

# CARBON BLACK: Sub-Micron Dispersion

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One of the most important parameters of a given rubber compound reinforced with Carbon Black is the micro dispersion of the filler. This micro dispersion governs the fundamental viscoelastic response of the compound. Indeed this micro dispersion is responsible for a ratio of the filler-filler to polymer-filler interactions. It is shown in this paper that the electrical measurements are well adapted to give valuable information on the state of micro dispersion of the Carbon Black.

## 1. INTRODUCTION

The way a new product is developed, especially on the ever-narrowing time constraint, has influenced the demands on basic technology.

One of the keys of today's success is to understand the material behavior and the relationships existing between its fundamental physicochemical properties and the quality of the final product.

Far from solving all of the aspects of an important segment of tire technology, the present paper proposes to shed some light on the influence of the Carbon Black micro-dispersion on the compound properties.

## 2. THE RUBBER COMPOUND

The main component of a pneumatic tire is the rubber compound. Composed of a mixture of an elastomeric matrix and rigid filler, its exact composition will depend on its role in the tire architecture. Other chemicals are used to crosslink the elastomers, avoid oxidative degradation, ease processing, etc.

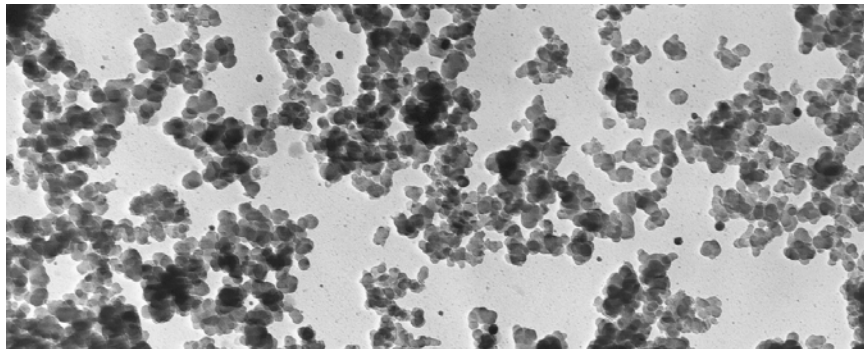


Figure 1

In spite of all these variations, all rubber compounds can be described as two interpenetrating networks. From Figure 1 (TEM image) it clearly appears that some microvolume of polymeric networks are totally unaffected by the filler whereas the filler

itself appears as a network of clusters of different sizes. One still remaining important question is the presence or absence of polymeric chains in the filler cluster voids. Because of the densification of the filler during manufacture it may be quite reasonable to hypothesize that some of these clusters are not filled with polymeric chains.

The local variation of filler cluster density may be considered as the “filler dispersion” and it is being shown in this paper that this dispersion is by far the most important parameter influencing the physical behavior of the rubber compound.

It is also obvious that a lower local cluster density, a good micro-dispersion, will allow more filler surface to be in contact with the polymeric matrix, forming a less compact filler network.

It is also to be noted that the filler mono-unit, in this case an aggregate of carbon black, is a rigid object. The clusters or agglomerate, which make up the carbon black network, is what is being deformed upon strain energy input.

The polymeric network is composed of elastomeric chains characterized by a degree of mobility (depending on the elastomer structure, crosslink density, etc) and chemical unsaturation. These polymeric chains also undergo deformation upon strain energy input.

The filler-filler and the polymer-filler interactions are recognized as the important parameters of the physical properties of the final product. The micro-dispersion of the filler will govern the ratio of these two types of interactions.

### 3. THE CARBON BLACK SURFACE

A considerable amount of work has been done in the last 50 years to better define the exact nature of carbon black.

The usage of the TEM as an analytical tool has provided important information concerning carbon black's shape, size and structure. The reader is referred to the numerous publications of W. Hess, which were published for the last twenty years in the ACS Rubber Division journal: Rubber Chemistry and Technology.

Other techniques such as X-Ray scattering begun in the late thirties shed some fundamental light on the crystallographic nature of the carbon black.<sup>[1]</sup> These types of studies have been redone in the late 80's with similar findings.<sup>[2]</sup>

The advent of the Scanning Tunneling and Atomic Force microscopy has provided additional information on the nature of the surface of carbon black. The pioneering work of Prof. Emeritus J. B. Donnet<sup>[3]</sup> has opened the door to a large number of publications using these modern techniques.

At the same time, small angle neutron (SANS) and X-Ray (SAXS) Scattering techniques have contributed to further understanding this material.<sup>[4,5]</sup>

Raman Spectroscopy, another interesting technique, was used by Prof. Zerda<sup>[6]</sup> to confirm the existence of several carbon species on the surface of the carbon black.

It is absolutely remarkable to realize that all furnace grade carbon blacks have very similar surfaces. Indeed, it has been shown by numerous methods that crystallites have a stacking height  $L_c$  varying from 12 to 16 Å (depending on the grade of carbon black, the finer black having the smaller  $L_c$ ) and an  $L_a$  dimension (width of the crystallite) of around 25 Å for all grades. [7]

The amorphous carbon, which can be described as a highly “defective” graphitic plane, which may also contain  $C_5$  and  $C_7$  rings, is characterized by the presence of  $sp^3$  carbon hybrid. This makes the content of the hydrogen on the surface of the carbon black a very informative parameter.

The conduction electrons associated with the graphitic structure plays an important role in the amount of energy associated with these sites. Recently Schroeder and Schuster [8] have quantified the energies at similar sites on the surface of carbon black.

Using FTIR spectroscopy and volumetric gas adsorption, they have identified four different sites characterized by 4 different characteristic energies. Figure 2 represents these different sites and their corresponding energies, ranks as follows:  $I < II << III \square IV$ .

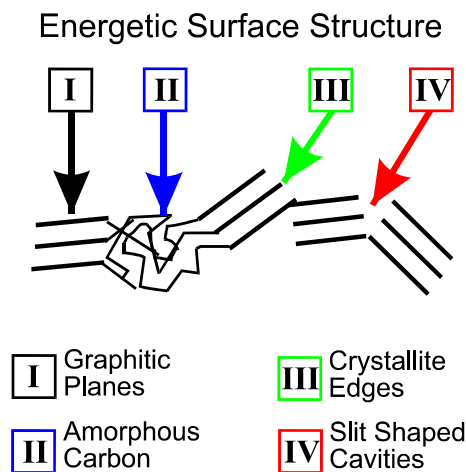


Figure 2

These sites are responsible for the filler network formation and for the polymer-filler interactions. Because of the relatively low energies of these sites, weak interactions between sites on the carbon black surface and the unsaturation in the polymer backbone may prevail (London, Van der Waals...). However, due to the large number of such sites the cumulative effect is significant.

#### 4. THE ELASTOMERS

The rubber industry, in particular the tire industry, is using elastomers which are characterized by a relatively low modulus but extremely high elongation at room temperature when compared to most ordinary materials.

The most commonly used of the elastomers in the tire industry are

- Natural Rubber (NR)
- Styrene-Butadiene Rubber (SBR)
- Butadiene Rubber (BR)

The materials are characterized by long, flexible chains. All these elastomers are used in their rubbery plateau and their glass temperature transition (DSC measurements) varies from around  $-100^{\circ}\text{C}$  for the BR to around  $-25^{\circ}\text{C}$  for special SBR's. Also, all these chains possess unsaturations in their backbone and for some dangling styrene or vinyl groups. These groups and the unsaturated segments of the backbone provide a source of  $\pi$  electrons ( $sp^2$  carbon atoms) susceptible to interact with the  $\pi$  electrons on the surface of the carbon black as described above.

This unsaturation in the backbone also plays an important role in sulfur vulcanization. [9] It is to be noted that only a relatively small amount of unsaturation (less than 5%) is used for crosslinking. Therefore the remaining unsaturation plays an important role in polymer-carbon black interactions.

## 5. FILLER DISPERSION

Carbon black is used in form of pellets. These pellets are obtained by mechanical densification of the original "fluffy" material and have an apparent specific gravity of  $0.4\text{g/cm}^3$ .

These pellets are normally introduced into the rubber mixer (i.e., banbury) once the polymer has been masticated. The "destruction" of the pellets is essentially obtained by shearing forces created by the mixer blades. It is possible to imagine that, once the pellet has been reduced to a much smaller size, the shearing forces are no longer effective for further size reduction. This may result in aggregates which are not distributed in the matrix of polymer since they are part of an original agglomerate.

It is most likely that at this stage of the process the interactions between the filler surface and the polymer chains has the largest influence. The more interactions, the more carbon black will be taken away from the original pellet and be distributed in the rubber matrix. This mechanism may explain the mode of disintegration of the pellets. [10] It is therefore appropriate to evaluate filler dispersion at a scale adapted to the aggregate size, the submicron length.

Several techniques exist [11] to approximate the degree of dispersion, but an absolute quantification of that dispersion of aggregates in 3-D space is still missing. A review of the possible methods [12] to assess dispersion highlight the following techniques:

- Microscopy
- Reflectometry
- Mechanical Scattering Microscope
- Electrical Measurements...

As indirect method, electrical resistivity measurement, have been used successfully to assess the degree of dispersion of carbon black in rubber. In particular it has been shown [13] that the electrical percolation threshold  $E_p$  is linked to dispersion.  $E_p$  being the smallest amount of carbon black required to attain percolation (Figure 3). The larger this  $E_p$  for a given carbon black, the better the dispersion.

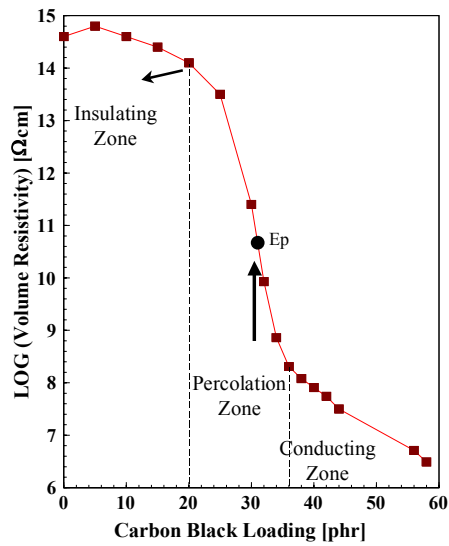


Figure 3

The result on Figure 4a indicates that this threshold is polymer dependent. The results show that Sn-SSBR disperses a given carbon black much better than NR for example. It is also remarkable to realize (Figure 4b) that this percolation threshold is directly related to the polymer solubility parameter<sup>[14]</sup>. This solubility parameter  $\delta$  being related to the unsaturation of the polymer chain it is reasonable therefore to relate the elastomer ability to disperse carbon black to the interactions between the carbon black surface and the polymeric unsaturations. In particular as shown in Table 1 the styrene content of the solution SBR is related to the percolation threshold  $E_p$ .

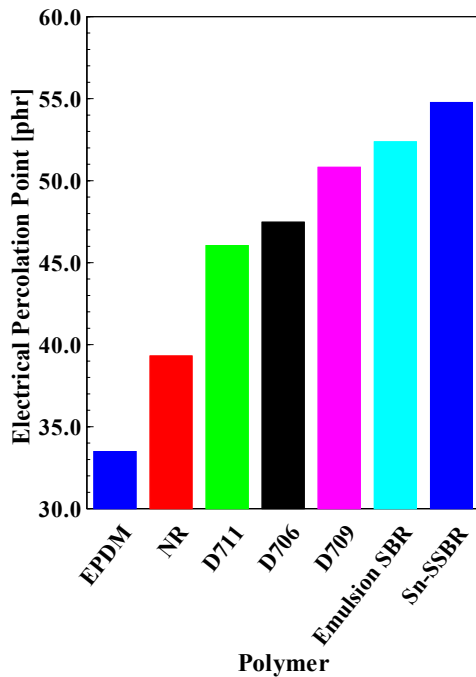


Figure 4a

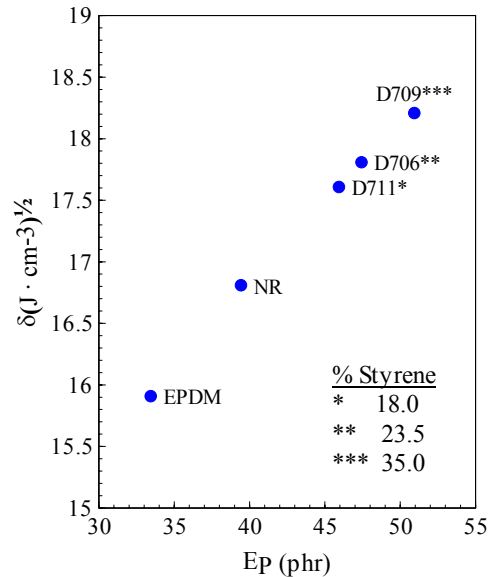


Figure 4b

% Styrene	EP (phr)	$\bar{\delta}$ (sol. parameter)
18	46	17.6
23.5	47.5	17.8
35	51	18.2

Table 1

On the other hand, the usage of electrical resistivity around the percolation threshold is also useful to determine the potential and/or the kinetic of dispersion for a given polymer.

As an example, Figure 5 highlights such a behavior showing that Sn-SSBR disperses the filler faster than solution SBR-D706. Indeed, as a function of mixing time, the depercolation effect is much faster with the first polymer than with the second one; hence a better dispersion. Where depercolation is defined as a breakup of a continuous electrical current, because of the separation of initial percolated agglomerate.

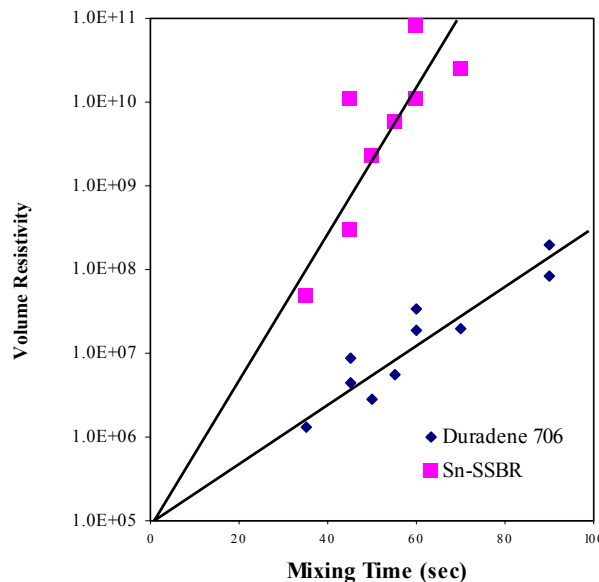


Figure 5

This again may be attributed to the interaction of the filler surface with the polymer. Obviously in this particular case, the nature of the polymer's microstructure must also play an important role.

## 6. ROLE OF THE CARBONBLACK DISPERSION IN RUBBER COMPOUNDS

The Carbon Black dispersion governs the compound material interactions.

- At low frequency and for strains below 50%, the filler-filler interactions play the major role. The effect of these interactions is to create a filler network which upon straining dissipates energy (friction) in the form of heat.

This may be beneficial if one wants to avoid any undo amount of stored elastic energy, which could be responsible for crack formation and propagation. But in today's world, where fossil fuel has to be spared, this energy dissipation can be viewed as a negative (i.e. high hysteresis).

This negative can be addressed by a less dense filler network, which may be achieved by a better dispersion of the filler.

- At high frequency, characteristic of the road/tire tread interface where the deformation is very minute, the reduced mobility of the polymeric chains, due to their interaction with the carbon black, is responsible for energy dissipation required for good traction.

This can be enhanced by increasing these types of polymer-filler interactions. Once again, a good filler dispersion will allow more carbon black surfaces to be in contact with the polymeric matrix, hence increasing the desired interactions.

- It appears therefore that a better filler dispersion will be beneficial for both of these fundamental characteristics of a tire: Rolling Resistance and Traction

It is interesting to note that in order to achieve a better dispersion during mixing, the interactions between the polymer and the fillers may play an important role besides the mechanical aspect of mixing.

## 7. CONCLUSIONS

Considering a modern tire compound, it has been shown that the materials interactions play a very significant role. This paper also indicates that a good dispersion may well solve the problem of the so-called magic triangle. Indeed a good dispersion improves all fundamental tire properties.

To achieve a good dispersion obviously both the carbon black and the polymer have to be fine-tuned. This is certainly one of the key objectives of the producers of these materials.

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