect on the physical properties of the vulcanizate. If weak bonds are formed, the maximum reinforcement for the stock cannot be obtained from the black. The relative strengths of these bonds can be determined by electron microscopy.

When a rubber stock is frozen and fractured the propagation of the fracture will proceed along the path requiring the least amount of energy.

If the bond between the black and the polymer is a zone of relative weakness, the advancing fracture will travel along this polymer–black interface. Just ahead of the primary fracture front a stress field is generated which causes secondary failures to occur in the matrix around the black particles. This therefore results in exposing the black as smooth spherical particles, shown in Figure 3. The presence of strong carbon black–rubber bonds results in a less random movement of the fracture through the masterbatch rather than from one filler particle to an adjacent one, as results with weak bonding. In this manner, the particles are exposed as simply bumps or rough spots in the masterbatch rubber than spheres. An HAF masterbatch exhibiting good black–rubber bonding is shown in Figure 4.

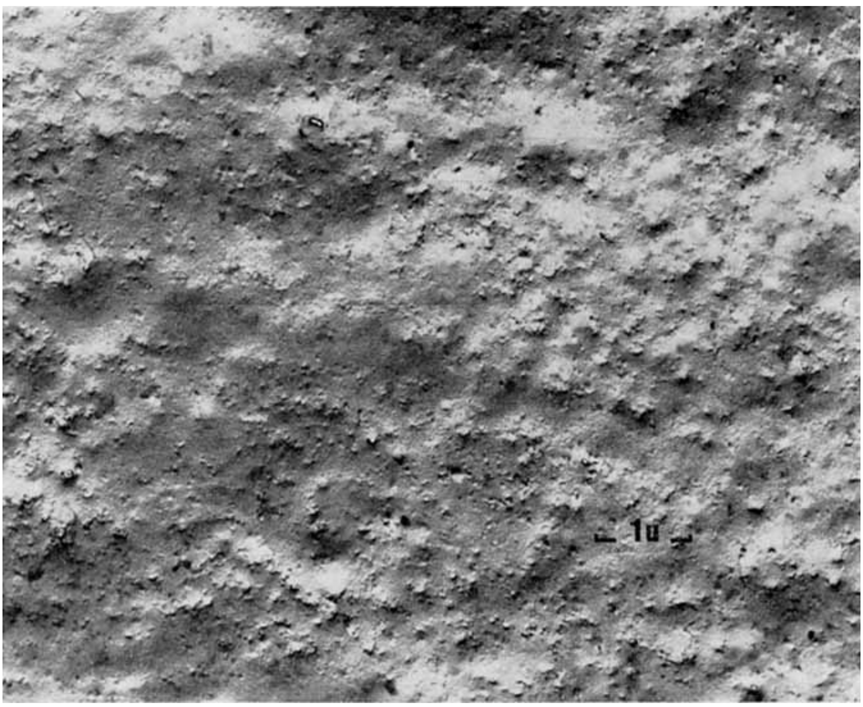

Fig. 4. Good dispersion, grinding, and bonding.

This observed difference in the physical appearance of the exposed carbon black particles was correlated with amounts of carbon gel complex in the masterbatch. The chemical determination of gel has been described elsewhere.[8] Typical results are (*1*) 15.2% bound rubber on samples showing poor bonding, as in Figure 3, and (*2*) 28.7% bound rubber on samples showing good bonding, as in Figure 4. These data indicated that the relative quality of the carbon black–rubber bond can be determined with the electron microscope.

The microscopic evaluation of bonding has the advantage of allowing determinations to be made on stocks of unknown origin. The chemical test for bound rubber, however, requires exact knowledge of the composition of the stock.

Results have shown that poor bonding is generally associated with poor grinding (Fig. 2); it can, however, occur with finely ground black also (Fig. 3). Samples showing poor bonding appear to produce vulcanizates with poor physical properties no matter how well dispersed or finely ground the black is.

The Role of Reinforcement Criteria in Vulcanized Properties

The evaluation of the effects of these reinforcement criteria on the valcanizate properties of wet-type masterbatches was made on stocks containing HAF black or SAF black. The masterbatch composition was as shown in Table I.

TABLE I
Black Masterbatch Composition

Masterbatch type	HAF	SAF
Polymer type	1500	1500
Black (phr)[a]	52	40
Processing oil (phr)[a]	10	5
Polymer Mooney viscosity	52 ML_4	52 ML_4

[a] Parts per hundred rubber.

The effect that each one of the reinforcement criteria has on the raw Mooney viscosity of the stock is shown in Figure 5. It can be seen that better carbon black incorporation results in increased Mooney viscosity.

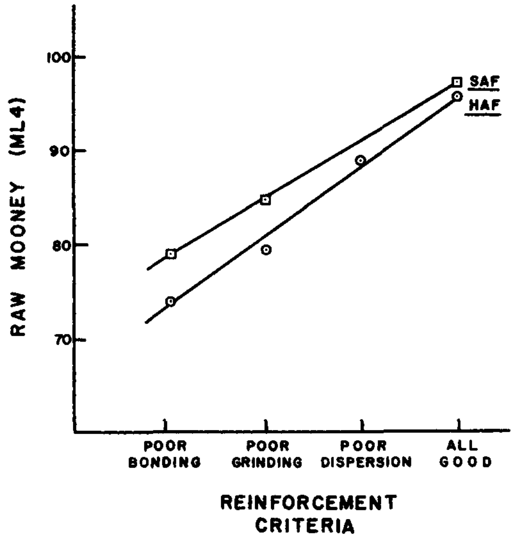

Fig. 5. Effect of reinforcement criteria on raw Mooney viscosity.

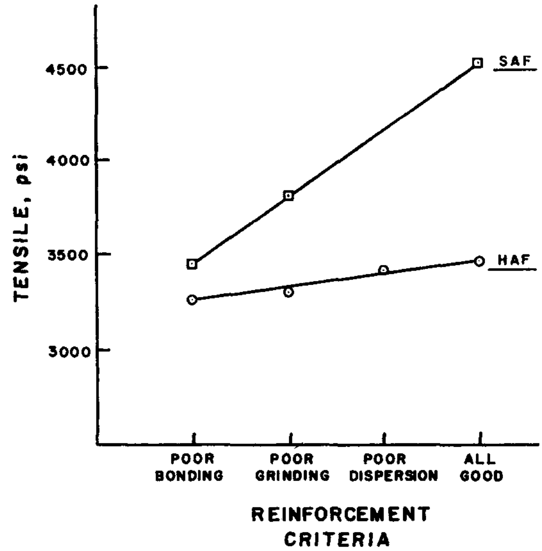

Fig. 6. Effect of reinforcement criteria on tensile strength.

For a given base polymer and carbon black it therefore appears possible to predict the quality of carbon black incorporation in the polymer from the measurement of the raw Mooney viscosity of the stock.

Variation in tensile strength of the vulcanizates with reinforcement criteria is seen in Figure 6. Increased black incorporation produces higher strengths. The greatest effect is seen with SAF-type blacks. This is probably due to the fact that the amount of the black surface available for the formation of the carbon gel complex is greater in SAF than in HAF

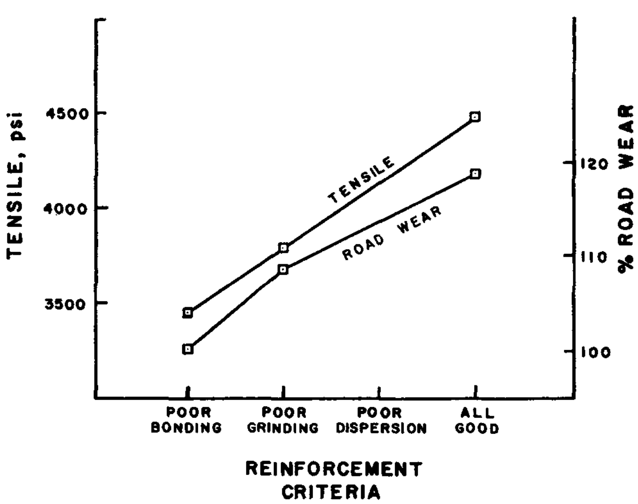

Fig. 7. Effect of reinforcement criteria on tensile strength and road wear.

blacks, the surface average diameter for SAF being approximately 225 A. as against 425 A. for HAF black.

The results of a program relating reinforcement criteria, tensile, and road wear are presented in Figure 7. Failure to obtain good dispersion, grinding, or bonding produces a striking decrease in road wear. Similar results were found in the case of stocks reinforced with HAF blacks.

Conclusion

With the advent of wet masterbatching methods, which provide a preliminary dispersion of carbon black in latex, techniques for the microscopic evaluation of the quality of this incorporation proved inadequate. Three reinforcement criteria were developed for such evaluations: dispersion, grinding, and bonding.

By using these reinforcement criteria the performance characteristics of a trend stock made with such masterbatches can be predicted fairly reliably.

The correlation of reinforcement criteria and the raw Mooney viscosity of the masterbatch reveals the striking effect of improved carbon black incorporation on this property. With this correlation it should be possible to evaluate masterbatch production on a continuous basis.

References

1. Sweitzer, C. W., W. M. Hess, and J. E. Callan, *Rubber World*, **128**, 869 (1958).
2. Leigh-Dugmore, C. H., *Rubber Chem. Technol.*, **29**, 1303 (1956).
3. Braendle, H. A., *Rubber World*, **136**, 835 (1957).
4. Samuels, M. E., *Rubber Age*, **86**, 649 (1960).
5. Andrews, E. H., and A. Walsh, *J. Polymer Sci.*, **33**, 39 (1958).
6. Ladd Research Industries.
7. Sweitzer, C. W., W. C. Goodrich, and K. A. Burgess, *Rubber Age*, **65**, 651 (1949).
8. Medalia, A. I., and I. M. Kolthoff, *J. Polymer Sci.*, **6**, 433 (1951).

Synopsis

A study was made to establish and define reinforcement criteria for the evaluation of the incorporation of carbon black in black masterbatch. Using replica electron microscopy, examination of the fractured surfaces of black masterbatches indicated that three terms were needed to correlate the quality of this black incorporation with the physical properties of the masterbatch. These are, in order of increasing effect on vulcanizate properties: dispersion, grinding, and bonding. Using these reinforcement criteria the performance characteristics of a tread stock made with such masterbatches can be predicted with good reliability.

Résumé

Nous avons effectué une étude en vue d'établir et de définir un critère de renforcement pour évaluer l'incorporation de noir de fumée dans un masterbatch de noir. Par l'emploi de la technique de microscopie électronique duplicative nous avons examiné les surfaces fissurées de ces noirs et établi trois conditions pour relier la qualité de l'incorporation du noir animal aux propriétés physiques du masterbatch. Ces conditions sont, dans l'ordre d'augmentation des propriétés vulcanisantes: la dispersion, le broyage et la pouvoir liant. L'utilisation de ces critères de renforcement permet de prévoir avec une bonne reproductibilité les performances caractéristiques d'un stock obtenu à partir de tels masterbatches.

Zusammenfassung

Die Aufstellung und Definierung eines Verstärkungskriteriums zur Bewertung des Einbaus von Russ in Kautschuk-Russmischungen wurde untersucht. Die Prüfung der Bruchflächen der Mischungen mit Replica-Elektronenmikroskopie zeigte, dass man drei Terme benötigt, um die Güte der Russaufnahme mit den physikalischen Eigenschaften der Mischung in Beziehung zu bringen. Diese sind, in Reihenfolge des steigenden Einflusses auf die Vulkanisateigenschaften: Dispersion, Mahlung und Bindung. Unter Verwendung dieser Verstärkungskriterien kann die Verwendungscharakteristik eines aus diesen Mischungen erzeugten Materials verlässlich angegeben werden.

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