

POLYMER/FILLER INTERFACE – ENERGY DISSIPATION

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INTRODUCTION

A tire undergoes various types of deformation when rolling on a road. Part of the strain energy input in such a moving object will be momentarily stored while the remaining is dissipated. This partition of the strain energy input depends both on the carbon black and the polymer and the interface between these two main components of the tire. The energy dissipation in particular appears to be mainly occurring at the interface of the constitutive materials.

I. RUBBER COMPOUND COMPONENT

Rubber compounds are obtained by mixing an elastomer with filler followed by the incorporation of a curing package. Therefore a rubber compound is constituted mainly by two essential and distinct materials: the crosslinked elastomer and the filler (carbon black in this paper).

Historically carbon materials (soot) were used as dilutant for the expensive natural rubber but it was also found to impart outstanding tire wear performance.

Tires are highly sophisticated objects which have to not only last longer (better wear) but also be safe (handling and traction) and energy efficient (rolling resistance). It is therefore normal that a great emphasis is put on studying the role of the carbon black in the rubber matrix in order to better understand the mechanism(s) of reinforcement. This word reinforcement can take different meaning depending on what aspect of a tire is studied. For example it may mean a higher stress at break, a higher adhesion to cords, a better wear, etc....

It is proposed, in order to encompass all of the above, to define reinforcement as being the way a viscoelastic rubber compounds respond to dynamic strain energy input. Upon deformation it will store and dissipate energy. The objective of this paper is to show that both carbon black and polymer play a major role in this energy partition which may be considered as "reinforcement."

A. Carbon Black

During the last 20 years a large number of studies have allowed a better understanding of carbon black. In spite of all these efforts a lot has still to be learned about this unique filler. The monounit of carbon black is the aggregate, a submicron object of complex shape.

1. Aggregate Shape and Size

Since the availability of the Transmission Electron Microscope (T.E.M.), around fifty years ago, the image of a carbon black aggregate is available. Fig. (1) shows such an image observed with today's state-of-the-art T.E.M. instrument.

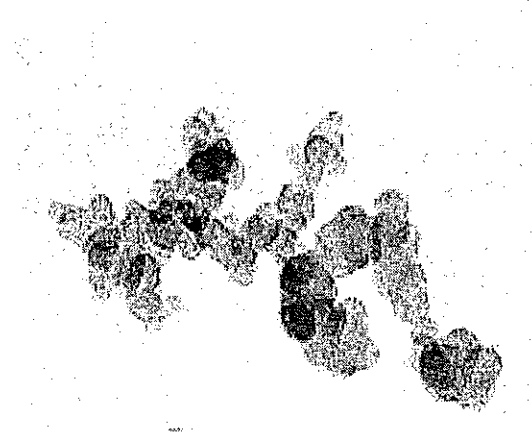


Fig. 1 T.E.M. Image of Carbon Black

One of the limitations of such an image is that it shows only a planar 2-D projection of a 3-D object. On the other hand, and this will always remain a source of uncertainty, it is almost unfeasible to unequivocally determine the number of aggregates in such a picture. Nevertheless, it is possible to hypothesize after having taken all necessary steps in the preparation of the T.E.M. grid, that only one aggregate is observed. Once such an hypothesis is made it is feasible by consideration of 3-D modeling techniques to assess the shape of this object. This is well described in ref. (1), (2).

Data are acquired from two-dimensional projections taken with the aggregates at two different orientations with respect to the electron beam. Computerized aggregate models are generated using data from T.E.M. projections (3). Aggregates exhibit planarity; that is, their breadth in a particular plane is consistently greater than their thickness perpendicular to that plane.

Basically it was found that all conventional furnace carbon black exhibit a flat complexion. This flatness confers to the carbon black a tendency to form a stronger filler-filler network which may not be beneficial, as it will be shown later.

Depending on the grade of carbon black the overall size of the aggregate ranges from 50nm to almost a micron for the so-called "Carcass Grades".

In conclusion, a carbon black aggregate is a sub-micron 3-D object of varying size. The flatness of the aggregate may be of prime importance, since it may be correlated to the in-rubber performance of this filler.

2. Aggregate Structure

2.1. The Aggregate Surface

Since the early work by X-ray Scattering (4, 5, 6) the crystallographic structure of the aggregate was revealed. Indeed these scattering results showed the presence of graphitic structures and a density decrease from the outside of the aggregate toward the inside.

Most recently Raman spectroscopy has been a very important tool to confirm (7) the presence of amorphous carbon as detected by Tunneling Electron Microscopy (8). From all the studies it appears that the surface of the carbon black is characterized by the existence of crystallites and amorphous regions.

The crystallites, described as turbostratic structures, possess an average width L_a of 25 Å and a stacking height L_c of 12 Å to 17 Å depending on the grade. These non-symmetrical structures are characterized by a d_{002} value always larger than the 3.354 Å characteristic for graphite. This implies that in carbon black the graphitic planes randomly distributed with respect to each other are further apart than in graphite. This is a direct consequence of the process of manufacturing the material. Indeed the reaction time in the furnace is very short and a thermodynamic equilibrium is never reached. Entropy processes may better describe the carbon black formation. This may also explain the presence of amorphous carbon obtained due to incomplete dehydrogenation. The presence of these "amorphous" structures is of great relevance for understanding and monitoring the energetic sites on the surface of the carbon black aggregate.

Fig. (2) shows a typical Raman Spectrum obtained using an untreated sample. The two main peaks at 1300 cm^{-1} (A_{1g}) and 1550 cm^{-1} (E_{2g}) are characteristic of the crystallites whereas the response around 1500 cm^{-1} is due to the amorphous regions on the carbon black surface. This last peak is the signature of a sp^n bonded carbon. This sp^n nomenclature may represent carbon in graphitic type species highly dislocated. At the dislocation sites sp^3 bonded carbon are present with additional hydrogen. In fact these additional hydrogen atoms are used to quantify the presence of amorphous carbon and can be used to monitor the amount of amorphous carbon during the carbon black formation.

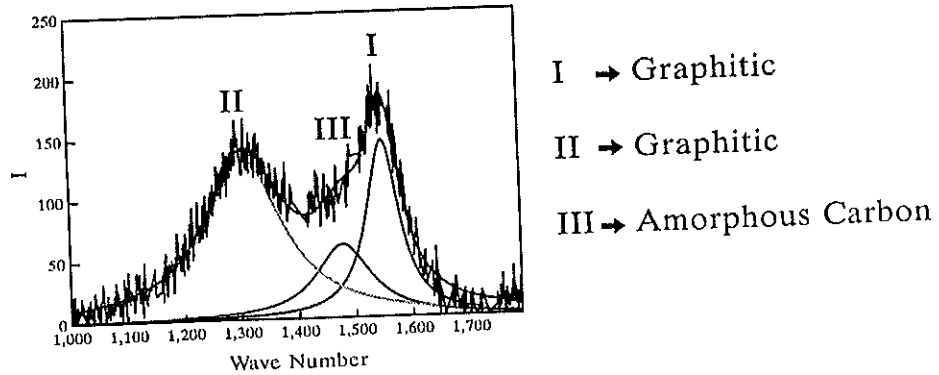


Fig. 2 Carbon Black Raman Spectrum

As far as the surface activity of the aggregate is concerned, it is hypothesized and widely accepted, that the boundaries between crystallites, with a high density of π electrons, are the active sites which will be responsible for both the networking of the filler and also the interactions with the unsaturation of the elastomer backbone as it will be discussed later.

It is therefore feasible to monitor the aggregate surface activity by a judicious increase (or decrease) of the amount of amorphous phases and regulate surface activity depending on the end usage of the filler (9).

2.2. Aggregate Surface Group and Microporosity

It is common to see in past literature that carbon black is represented as a "hairy" entity and that all kinds of surface groups are present on its surface. (i.e. quinone, lactone, carboxylic groups etc....)

This was without doubt, justified for carbon black from the generation before the furnace process, in particular for channel blacks containing 3 to 8 percent oxygen (10) whereas the furnace black total oxygen content is around 0.1%.

Using identical wet chemistry methodologies as in the above reference (10), the total amount of groups on the surface of the furnace black was found (11) to be only between 10 and 40 milliequivalent per 100g of carbon black. This contributes a very small amount (~2%) of surface coverage by chemical groups.

The same can be said for microporosity, which seems to be absent of the surface of furnace type carbon black (12, 13, 14, 15, 16).

It is not in the intent of this work to further comment on these two common misleading statements regarding the surface of furnace black, but one has to realize that neither the presence of surface groups nor the microporosity should be advocated to describe interactive phenomenon observed with furnace black and elastomer. Of course any oxidative post treatment of carbon black may induce both microporosity and surface

groups but in general the carbon black used in today's rubber industry is not post-treated and therefore has to be considered not microporous and with a negligible amount of surface groups. On the other hand, the type and amount of hydrogen atoms present on the surface may be very important (17).

3. Aggregate Model

In conclusion an aggregate of furnace black is characterized by a shell-core like structure. The shell surface is formed by turbostratic graphitic crystallites and some regions rich in highly disordered structures that are referred to as amorphous carbon. The inside of the shell, the core, is of much lower density.

Fig. (3) summarizes the Sid Richardson Carbon Co. model of an aggregate. The darker area represents the crystallites and the lightest one the area rich in amorphous carbon.

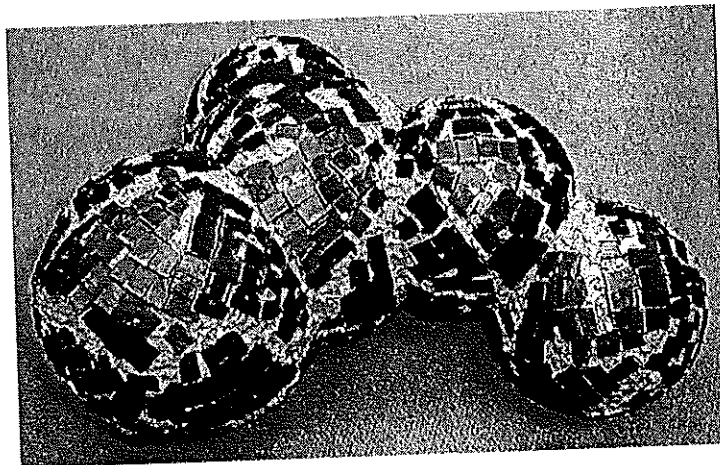


Fig. 3 Sid Richardson Carbon Black Aggregate Model

B. **The Elastomer**

The most important property for an elastomer is exhibiting rubber-like viscoelasticity. It consists of long, flexible chain-like molecules that can undergo rapid rotation as a result of thermal motion. This means it is a high molecular weight polymer well above its quasi-insoluble transition temperature T_g . A further requirement is that the long linear molecules must be crosslinked by a few intermolecular bonds in order to form a quasi-insoluble three-dimensional network.

In today's tire industry the most commonly used elastomers are unsaturated (NR, SBR, BR...) It is through these interactions in the polymer backbone that the crosslinking is done via mono/di/polysulfidic bonds depending on the "cure package." In order to keep its rubbery behavior the amount of crosslinking must be low which leaves a lot of unsaturation on the polymer backbone.

It is hypothesized that these site of unsaturations (π bonds) are responsible for the physico-chemical interactions between the polymer chain and the carbon black. These

interactions are most likely van der Waals type bonds due to the de-localized electrons from the polymeric double bands and the conduction electrons on the surface of the carbon black

Obviously, other phenomenon may exist like entanglements, transient dipoles, etc., and can also play an important role in rubber compounds.

It will be shown that it is the interface of the constitutive materials of the compound that dictates its properties.

II. 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.

This explains why that in the past two decades the dynamic testing of rubber compounds has undergone extensive 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.

A. 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 (18, 19). 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 (Fig. 5a). 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 (Fig. 4a-4b).

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

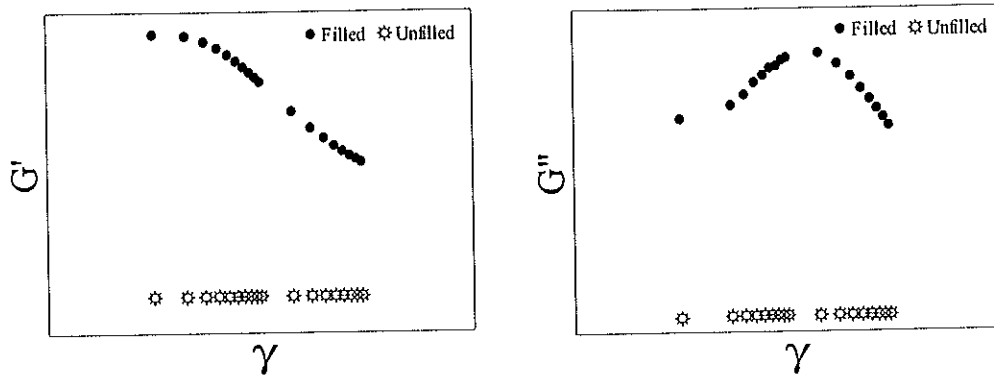


Fig 4a

4b

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. Fig. 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'' (18, 19). 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 (Fig. 5) is referred to as <G-Plot>(20) and allows for a more insightful understanding of the mechanism of carbon black reinforcement.

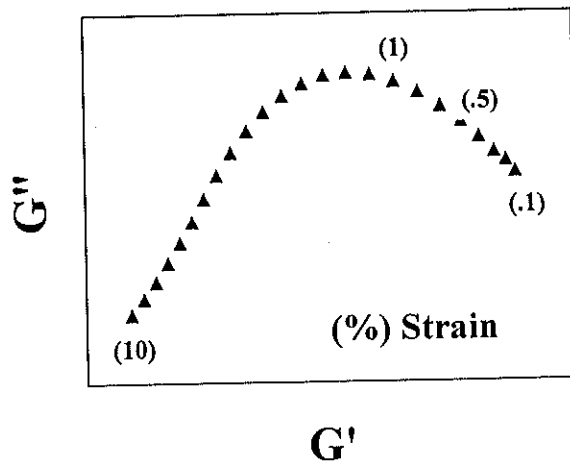


Fig. 5

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

It was shown (21) 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 this 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 γ .

It was also previously shown (22) 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' (Fig. 6). 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.

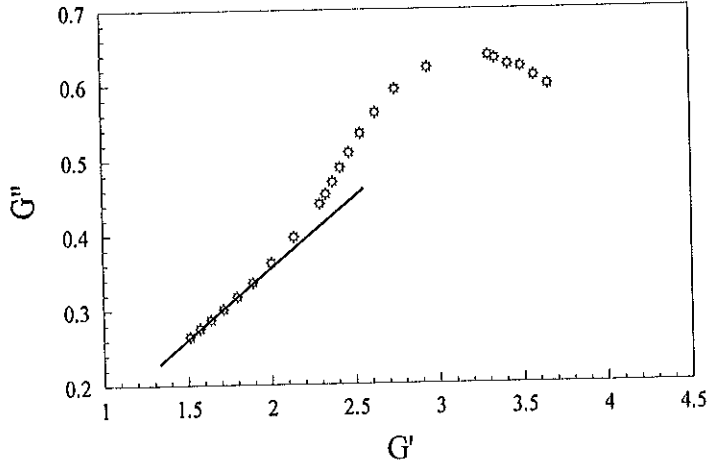


Fig. 6

An important property of the tire, namely 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.

B. Role of Carbon Black on Compound Viscoelasticity at High Frequency

The WLF equation (18) is employed to understand and predict behavior of polymers subjected to high frequency deformations. It has been shown that once filled with carbon black, the WLF principle no longer holds true 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. (23)

The sample subjected to an ultrasonic wave experiences 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 Fig. 7.

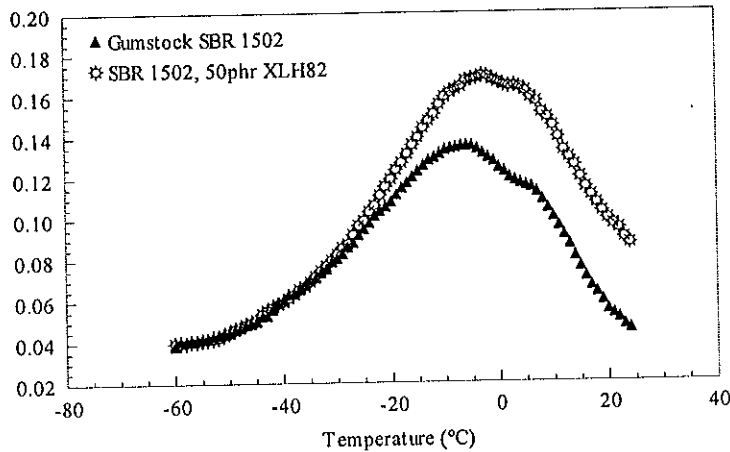


Fig. 7

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 (24) that the best way to observe this polymer/filler interaction is to evaluate the shift of T_g of the polymer at high frequency. Fig 8a shows the shift in T_g and broadening of the response when an SBR polymer is filled with carbon black, whereas with butyl rubber, Fig. 8b, the T_g value is not affected indicating the absence of this type of polymer/filler interaction.

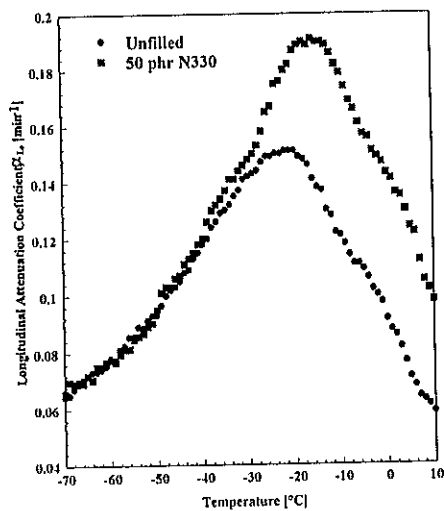
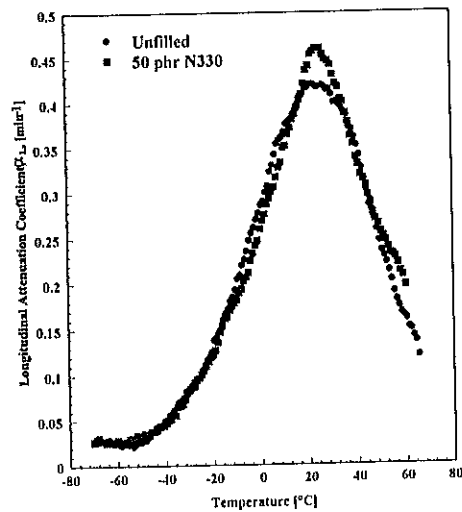


Fig. 8a



8b

C. 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.

Fig. 9a 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 Fig. 9b 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).

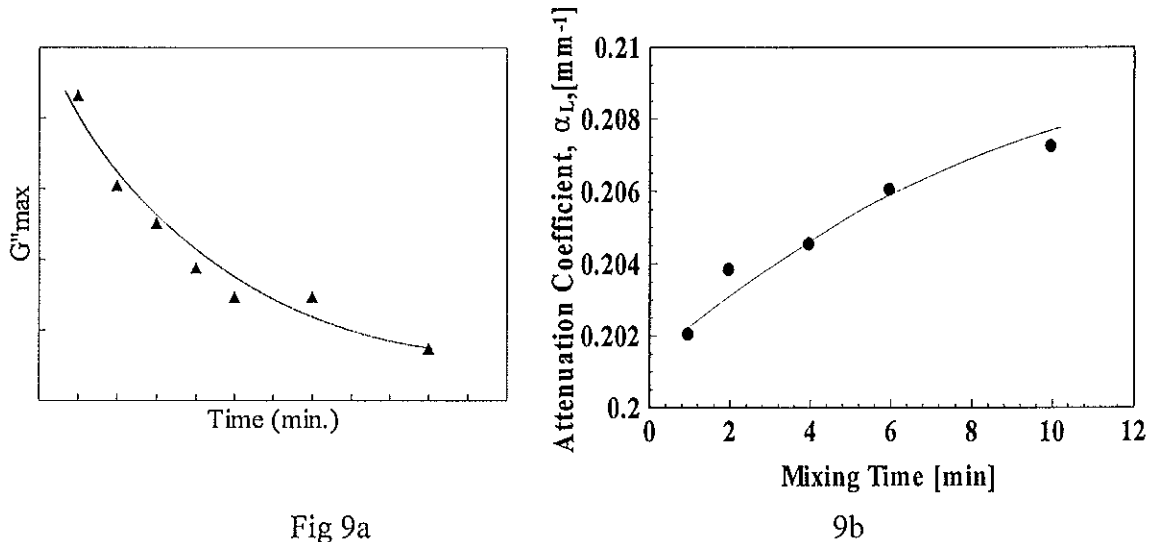


Fig 9a

9b

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.

Fig. 10 indicates the relationship existing between the instrumentation available and the length scale at which the dispersion has to be assessed.

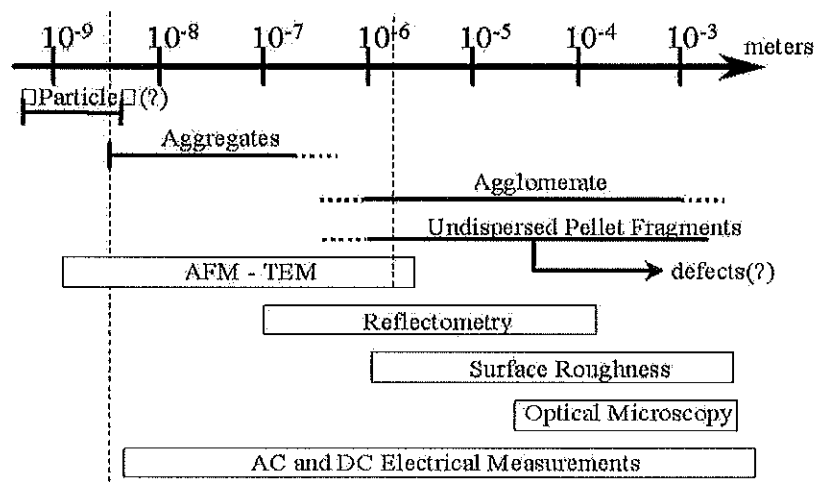


Fig. 10

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 (25, 26).

However, the filler dispersion is of utmost importance. It improves tire rolling resistance, traction, and tread wear (27).

All these effects can be explained by the fact that improved dispersion decreases the filler network density, and increases the amount of possible interaction of filler/polymer that 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 (28) 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 (Fig. 11).

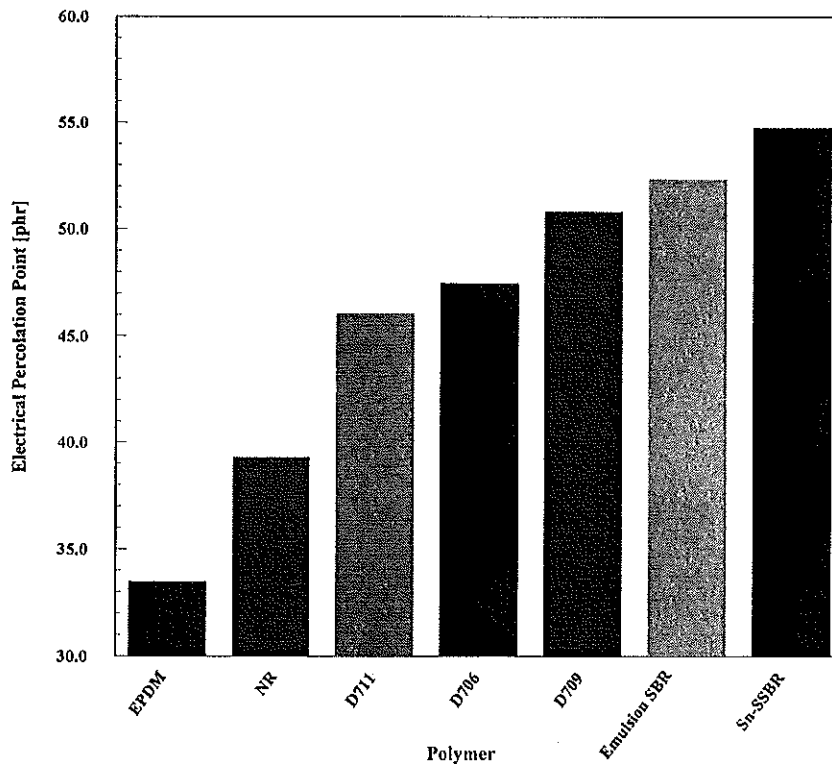


Fig. 11

The solubility parameter δ of five of the polymers shown in Fig. 11 were evaluated (29). It is remarkable to observe Fig. 12 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.

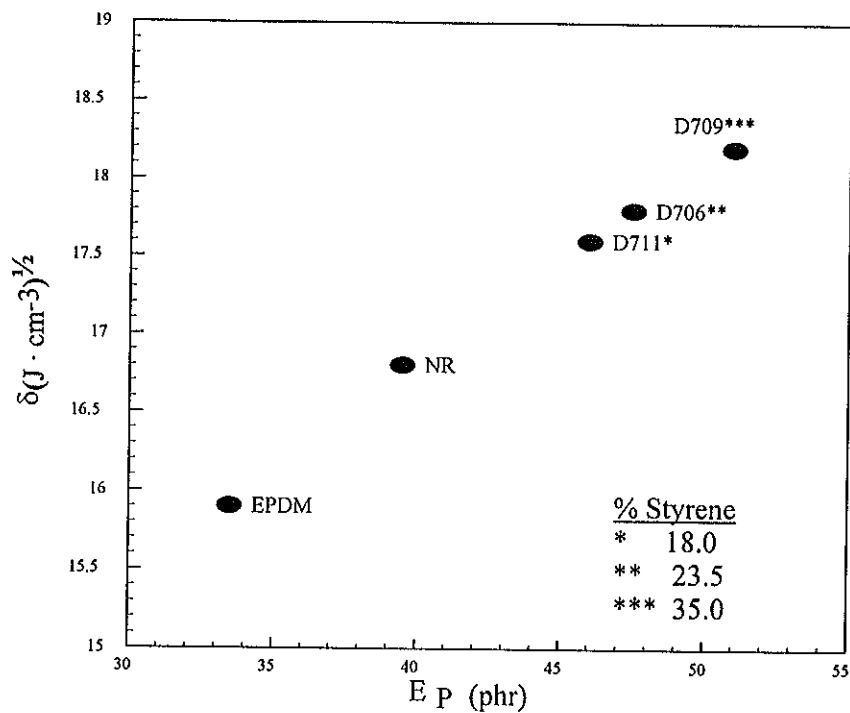


Fig. 12

D. 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 carbon black agglomerate size and shape.

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