

# CARBON BLACK-ELASTOMER COMPOSITES

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## **Generalities**

In the rubber industry Carbon Black is, in general, used combined/mixed with an elastomer. This composite also contains other ingredients such as the extenders (oil), the anti-degradant and accelerating agents. Such a composite is referred to a Rubber Compound.

The change in the mechanical and dynamic properties of tire compounds imparted by the incorporation of fillers in the elastomer matrix is known since almost a hundred years. This phenomenon is vital to modern tire technology and is still not described in a perfectly satisfactory manner although a huge amount of research work has been devoted to it.

It has been shown (1,2) that the surface of the aggregate is covered with turbostratic crystallites of finite dimensions and regions of a lesser order referred as amorphous carbon. Such a surface is characterized by a highly heterogeneous distribution of so called "active sites". These "active sites" are located at the edge of the crystallites and are essentially areas rich in conduction electrons. These active sites are the key to understand the material interactions within a carbon black containing rubber compound

### **A. Reinforcement**

There have been many review papers published in the last decades and they have to be referred to for more details (3, 4, 5).

Since these first important publications a large amount of work has been done to understand the mechanism(s) by which Carbon Black modifies the physical properties of filled Rubber Compound.

In 1993, a comprehensive review (15) was published and all the experts who have contributed to this book have spent a considerable amount of time and

energy towards this fundamental endeavor, which is to explain the reinforcement mechanism of Carbon Black. This book certainly constitutes today the reference of choice for material scientist interested in this subject.

### **1. Dynamic Responses of Rubber Compounds**

The demanding requirements of modern tires have been the source of a large amount of research for improved tire compounds, in particular tire treads. Tires that must exhibit a low rolling resistance (low energy dissipation through heat) good traction and excellent wear performances are all characterized by the fact that those characteristics will depend on the dynamic and not static response of the filled rubber compound.

This explains why that in the past two decades the dynamic testing of rubber compounds has undergone extreme development. This type of testing, using advanced techniques is becoming more and more mandatory since a running tire is subjected to cyclic deformations of its components.

When considering the tread compounds specifically, it is easy to understand that this part of the tire will undergo two different types of deformation.

- a) A low frequency deformation corresponding to the overall tire rotation (less than 25 Hz).
- b) A very high frequency deformation at the tire/road interface.

The response to these two fundamental and different types of deformations is required to explain the overall tread performance. It is therefore judicious to study a rubber compound under these two types of deformations to understand the contribution of Carbon Black.

#### **1.1 Role of Carbon Black in Compound Viscoelasticity at Low Frequency**

**Generalities:** The viscoelastic nature of elastomers has been the subject of tremendous amount of work and theories, all of which are well documented in the literature (6, 7). It would be quite a task, and it is not the object of this paper, to review all of these studies and theories, which still today constitutes a very active field in polymer physics.

It is clear that the elastomers commonly used in tires are, at low frequency deformation, operating in their rubbery plateau. An unfilled elastomer in the rubber plateau when undergoing a dynamic strain sweep,  $\gamma = \gamma_0 \sin(\omega t)$ , exhibits in general and in first approximation a linear behavior translated by a complex modulus

$$G_u^* = G_u' + iG_u''$$

which is independent of the strain amplitude (Figure 1). This fact is also verified when the elastomer is crosslinked with conventional vulcanizing agents.

The presence of Carbon Black in quasi-linear viscoelastic elastomer changes its linear characteristic to non-linear behavior, clearly described by the strain dependence of the complex modulus on the strain amplitude (Figure 1-2).

$$G_f^* = G_f'(\gamma) + iG_f''(\gamma)$$

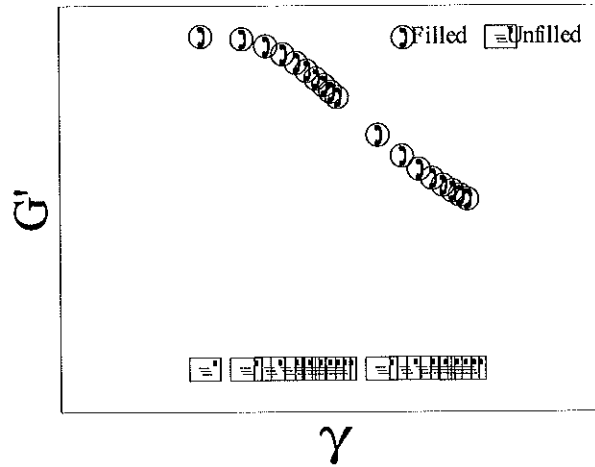


Figure 1.

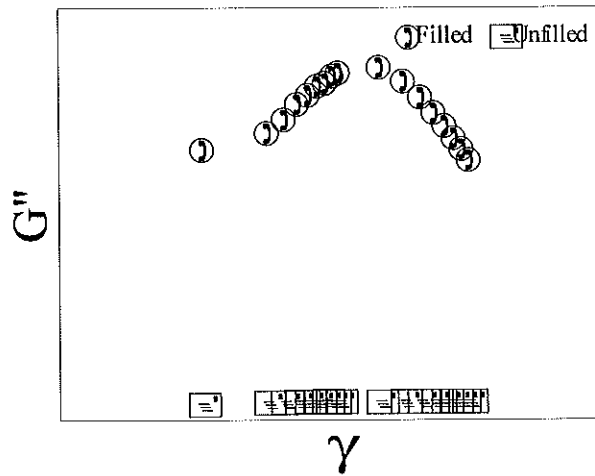


Figure 2.

The strain therefore appears to be the most important testing parameter to study the role of Carbon Black in rubber compounds subjected to low frequency deformation. Figure 2 clearly indicates that both  $G'_f$  and  $G''_f$  are strain dependent, and both are relevant to characterize the filler reinforcement potential.  $G'_f$  is indicative of stored elastic energy whereas the dissipated energy is proportional to  $G''_f$  (6, 7). It therefore appeared judicious to consider  $G'_f = f_1(\gamma)$  and  $G''_f = f_2(\gamma)$  as a parametric representation of a more general equation

$$G''_f = F_3(G'_f)$$

The representation of this last equation (Figure 3.) is referred to as <G-Plot>(8) and allows for a more insightful understanding of the mechanism of Carbon Black reinforcement.

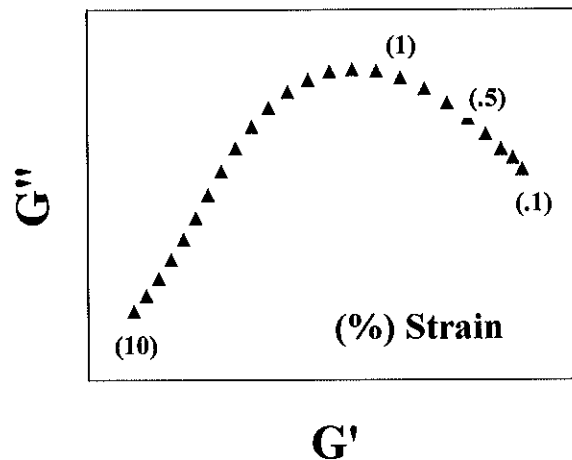


Figure 3.

**At Low Strain (below 10%):** all furnace Carbon Black and elastomers generally used in the rubber industry behave the same way.

It was shown (9) that by considering individual <G-Plots> one was able to shift all these <G-Plots> to a "master curve", indicating that whatever the type of Carbon Black employed the mechanism responsible for the variation of  $G'$  and  $G''$  with strain is unique and similar in nature for all Carbon Black. Nevertheless the magnitudes of these modulus are, as one would expect. Carbon Black type dependent.

This observation allows one, within the strain range studied, to postulate a unique reinforcement mechanism for all grades of Carbon Black. The proposed mechanism is that once mixed in a rubber compound and after percolation, the filler forms a continuous network, which upon straining is disrupted. This breakdown of the continuous network is responsible for both the decrease of  $G'$  and the "bell shaped" curve of  $G''$  when plotted against strain  $\gamma$ .

It was also previously shown (10) that this network, when tested at a very low strain (0.1%) can be disrupted by thermal motion. In fact the Carbon Black network exhibits a typical temperature dependency with a statistical breakdown around 90°C to 100°C. A well marked transition point of the  $\ln G'$  vs.  $1/T$  plot is present at these elevated temperatures, indicating that the sample passes from a state characterized by a continuous filler network to another in which the network is thermally disrupted.

From the initial slope of the  $\ln G'$  vs.  $1/T$  plot it is also possible to quantify the networking energy of Carbon Black. In all cases the energy is in the range units of the Van der Waals or London dissipative type force.

**At High Strain (>10%):** The test results showed that once the network is broken (6%-8% strain) all <G-Plots> exhibit a linear dependence of  $G''$  vs.  $G'$  (Figure 4.). The slope of that straight line is Carbon Black dependent, but once again, a similar type of behavior is observed for all type of Carbon Black studied.

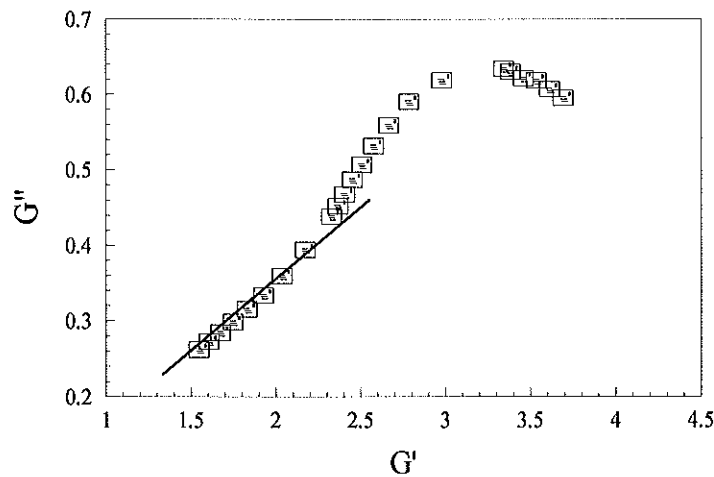


Figure 4.

That linearity in fact extrapolates to the origin of the axes indicating that if the strains tends to infinity the modulus vanishes. Obviously this has no applicable effect since the compound cohesion will at higher strains (>150%) depends on the polymeric chains and the modules will increase again until the sample breaks (maximum of stored elastic energy)

An important property of the tire hystereses depends primarily on lower strain behavior of the carbon black network. The linearity of  $G'$  vs  $G''$  after the breakdown of the network can be explained by dissipation of strain energy at the interfaces between the filler and the polymer. That energy dissipation may be further explained by momentum transfer through fractal interfaces (11).

## 1.2 Role of Carbon Black on Compound Viscoelasticity at High Frequency

The WLF equation (6) is employed to understand and predict behavior of polymers subjected to high frequency deformations. Indeed the equivalence temperature-frequency principle allows one to study polymers at low temperature and low strain and predict high frequency responses. It has been shown that once filled with Carbon Black, the WLF principle no longer holds true valid and experimental results confirm the fact. The small segment of the tire tread in contact with the asperities of the road surface undergoes high frequency deformation. It was therefore judicious to measure the rubber compound high frequency behavior at low strains. One method to accomplish this is using acoustic waves in the MHZ range. (15)

The sample subjected to the ultrasonic wave is experiencing a very low strain well below the strain energy able to disrupt the Carbon Black network. Therefore it seems that the main effect of this wave is to probe the mobility of the polymeric chains. In general the less mobile the polymeric chains the higher the ultrasonic wave attenuation coefficient of the rubber compound. It follows that an increasing polymer/filler interaction will immobilize more polymeric chains and therefore increase the acoustic energy absorbed by the system. This is particularly highlighted by the results shown on Figure 5.

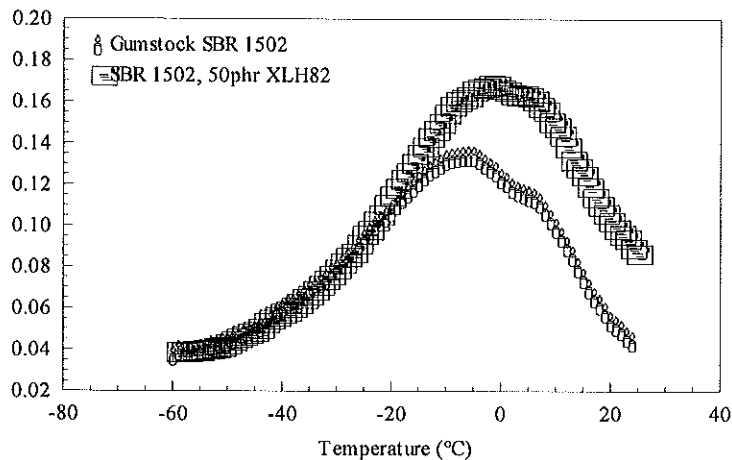


Figure 5

A better dispersion (increased mixing time) exposes more Carbon Black surfaces to polymeric chains, immobilizing them via Van der Waal's type interactions thus increasing the attenuation coefficient. It has been found (16) that the best way to observe this polymer/filler interaction is to evaluate the shift of  $T_g$  of the polymer at high frequency. Figure 6a shows the effect of this interaction with an SBR elastomer (shift in  $T_g$  and broadening of the response) whereas with butyl rubber, Figure 6b,  $T_g$  value is not affected indicating the absence of polymer/filler interaction

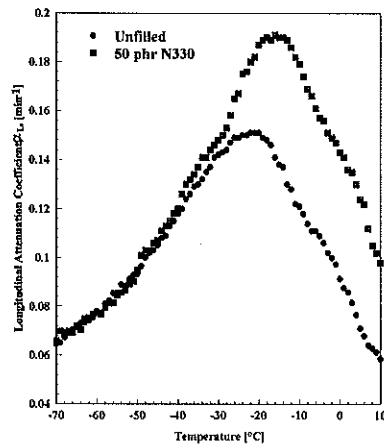


Figure 6a

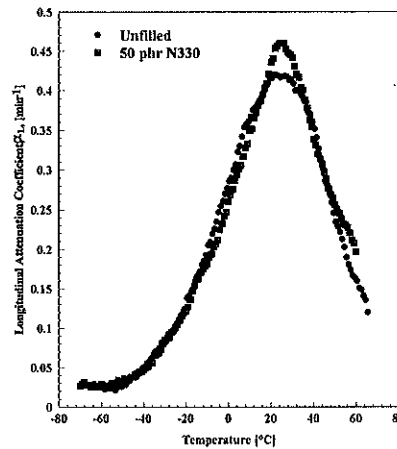


Figure 6b

It has been shown elsewhere that these high frequency viscoelastic properties (1 MHz, very low strain) correlate very well with tire traction.

In summary, in the high frequency region of compound solicitation the Carbon Black plays an important role not through its filler network but through its interaction with the polymer. This highlights the very important effect of the Carbon Black dispersion in the elastomeric matrix.

## 2. Modeling of Low Strain Dynamic Responses

The model of the filler network, interpenetrating the polymer network is not a new one. This hypothesis was already studied in the 70's and all the initial works were reported (4).

The mathematical modeling of this filler networking was made initially in the early 70's (13). More recently (12, 13) a new model was proposed that fits very well the experimental data. This model expresses the complex modulus  $G^*$  as a function of one material dependant weighing function  $W(\gamma)$ .

This W function is used as a measure of the number of interaggregate contacts surviving the strain ( $\gamma$ ) deformation. As the strain amplitude is increased, a greater number of interaggregate contacts are disrupted and therefore the W function is determined by the strength of interaggregate contacts as affected by the surface characteristics of the filler.

The W function is found to increase with the so called nitrogen surface area of the filler and filler loading and decrease with increasing degree of filler dispersion (mixing time) and temperature. At a filler loading of 50 phr, the weighing functions as a function of strain appear to be superposable by a vertical shift, regardless of the filler characteristics, filler dispersion, temperature, and frequency. This observation suggests that the filler reinforcement mechanism is unique and only the magnitude of the reinforcement differs. The magnitude of the vertical shift was found to correlate well with the normalized excess modulus  $\Delta G'$ . The most striking observation is that it appears that regardless of the grade of Carbon Black the behavior at low frequency deformation is similar. The values of the measured modulus are grade dependent but their variations are affined.

This is in parallel with the fact that all Carbon Black surfaces are similar and that only the shape and the size of the aggregate vary for the different grade.

This implies that, if one accepts the hypothesis of a filler network that its behavior will be similar for all grades but its local density fluctuation will vary for different samples.

This density variation is not only a function of the aggregate geometry but also highly dependant on the dispersion of the filler in the elastomeric matrix. This point highlights the essential effect of the mixing process but also emphasizes the filler/polymer interaction, as it will be discussed in the last part of this chapter.

Although this model is generally accepted other models exist. One of the interesting alternative refers to strong and weak adsorption of polymer chains to the surface of the Carbon Black. (14)

Whatever the real mechanism is, it is obvious that it is the conduction electrons on the surface of the Carbon Black, which are responsible for the observed dynamic behavior at low frequency.

## **B. Carbon Black Dispersion**

It has been shown in previous paragraphs that the dispersion of the carbon black is very important and affects both the low and high frequency testing response of the rubber compound. The degree of dispersion affects the local density fluctuation of the carbon black network as well as the amount of carbon black surface available to interact with the polymer.

Figure 7 clearly shows that the better the dispersion (increasing mixing time) the lower the complex modulus (i.e.,  $G'_{max}$ ,  $G''_{max}$  are lower). The data in

Figure 8 clearly indicates that the better the dispersion the higher the attenuation coefficient obtained at 1 MHz testing. This will be translated into lower tread rolling resistance (lower  $G''_{max}$ ) and better traction (higher attenuation coefficient).

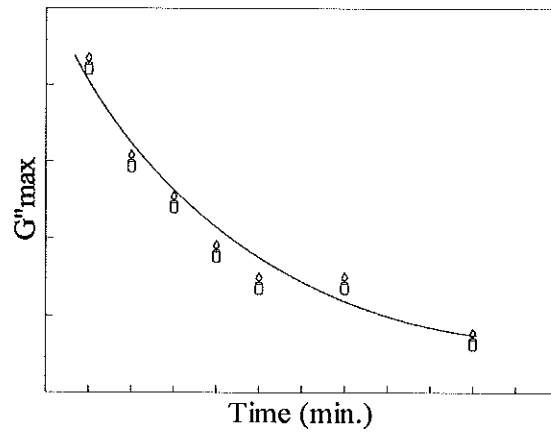


Figure 7.

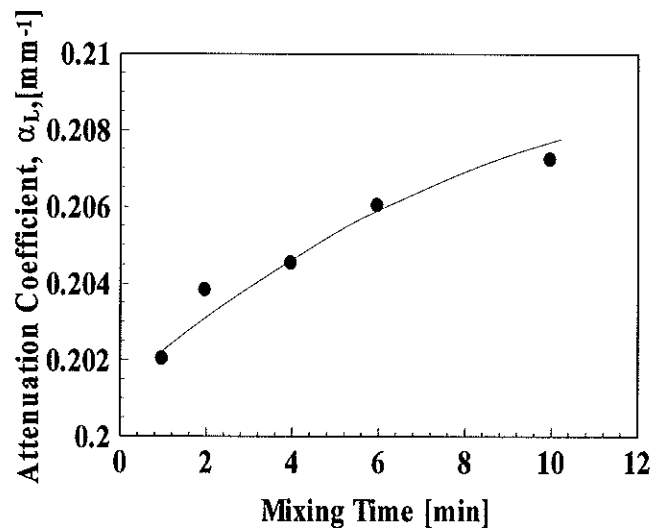


Figure 8.

For other applications, like resistance to crack propagation, a worse dispersion may be preferable. Indeed large agglomerate of undispersed carbon

black may stop the crack propagation, as it is well known in material technology.

The dispersion of the filler is therefore a very, if not the most, important parameter to control during compounding.

One of the challenges to be addressed is the appropriate definition and measurement of the dispersion. Since the aggregate is the mono-unit of carbon black and since it is its surface which plays the active role (both for filler networking and filler-polymer interactions), the dispersion has to be defined at the scale of the aggregate: a sub-micron object.

Figure 9 indicates the relationship existing between the instrumentation available and the length scale at which the dispersion has to be assessed.

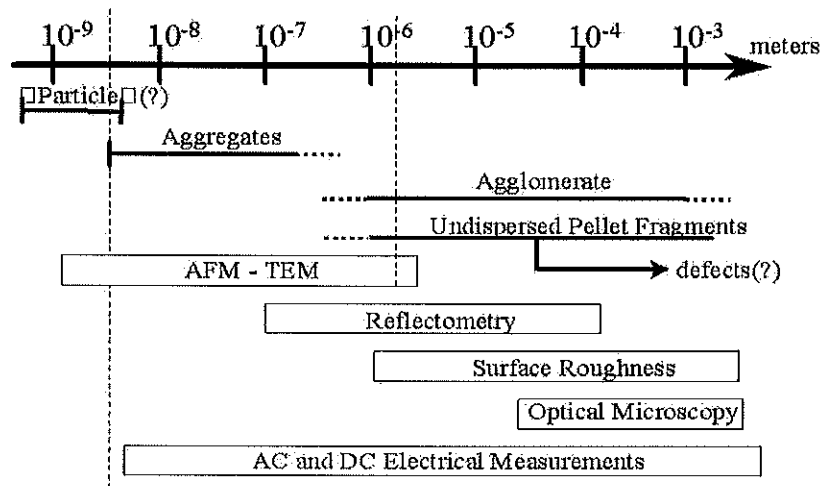


Figure 9.

One can appreciate that the smaller the scale to be investigated the more sophisticated the equipment needed to evaluate it.

If one realizes that in compounds using polymer blends not only the dispersion within one elastomeric phase is relevant but also the distribution of the filler between the different phases is as important, it is easy to understand the complexity of this dispersion measurement of the filler.

Once again it would be too voluminous to cover the whole subject in this chapter. Therefore the reader interested in knowing more on the subject should find interesting articles in the recent literature (17, 18).

However, the filler dispersion is of utmost importance. As far as Tire Rolling Resistance is concerned as well as traction properties it has been shown Figure 13a and 13b that a better dispersal will impart improved properties. As far as tread wear is concerned it was also shown that a better dispersion will improve wear (19).

All these effects can be explained by the fact that improved dispersion increases the amount of possible interaction of filler/polymer, which has a beneficial impact on all these fundamental tread characteristics. For improving filler/polymer interaction it obviously does not depend on the filler alone but also the polymer.

It was shown (20) that for a given family of carbon black an improved dispersion is translated by an increase of the amount of filler necessary to attain the electrical percolation point in a rubber compound.

At the same time it also can be shown that the percolation point for a given carbon black is polymer-type dependent (Figure 10).

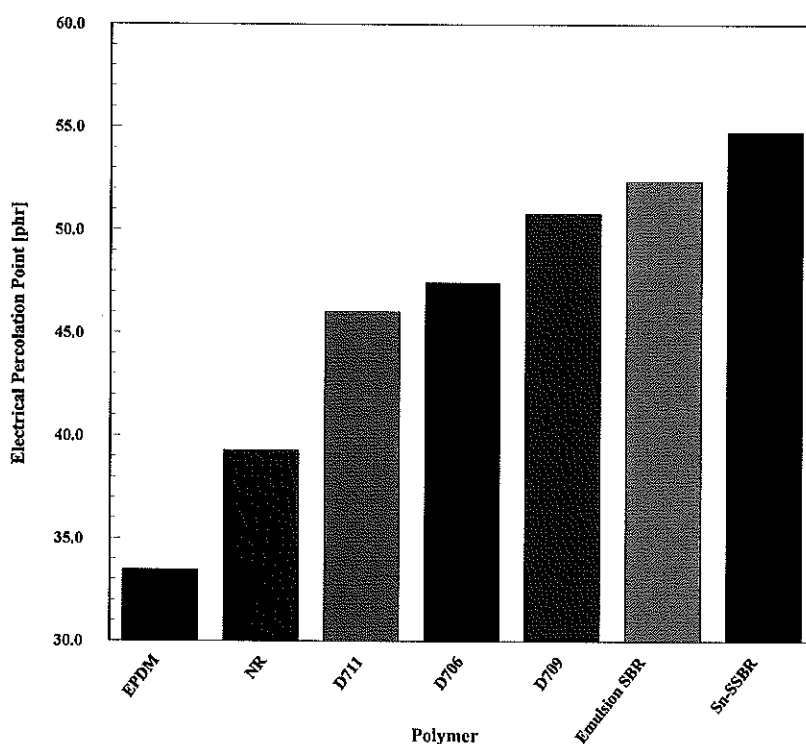


Figure 10.

The solubility parameter  $\delta$  of five of the polymers shown in Figure 10 were evaluated (21). It is remarkable to observe Figure 11 that a definite relationship exists between this solubility parameter and the percolation point. In particular, the more the quantity the conduction electrons in the elastomer the higher the percolation point. This is a clear indication that the more interaction (van der Waal bonds) between the polymer and the filler the better the

dispersion. This highlights the essential role during mixing (filler distribution within the elastomeric matrix) of the polymer/filler interaction.

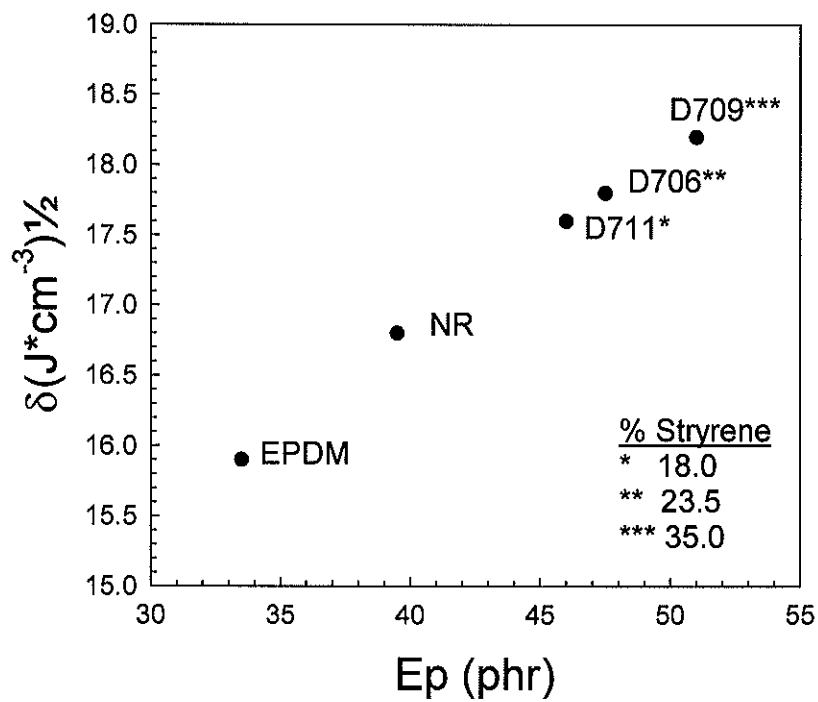


Figure 11.

### C. Conclusion

Carbon black is a very interesting object of fundamental research. Its surface structure is responsible for its interactions with neighboring aggregates and/or polymer chain. These two types of interactions govern the behavior of carbon black in the elastomeric matrix.

The amount of these interactions are polymer-dependent as well as a function of the agglomerate size.

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