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TIRE COMPOUND MATERIALS INTERACTIONS

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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. The balance between these two types of interactions is dictating the most relevant properties of the finished product like a tire.

Introduction

The way a new product is developed, especially on the ever-narrowing time constraint, has influenced the demands on basic technology. In the past the trial and error approach was accepted as a mean of developing materials necessary to satisfy the industrial demand. This is no longer true.

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. This requires fundamental research.

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Far from solving all of the aspects of an important segment of tire technology, the present paper proposes to shed some light on the materials interactions in the rubber compound.

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. It is not uncommon to have more than half a dozen different compounds in a tire; they vary by their polymeric composition (types, blends...) and the type and amount of filler to only mention the most important component of such a compound. Indeed other chemicals are used, i.e., to crosslink the elastomers, avoid oxidative degradation, ease processing, etc.

In spite of all these variations, all rubber compounds can be described as two interpenetrating networks. From Figure 1 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 questions 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.

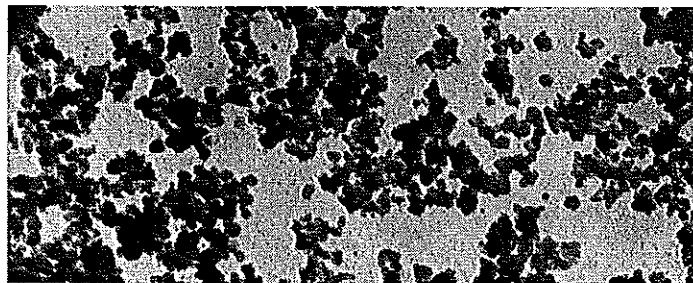


Figure 1. TEM image. (20,000x)

The local variation of filler cluster density may be considered as the “filler dispersion” and it will be seen later 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 will allow more filler surface to be in contact with the polymeric matrix. Therefore it appears that the

magnitude of material interactions, filler-filler; and polymer-filler will be paramount to the physical properties of the composite.

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. A poor micro-dispersion will favor the Filler-filler interactions; whereas a good micro-dispersion will enhance the polymer-filler interactions.

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.⁽¹⁾ These types of studies have been redone in the late 80's with similar findings.⁽²⁾

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⁽³⁾ 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.^(4,5)

Raman Spectroscopy, another interesting technique, was used by Prof. Zerda⁽⁶⁾ to confirm the existence of several carbon species on the surface of the carbon black.

The Sid Richardson model of a carbon black aggregate, in Figure 2, intends to summarize the nature of that surface where turbostratic graphitic crystallites are present beside areas of amorphous carbon.⁽⁶⁾

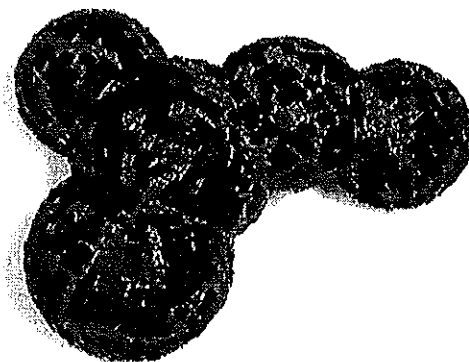


Figure 2. Sid Richardson model of a carbon black aggregate.

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 above mentioned crystallites and amorphous areas appear to be the major component of the carbon black surface. Indeed, microporosity and chemical groups containing hetero atoms are very minimal, if any, and do not seem to play an important role as is sometimes mentioned in the literature. (This most likely is a holdover from early studies made on Channel black which did contain a lot of oxygenated groups).

In considering this type of surface, different sites can be assigned.

- The boundaries between two crystallites
- The boundaries between crystallite and amorphous areas
- The graphitic surface of a crystallite
- The surface of the amorphous carbon

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 3 represents these different sites and their corresponding energies, ranks as follows: $I < II \ll III \leq IV$.

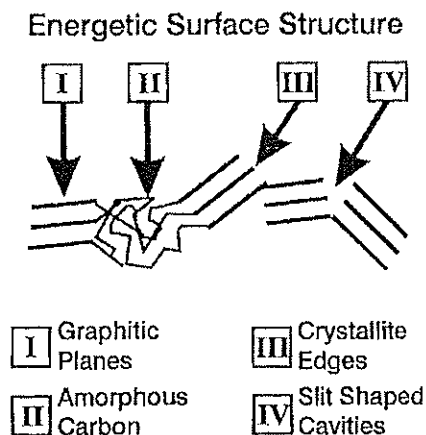


Figure 3. Energetic Surface Structure.

It is reasonable to hypothesize that these sites will play an important role in the material interactions in a carbon black-filled rubber compound. In particular, 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/or the unsaturation in the polymer backbone may prevail (London, Van der Waals...). However, due to the large number of such interactions the cumulative effect is significant.

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°C for the BR to around -25°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 π electrons (sp^2 carbon atoms) susceptible to interact with the π 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.

The Materials Interactions

An excellent review of the subject was given by Waddell ⁽¹⁰⁾ for carbon black and non-polar elastomers such as natural rubber, styrene butadiene, and butadiene rubber; the dispersive forces are the primary contributors to the attractive energy. In these systems, the polarizability of the electrons of the rubber molecule then can become an important consideration, explaining the stronger interactions observed between carbon black and styrene-butadiene rubber than for natural rubber and other nonpolar elastomers. The polarizability of styrene-butadiene is primarily associated with the delocalized π electrons on the phenyl ring.

One effect that such interactions will have on the elastomeric chain is to reduce its mobility. It will therefore affect the relaxation spectrum of the elastomer. This property will be used to quantify these interactions.

In a rubber compound, besides the polymer-filler interaction, the filler-filler and polymer-polymer interactions are also present. One also should keep in mind that mechanical entanglement may also play an important role, but it will not be discussed in this paper. The following comments are directed to the interactions involving carbon black.

Filler-Filler Interactions

The effect of the filler-filler interactions is very well known, and its effect is sometimes referred to as the Payne effect. Numerous studies have been published on the subject.^(11,12)

Figure 4 highlights the effect of these filler-filler interactions on the response of a typical carbon black filled compound to low frequency dynamic strain energy input (rotational shear, 1Hz. Strain Sweep, 0.1% - 10%). The graph referred to as a <G-Plot>⁽¹²⁾ can be divided into two domains.

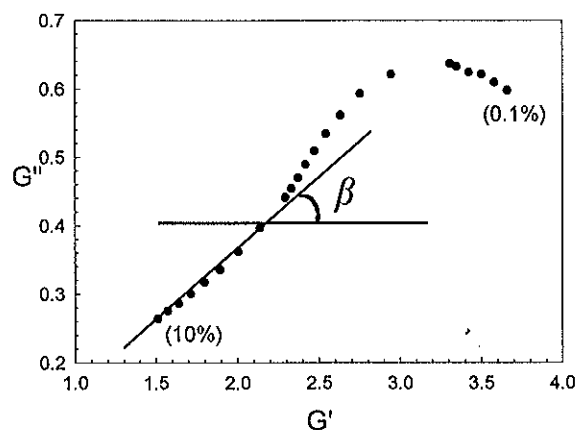


Figure 4. *G-Plot of a typical carbon black filled compound.*

- Domain I, Characteristic behavior when the initial filler network loses its cohesion at strains lower than 10%. G' and G'' are quadratically dependent (Cole-Cole).

- Domain II, For strains between 10 and 50%, the initial network is destroyed, and the carbon black aggregates are present in non-contacting clusters and not individual aggregates. G' and G'' are linearly dependent.

These clusters or sub-networks are further broken down in sub clusters (sub-subnetworks) under additional straining. ⁽¹¹⁾ It is worth mentioning that at these strains, the linear relationship between G' and G'' extends to the origin of the axes ($G' = G'' = 0$). This clearly indicates that for strains below 50% the filler plays the most important role as long as the frequency of deformation is small (< 100% Strain). This may well be explained by the relaxation spectrum of the polymers since at these frequencies the polymeric chains are in a quasi-relaxed state and have little input in energy dissipation. The situation reverses itself at very high frequencies as described below.

Filler-Polymer Interactions

In order to probe a rubber compound at high frequency it is necessary to have a system of excitation, which moves masses of material. Since the mechanical actuators are limited in frequency, an acoustic technique was developed. ⁽¹³⁾

In this technique, a frequency of 1MHz is used and the corresponding deformation is very small (10^{-9}). In this type of strain energy input, the integrity of the network of carbon black in the rubber compound is not affected. Nevertheless, at these frequencies, the mobility of the polymeric chains is probed. In particular, as it is very well known, an increase in the testing frequency shifts the polymer " T_g " towards higher temperature.

Figure 5a shows the variation of the attenuation coefficient with temperature. When compared to the unfilled compound, the shift for the filled SBR compound of the maximum of the attenuation coefficient and the larger Full Width at Half Maximum (FWHM) of its " T_g " peak can be explained by a reduction in the polymer chain mobility. This reduction in mobility is the signature of the interaction of the polymer and the carbon black surface

Figure 5b shows the same type of measurement for a system using a butyl rubber known to have very little amount of unsaturation before vulcanization and practically none after. This result indicates that in the absence of possible interaction between the polymer and the filler, the overall polymeric mobility is not affected.

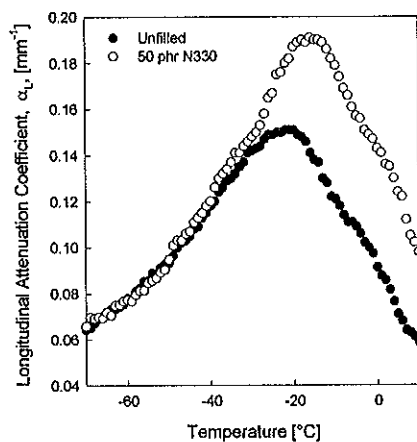


Figure 5a. EPDM

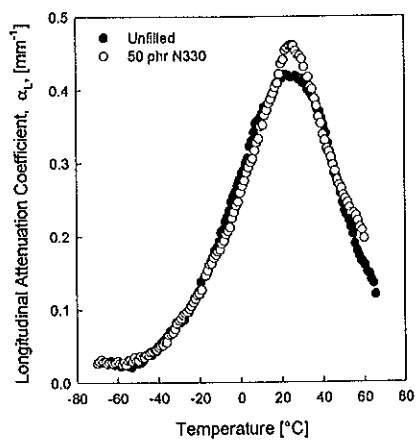


Figure 5b. Butyl

Figure 6 shows the result of a study made with one polymer (S-SBR) and different fillers. (Table I) It clearly shows that the carbon black with a higher specific surface area immobilizes more of the polymeric chains because of the larger total surface available per unit mass. The case of the XLH82, which has an intermediate surface area (smaller than N299), exhibits a higher FWHM. This may be explained by the outstanding dispersability of this carbon black in this elastomeric matrix.

Table I. Specific Surface Areas (N_2 SA)

| Filler | Specific Surface Area (m^2/g) |
|--------|-----------------------------------|
| N234 | 120 |
| XLH82 | 80 |
| N660 | 35 |
| N772 | 31 |

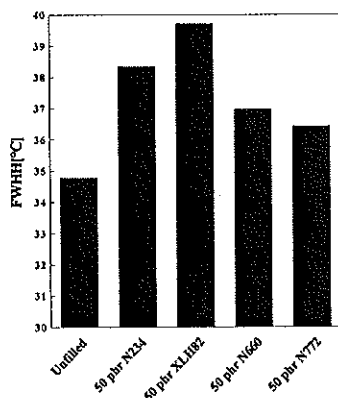


Figure 6. S-SBR

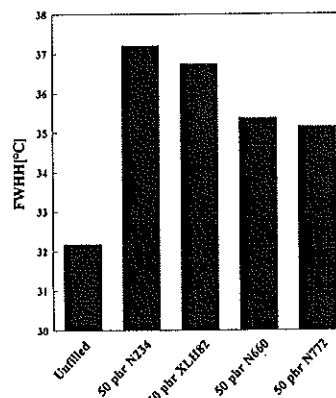


Figure 7. Sn-SSBR

This phenomenon is nevertheless polymer dependent. Figure 7 shows identical results as in Figure 6, but using a polymer (Sn-SSBR) which is known to disperse fillers well.

The two above-mentioned results outline the most important properties of the materials used to make a rubber compound.

- Dispersibility of Carbon Black
- Dispersion potential of the polymer

The following describes these two fundamental properties, which depend on material interactions.

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 0.4g/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.⁽¹⁴⁾ It is therefore appropriate to evaluate filler dispersion at a scale adapted to the aggregate size; the submicron length.

Several techniques exist⁽¹⁵⁾ to approximate the degree of dispersion, but an absolute quantification of that dispersion of aggregates in 3-D space is still missing.

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⁽¹⁶⁾ that the electrical percolation threshold E_p , the loading at which a sudden decrease in electrical resistivity occurs, is linked to dispersion. E_p being the smallest amount of carbon black required to attain percolation (Figure 8). The larger this E_p for a given carbon black, the better the dispersion.

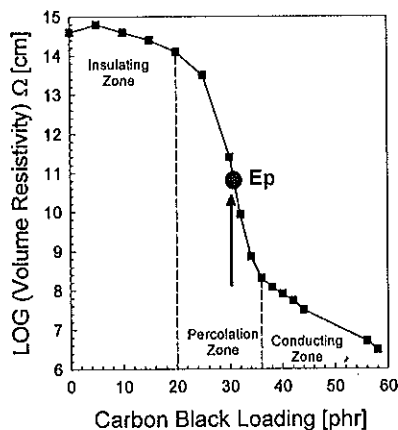


Figure 8. Percolation Point

The result on Figure 9a 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 9b) that this percolation threshold is directly related to the polymer solubility parameter⁽¹⁷⁾. This solubility parameter δ 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 I the styrene content of the solution SBR is related to the percolation threshold E_p .

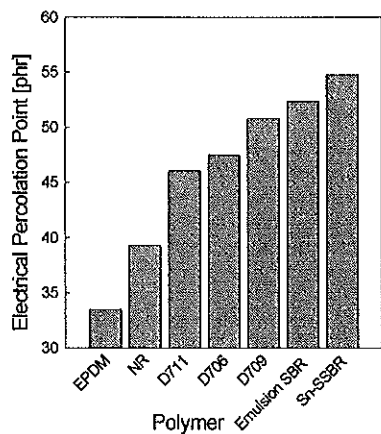


Figure 9a.

EP for Different Polymers

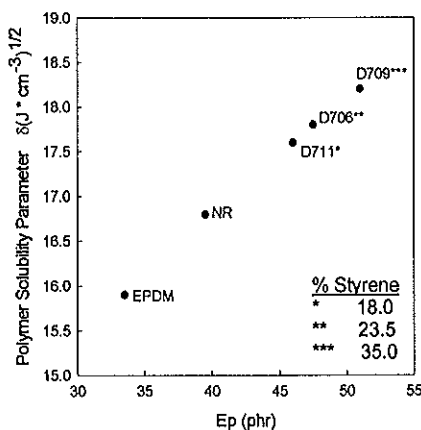


Figure 9b.

Ep vs. Polymer Solubility Parameter

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.

Table II. Percolation Threshold Relations

| % Styrene | EP (phr) | δ (sol. parameter) |
|-----------|----------|---------------------------|
| 18.0 | 46.0 | 17.6 |
| 23.5 | 47.5 | 17.8 |
| 35.0 | 51.0 | 18.2 |

As an example, Fig 10 highlights such a behavior showing that Sn-SSBR disperses the filler faster than solution SBR-D706 at a 40 phr level. 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.

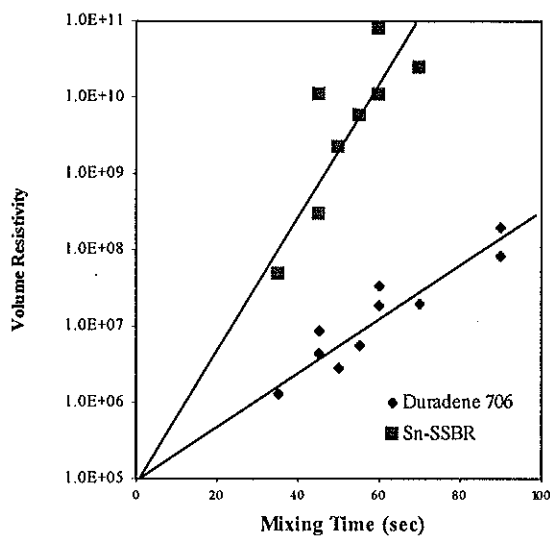


Figure 10. Polymer Dispersion

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.

Role of the Materials Interactions in the rubber compound

It is very clear that without these physico-chemical interactions, the cohesion of the rubber compound would be of a totally different nature. The complexity of the system due to all parameters of the materials present makes the mechanistic understanding a difficult endeavor. Nevertheless, these material interactions may explain some aspect of the mechanical behavior of carbon black loaded elastomers when subjected to strain energy input.

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 undue 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.

Therefore, it appears 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.

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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