

CARBON BLACK AND SILICA

Two Fillers with Similar Behavior in Rubber

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Abstract

A comparison of the two most used particulate fillers (carbon black and silica) in tire compounds shows that in spite of their inherent chemical differences, their behavior is the same when one considers the reinforcement mechanism of the rubber compound. For both of these fillers, in order to achieve their full potential, two identical challenges must be met:

- Reduction of the local fluctuation of the filler network density hence improving the microdispersion. (Improve low strain/low frequency properties; i.e. rolling resistance)
- Increasing the filler-polymer interactions (improves high frequency strain energy input, i.e. Traction, handling...)

For carbon black, these two important steps occur more or less naturally during mixing. The impact of the polymer microstructure/functionality is important to insure filler-polymer interactions.

For silica, a surface treatment is required to inhibit/remove the silanol groups on the surface. In general a silane is used. When this treatment is properly done, the silica/silane combination imparts certain improved performance properties to the tire: i.e. wet traction.

Latest developments in carbon black technology are aimed of reducing the performance gap (i.e. in wet traction performance) between these two fillers. Some experimental carbon black samples exhibit identical behavior to the silica/silane combination in overall tire performance.

A. Introduction

The employment of carbon black to reinforce tires is rapidly approaching its hundredth anniversary.

Silica, on the other hand, has only been utilized for less than 50 years in the tire industry and only for the last 20 years considered capable of duplicating the characteristics of carbon black in passenger tire tread applications.

The following compares these two fillers from a purely technical standpoint.

B. Material Definition

Carbon Black

The carbon black aggregate (the carbon black mono-unit) obtained today in the furnace process is a sub-micron object characterized from a geometric standpoint by an assembly of more or less spherical particles (Fig. 1a). This object has to be considered as rigid and, in general, relatively flat(1).

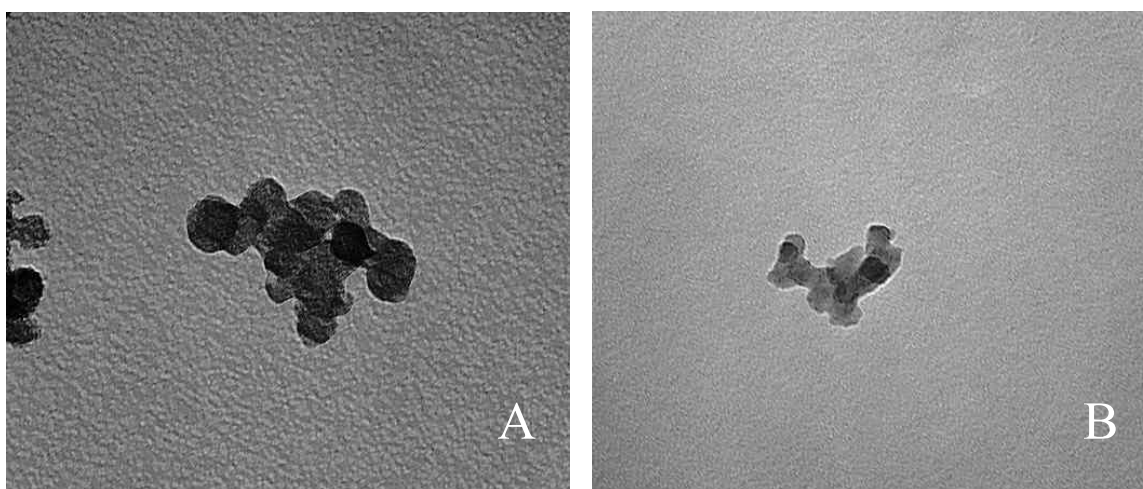


Figure 1. TEM Images of (A) carbon black and (B) silica

From a physicochemical standpoint, the aggregate surface: consists of two main constituents: turbostratic crystallites and amorphous carbon.

It should be noted that in some past literature, the surface of furnace black was described as similar to the surface of channel black (2). In fact, the opposite is true, the surface of furnace carbon black is characterized by the presence of very few chemical groups containing heteroatoms like oxygen, sulfur, etc. (3).

The surface of carbon black is in fact best described energetically as an heterogeneous distribution of π delocalized electrons associated with the boundaries of the turbostratic

C. Material Characterization

Carbon Black

In the past fifteen years the carbon black surface and structure was more accurately determined by methodologies like:

- X-ray, neutron scattering (5,6)
- Raman spectroscopy (7)
- TOF SIMS (3)

In particular, these techniques allowed the preparation of a model of carbon black aggregate that is widely accepted today (Fig. 3).



Figure 3. Carbon Black Model.

Obviously, other more conventional techniques like N₂ adsorption, DBP absorption, CTAB, etc., have been used to characterize this material for everyday usage. It is not the intent of this paper to critically review the merits and drawbacks of these methodologies.

Silica

Silica has not been the subject of many academic investigations when compared to carbon black. Nevertheless, some authors (8) have studied in depth some aspects of this material. A technique of choice has been Inverse Gas Chromatography (IGC), which is capable of evaluating the surface energy γ_s of silica. In particular, the polar γ_p and the dispersive component γ_d have been investigated.

$$\gamma_s = \gamma_p + \gamma_d$$

It has been shown that for silica γ_p is very large, whereas for carbon black it is very low. The reverse being true for γ_d .

This in fact constitutes the essential differences between the two fillers. These particular characteristics are at the same time their strength and their weakness as will be shown later.

D. Dynamic Physical Properties of the Rubber Compound

In a typical tire application, the rubber compound (e.g. the tire tread) is subjected to periodic strain energy inputs. The properties of a tire will depend on the response of the rubber compound to these external stimuli.

It is well known today that particulate filler used in tires will form a network on its own when mixed in a rubber compound. The fluctuation of the filler local network density is essential to understanding the compound behavior subjected to low frequency deformation and reasonable low strain (typically 10 Hz and below 30%). This fluctuation is referred by the authors as filler micro-dispersion. The less fluctuation (the best micro-dispersion) the better the hysteretic response of the rubber compound (9,10)

For the purpose of clarification, if the rubber compound is tested at constant strain amplitude, $\tan \delta$ is not a predictor of the heat build-up (11).

For low frequency – high deformation or for ultrahigh frequencies (500 KHz to MHz) encountered by the rolling tire surface in contact with the road, it is the interactions of the

polymer with the filler, which is primordial. Indeed, the more interaction with the filler the more energy will be dissipated by the compound. This is translated into better traction and handling of the tire. It is to be noted that the WLF shift correlating low temperature behavior to high frequency deformation of the polymer unfilled is not applicable to filled compounds. Indeed the procedure to characterize the shift uses variable temperature and relatively low frequency testing under significant strain. In these circumstances the filler network cohesion perturbs the observed results and from a strictly scientific standpoint, the WLF shift is not attainable. High frequency viscoelastic testing has been developed to obviate this effect (12).

Therefore, regardless of the filler used, decreased local fluctuation of the filler network (improved micro-dispersion) and filler-polymer interactions is a prerequisite for optimal in-tire rubber compound properties.

If one accepts that a better micro-dispersion will reduce localized filler network density and allow more filler surface to interact with the polymer, hence more polymer filler interactions, then an optimized micro-dispersion should improve simultaneously the most important tire properties: rolling resistance, tread wear and traction.

E. Microdispersion and Polymer-Filler Interaction

Micro-dispersion is an easily understandable concept, but very difficult to quantify. The difficulty resides in the fact that one has to quantify in 3-D space the location of objects of submicron size.

Many of the submicron measuring techniques analyze the dispersion in a 2-D mode (TEM, ATM, Submicron roughness, etc.). The ideal solution would be to employ scattering techniques using visible light (the wavelength being similar to the size of the object to be studied). These techniques are of very limited application due to the nature of carbon black (absorption) and opacity of the compounds used in the tire industry (high filler loading).

For the carbon black compound, electrical resistivity techniques may provide some information (13). This of course is not feasible with silica.

The quest for a quantitative measuring technique continues.

Role of Mixing

Mixing filler in an elastomer, in the commercial production of tires, requires large pieces of equipment capable of creating forces capable of breaking down the filler delivered in the form of pellets and ideally distributing the individual aggregates of filler pellets within the elastomer matrix. When the “eroded” pellet, due to shearing in the mixer, has attained a small sub-pellet dimension the shear field may no longer have sufficient energy to achieve ideal dispersion.

Furthermore, the cohesion of the initial pellets may hinder adequate microdispersion. This is especially true of silica, where special drying processes are required to reduce internal cohesion and obtain highly dispersible silica (HDS). The drying process of choice is spray drying. It is designed to remove the moisture at relatively low temperature but at very high rate. This avoids the formation of “hydrates” obtained by more conventional heat drying. These hydrates, by hydrogen bonding, give a much higher cohesion to the silica pellets. The same phenomenon may occur in conventional carbon black drying but no studies showing that effect have been published.

One has also to consider the forces, which tend to keep the aggregate together in both silica and carbon black pellets. The forces in carbon black, beside some effect of pellet binder, are mainly Van der Waals type due to the high density of π electrons on the surface of this filler. These forces are relatively weak and can be overcome by the mixing shearing forces and interactions with polymer.

In the case of silica, the high concentration of $-OH$ groups at the surface create a large amount of hydrogen bonding which confers to the system a much stronger cohesion than that of carbon black. This difference in cohesion strength can be used to prepare blend of rubber filled compounds with poor micro-dispersion of silica imparting to the final product a better resistance to tear and cut growth.

In modern tire technology (10,14) silica has to be well micro-dispersed. The usage of silanes (i.e., Si69) which reduces the silanol group on the surface of silica has proven every efficient (Fig. 4). Considering the smaller size of a silica aggregate compared to carbon black, it is easily understood that under these conditions silica should better micro-dispersed. (3-D dispersion in an elastomeric matrix).

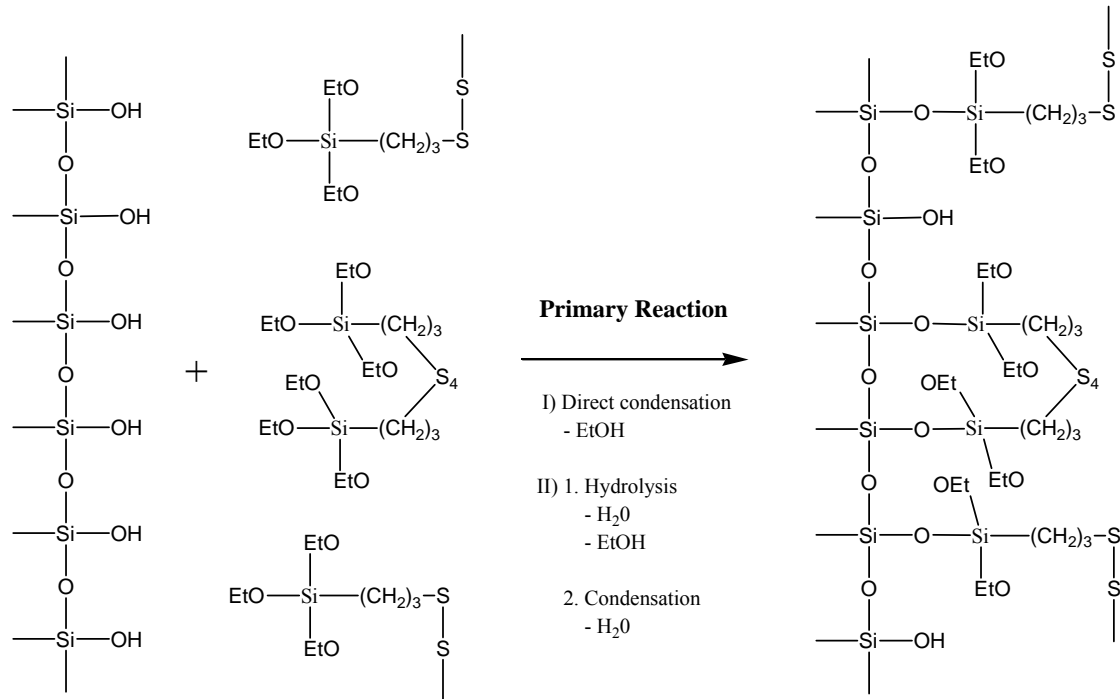


Figure 4. Silica/Silanes reaction.

Polymer Filler Interactions

After the initial shearing effect, breaking down the original pellets, the surface of the Carbon Black aggregate may interact with the polymer chains. These polymer-filler interactions depend on the microstructure of the polymer and affect the micro-dispersion, measured as the loading at percolation. (15). Fig. 5 shows this very typical effect.

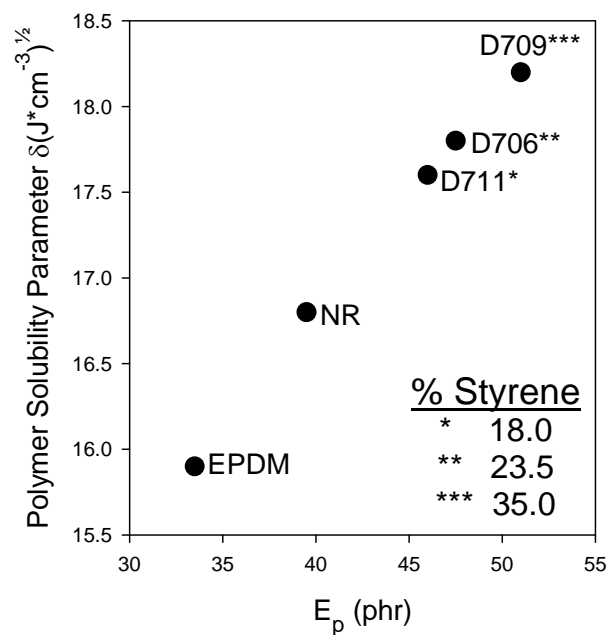


Figure 5. Effect of polymer type on E_p

In the case of silica, a large amount of literature (16) indicates that the resulting initial silane/silica reaction (removing the silanol group) is followed by a “covalent” bonding between the elastomer and the modified silica as shown in Figure 6.

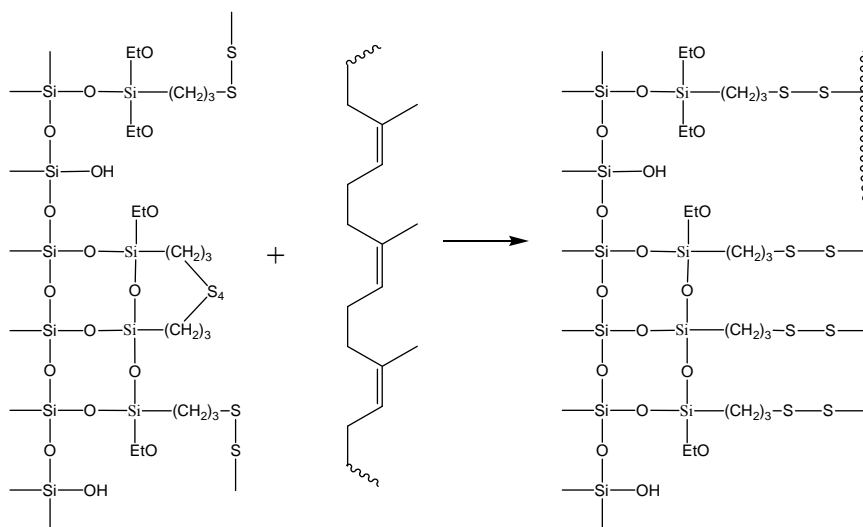


Figure 6. Silica-Polymer reaction.

This has been proven in model formulations (17) but never unequivocally demonstrated in a real rubber compound. The results in tire performance however tend to confirm this hypothesize interaction in real compounds.

F. Application to Carbon Black vs Silica

Carbon Black

Figure 7 clearly indicates that a better microdispersion (assuming that mixing time is directly related to the degree of microdispersion) gives definitively a lower maximum loss modulus G''_{max} and higher energy dissipation at high frequency. This translates in tire properties as a lower rolling resistance and better traction respectively.

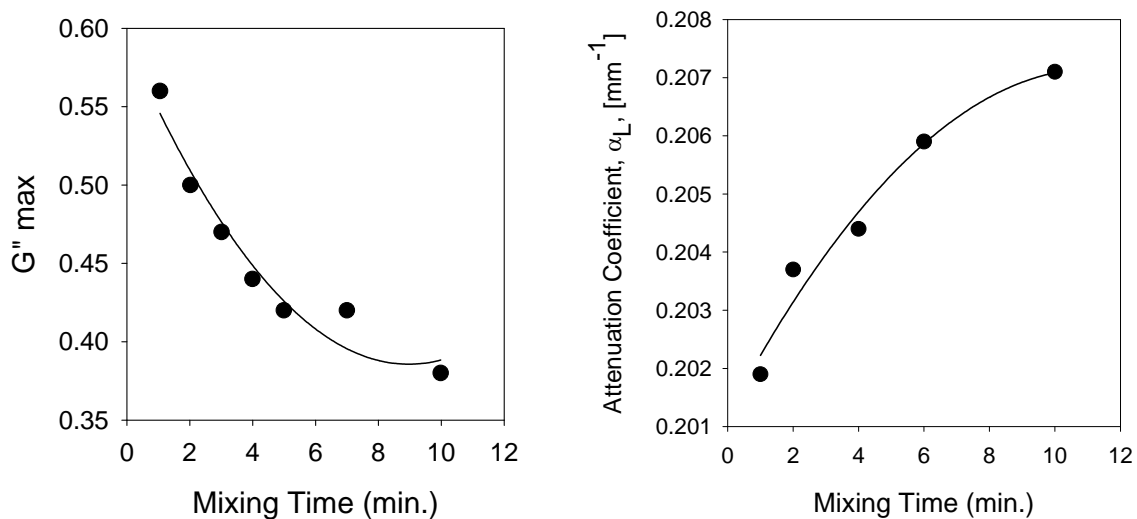


Figure 7. Effect of microdispersion on compound properties.

This may very well be explained by the fact that a better microdispersion decreases the local fluctuation of the filler network and therefore decreases G''_{max} but increases the amount of filler surface capable to “interact” with polymer: high filler-polymer interaction. The later may explain in simple terms that more polymer chains are immobilized by carbon black therefore the high frequency absorption coefficient increases.

Silica

Many investigations (16,17) using silica and silanes show identical results when comparing silica alone or silane treated silica. Indeed Figure 8 (16) clearly indicates that G' and G'' decrease significantly when silica is treated with silane or other chemicals capable to remove silanol groups from the silica surface.

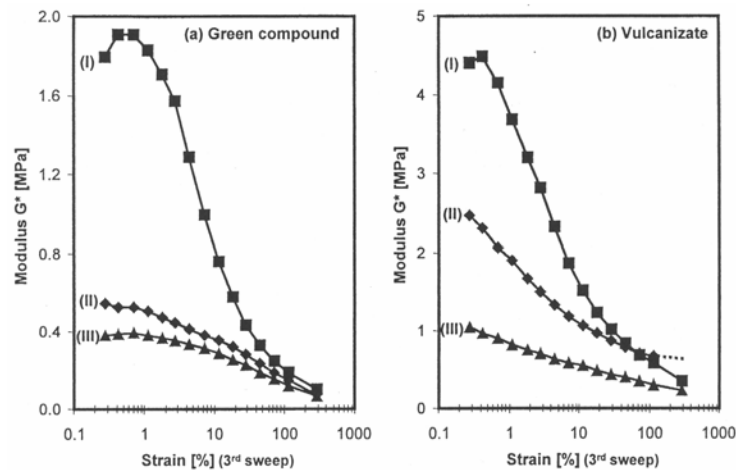


Figure 8. Shear modulus G^* vs. strain; (I) ■ without silane, (II) ◆ modified with 10phr TESPT, (III) ▲ modified with 8phr HDTES

This also explains, that by removing some of the silanol groups from the silica the microdispersion increases and through the bi-functionality of the silane the filler-polymer interaction is also enhanced.

This as shown in Figure 9 justifies the conclusion reached in another publication (18), which states:

“At smaller strain, the secondary structure of the fillers has an important effect on the stress-strain curve. At a larger strain, stress-strain curve is greatly affected by the interactions between filler and rubber matrix.”

It appears that the reinforcement mechanism of silica/silane combination is the same as for carbon black.

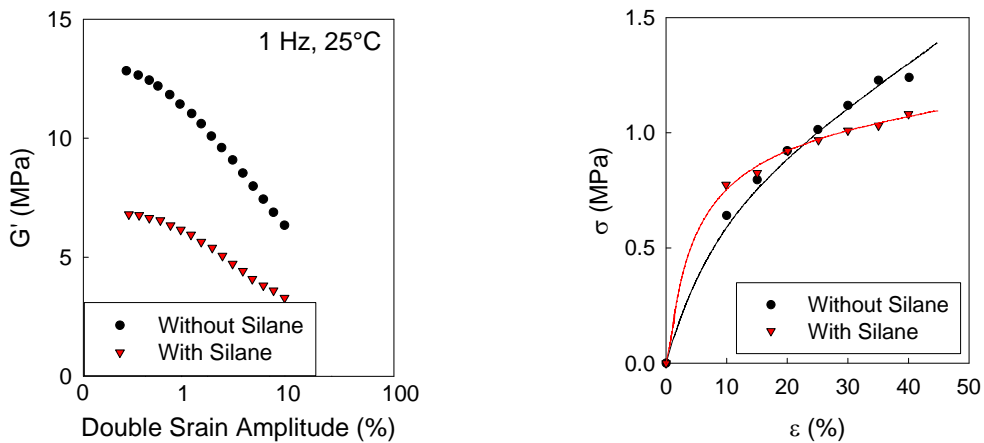


Figure 9. Silane effect on Silica.

G. Future Works

Since silica/silane combinations have been without doubt a successful endeavor, it has awoken the carbon black research community to expand its efforts to improve the performance of carbon black. The following data (Figure 10) indicates one such effort. Modifying the carbon black surface can reduce its low frequency viscoelastic response (better micro-dispersion) and at the same time increase the high strain response (increase polymer-filler interaction). This type of behavior is equivalent to the one observed with silica/silane combination.

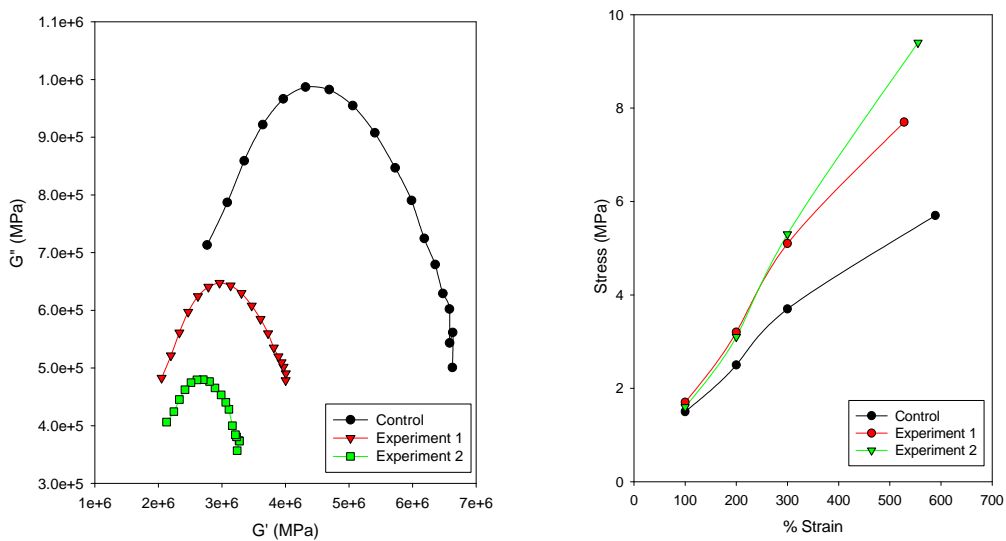


Figure 10. Results with experimental Carbon Black.

H. Conclusion

Both fillers, carbon black and silica, are similar but to optimize their individual usage additional modifications have to be undertaken. The ultimate goal is better microdispersion, which translates in less “filler networking” and more “filler-polymer interactions”.

Obviously the future modified filler surface may require specific polymer microstructure/functionalization.

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