

CARBON BLACK CHARACTERIZATION

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Introduction

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 T.E.M. instrument.

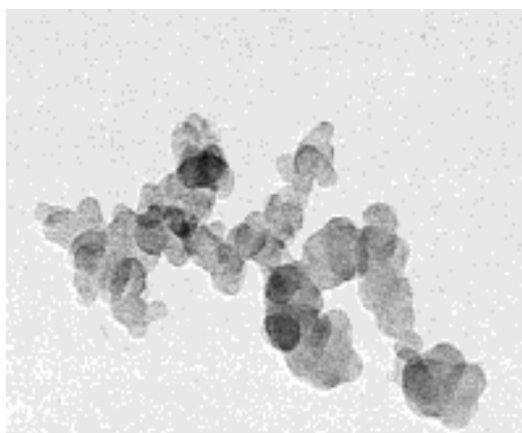


Fig. 1 T.E.M. Image of Carbon Black

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.

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 exhibits 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 strong filler-filler network

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\AA and a stacking height L_c of 12\AA to 17\AA depending on the grade. These non-symmetrical structures are characterized by a d_{002} value always larger than the 3.354\AA 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.

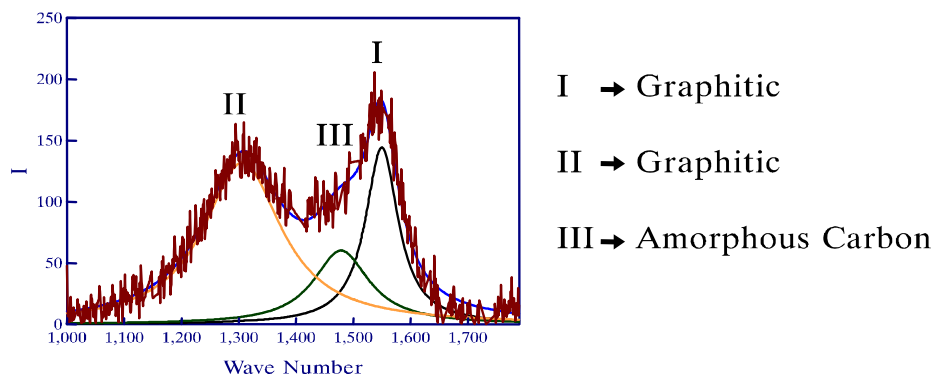


Fig. 2 Carbon Black Raman Spectrum

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.

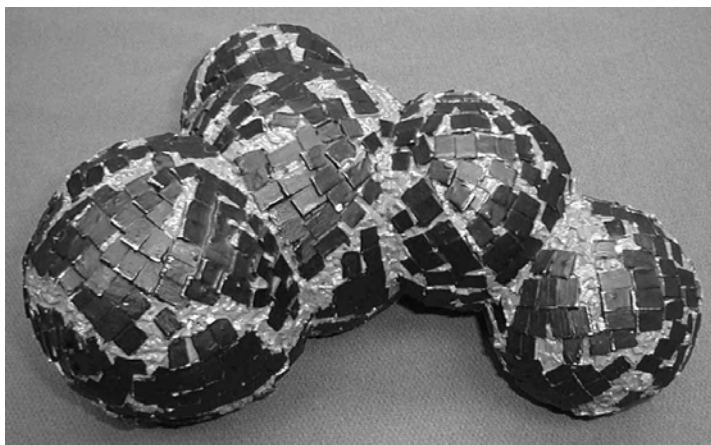


Fig. 3 Sid Richardson Carbon Black Aggregate Model

Bibliography

1. T. Grüber, T.W. Zerda and M. Gerspacher, *Carbon*, 31, 1209, (1993).
2. T. Grüber, T. W. Zerda and M. Gerspacher, *Rubber Chem. & Tech.*, 67, 280, (1994).
3. R. Rinewalt, L.D. Payne, C.A. Morgenstern and M. Gerspacher, *Rubber Chem. & Tech.*, 68, 169 (1995).
4. B. E. Warren, *J. Chem. Phys.*, 2, 551 (1936).
5. R. E. Franklin, *J. Chem. Phys.*, 47, 573, (1950).
6. R. E. Franklin, *Acta Cryst.*, 4, 253, (1951) 3, 107, (1950).
7. T. W. Zerda, W. Xu, H.H. Yang and M. Gerspacher, *Rubber Chem. & Tech.*, 71, 26, (1998).
8. J. B. Donnet, *Keynote Lecture, IRC, 95, Kobe, Japan.*
9. M. Gerspacher, *Patent Pending.*
10. R. C. Bansal, J. B. Donnet, 175 *"Carbon Black"* Marcel Dekker, New York, 1993.
11. W. A. Wampler, *private communication*, to be published.
12. J. B. Donnet, *private communication.*
13. D. C. Bansal, J. B. Donnet, and H.F. Stoeckli, *"Active Carbon,"* Marcel Dekker, New York 1988.
14. P. Bertrand, L.T. Weng, paper 38, *ACS, Rub. Div.*, Spring 1998.
15. H.F. Stoeckli, P. Rebstein, and L. Ballerini, *Carbon* 28, 907 (1990).
16. D. Huguenin and H. F. Stoeckli, *J. Chem. Soc. Faraday Trans.* 89, (1993).
17. L. Ballerini, D. Huguenin, P. Rebstein, and H.F. Stoeckli, *J. Chem. Phys.* 87, 1709 (1990).