

Fullerene-Like Structures as Interaction Sites between Carbon Black and Rubber

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Summary: Ball-milling of N660 carbon black and graphite causes a deep activation of its surface activity which can be measured by a significant increase in the bound rubber level and in the amount of grafted rubber in comparison to the pristine untreated samples.

The bound rubber measurement has been done also on a natural rubber masterbatch filled with extracted fullerene carbon black (EFCB). Also in this case extremely high levels of rubber grafting have been achieved in comparison to pure untreated graphite. It is discussed and demonstrated that the fullerene-like nanostructures in carbon blacks play a key role in the formation of bound rubber phenomenon and in grafting natural rubber on carbon black surface.

Keywords: carbon black; fullerene-like structures; grafting; rubber

Introduction

The interaction between carbon black surface and rubber is the basis of the reinforcement mechanism in rubber compounds. This interaction is not yet fully understood despite the large number of investigations dedicated to this subject.

In a series of papers we have shown that it is possible to increase the interaction between carbon black and rubber by a radiation treatment of the filler followed by the addition of the diene rubber.^[1-4] The explanation of the increased interaction lies in the structural changes induced by high energy radiation on the filler surface with creation of reaction sites under the form of free radicals and fullerene-like structures.^[4-5] A key parameter to evaluate the rubber-carbon black interaction is the bound rubber.^[3] The bound rubber is defined as the amount of rubber which remains irreversibly linked (adsorbed) to the filler surface after mixing and is no more extractable with any good rubber solvent.^[3]

We have proposed^[6] and discussed^[7-11] that a key role in this phenomenon is played by the fullerene-like structures (see ref.^[8] for a definition) which are present on carbon black surface. Furthermore, it has been shown that the concentration of the fullerene-like structures may

increase by the radiation-damage of graphene sheets.^[4-5] The fullerene-like structures on carbon black are naturally occurring topological defects in this disordered solid, as already demonstrated by J.B. Donnet and his group^[12-15]. Similar defects have been clearly detected by Ijima et al.^[16] in radiation-treated graphene layers and carbon nanotubes.

Since there are direct evidences about the reactivity of fullerenes with dienic rubber, as shown by us in other specific papers^[17-19] and by other authors with different types of rubbers and plastics^[20-24], then it is obvious to expect this chemical reactivity also between the fullerene-like structures present on the carbon black surface and the diene rubber. As stated in a previous paper^[8], it is theoretically expected a much higher electron affinity by the fullerene-like structures present on the carbon black surface than on a common C₆₀ fullerene which is already considered a free radical sponge.^[6-8,25]

Recently, considerable attention has been dedicated to the effects caused by ball milling on carbon materials, especially on graphite.^[26-34] The structural changes have been investigated by a number of different techniques from X-rays to Raman spectroscopy to TEM and SEM. In the case of graphite, the gradual increase in structural and surface disorder as function of the milling time has been very well documented.^[25-33] Carbon atom displacement caused by the intensive milling, with formation of dangling bonds has been reported for graphite.^[29] Graphene sheet planes rotation, basal plane stacking disorder, delamination and cracks have been reported in milled graphite as well as highly curved graphene sheets.^[30,32,33] Theoretically, we already know that to curl a graphene sheet it is needed to introduce one or more fullerene-like defects.^[8] Therefore milling is a relatively simple mean to introduce or create fullerene-like defects in graphite and to increase the concentration of these defects in disordered materials like N660 carbon black where the mentioned defects are naturally occurring.

It is expected that milling should cause the same surface activation of carbon fillers already observed and documented for the radiation-treated carbons.

Although numerous studies have been dedicated on the structural changes in the graphite and carbon materials under extensive milling^[26-34], no reports are available on the interaction between rubber and the activated carbon surfaces obtained after milling. The aim of the present work is to fill this gap. Thus, we have activated graphite and N660 carbon black by extensive milling and then have used the activated fillers to prepare a natural rubber masterbatch in a laboratory mixer. The bound rubber level has been measured by solvent extraction in comparison to rubber mixes prepared with the pristine graphite and N660 carbon

black. Furthermore, a sample of extracted fullerene carbon black has been mixed with natural rubber to study its reactivity with this polymer

Experimental

Materials

Graphite used in the present work was a synthetic type in powder form from Aldrich with a particle size of 1-2 microns. N660 carbon black was a standard industrial grade and was supplied by Columbian Carbon Co. Extracted fullerene carbon black (EFCB) consists of the soot formed during the fullerene synthesis in Kratschmer-Huffmann conditions^[35], after the extraction of C₆₀ and C₇₀ fullerenes with toluene. The resulting carbon soot still contains higher fullerene homologues which are not soluble in toluene and which are part of the soot together with its naturally occurring defects.

Ball-milling of Graphite and N660 Carbon Black

Ball milling conditions of graphite and carbon black have been already reported elsewhere.^[36]

Samples Preparation and Bound Rubber Measurements

The ball-milled carbon samples, the reference untreated pristine materials and the EFCB sample (which was used without milling) were compounded with natural rubber (cis-1,4-polyisoprene) using 100 phr of rubber for each 65 phr of carbon material. Use was made of a laboratory Brabender-type small mixer at 130 rpm with a fill factor of 0.7.

After mixing, a sample of 6g of each compound has been used to measure the bound rubber by solvent extraction. The details of the bound rubber measurements are reported in a previous work.^[36]

Surface Area Measurements

The surface area of the pristine and ball-milled carbon samples was estimated with the iodine absorption method using the standard procedure ASTM1510. The iodine absorption method measures the mg of I₂ absorbed by 1g of carbon sample. The conditions of the test have been selected purposely so that the iodine number of current carbon blacks is numerically equal to their specific surface area determined by the N₂ absorption method and expressed in m²/g.^[37]

Results and Discussion

Rubber-Carbon Interaction: The Bound Rubber Level

As discussed in a previous work^[3] the bound rubber is a measure of the interaction between diene rubber and a filler in general. When rubber is mixed with carbon black in a mixer, the compound obtained, called masterbatch, could be ingenuously expected to be only a mechanical mixture of rubber and carbon black. Thus, it is expected that rubber can be separated very easily from carbon with the aid of a good solvent of rubber. For instance toluene, which is a good solvent of rubber, should be able to dissolve completely the rubber leaving an insoluble residue of carbon. The experiment instead shows that only a fraction of the total rubber is extractable, while another fraction remains irreversibly bound into the carbon surface^[3]. The rubber fraction not extractable is called “bound rubber”.

The bound rubber has two components: the physical and the chemical component. This means that part of the rubber which is not extractable at room temperature from a rubber compound, is extractable with boiling toluene. Hence, the bound rubber fraction extractable exclusively at high temperature is attributed to the fraction physically adsorbed on the carbon surface while the fraction not extractable even with boiling solvent is assigned to the rubber chemically bound on the carbon surface. Of course physical adsorption implies adsorption involving only dispersive forces, physical occlusion and entanglements of polymer chains while chemical adsorption involves the formation of at least a chemical bond linking at least one polymer chain segment or a polymer chain end with the carbon surface. When a polymer chain is chemically linked on a carbon surface we can talk about grafting.

We will not enter into the detail of the polymer adsorption on surfaces or the general aspects of adsorption on carbon which are treated in good monographs.^[38,39] Instead we will focus on the experimental results generated in the present work. Before doing this, it is necessary to remember that carbon black is a paramagnetic solid^[40] and there are many possible reaction sites between rubber and its surface as assessed by many different techniques including inverse gas chromatography^[41] and gas adsorption.^[42] As proposed in earlier works^[1-11] these reaction sites include the fullerene-like structures.

Graphite is known to give very poor reinforcement due to its ordered structure, lack of adsorption sites and low surface area. However, after 10 h ball milling, graphite is transformed into a highly disordered solid.^[36] Its surface area increases dramatically and it has been well documented the formation of fullerene-like structures on its surface^[29-33, 36]. In Fig. 1 it is shown that graphite gives a total bound rubber level of 27.6% but after hot extraction

the chemical component of bound rubber is negligible: 2.5%. Instead, for the ball milled graphite the total bound rubber is 87.9% and decreases to 75.7% after hot extraction. This means that ball milling changes the graphite structure so that 75.7% of the rubber used in the masterbatch remains chemically grafted on its surface while for the pristine graphite this level was only 2.5%.

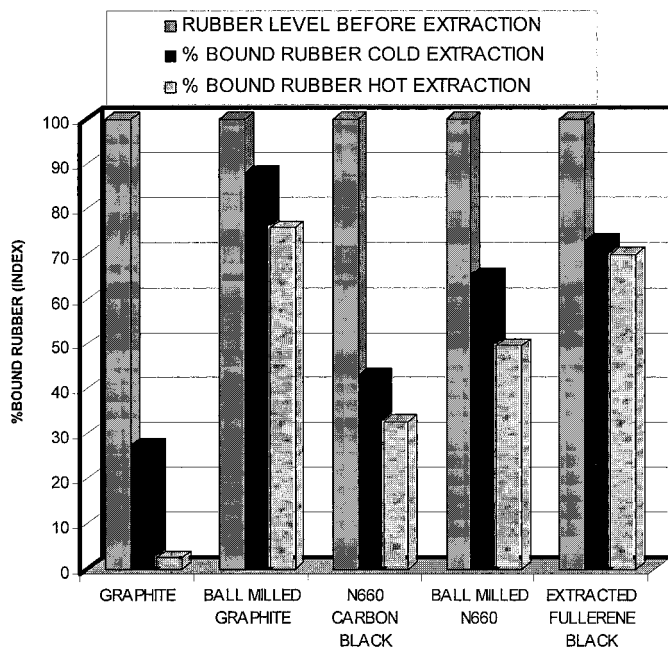


Fig. 1. Bound rubber values (index) of NR on different fillers having variable amounts of fullerene-like structures.

The ball milling experiment was also repeated on N660 carbon black. From the surface area measurements we know that after 6h ball milling the surface area of N660 does not increase as dramatically as graphite (see previous section). Notwithstanding this, the total bound rubber passed from 43.1% for pristine sample to 65.3% for the ball milled sample (Fig.1). The chemically bound rubber, i.e. the rubber grafted on the carbon surface, increased from 32.8% to 49.6%. The increased interaction in this case has been achieved practically without changing the surface area of the carbon solid.

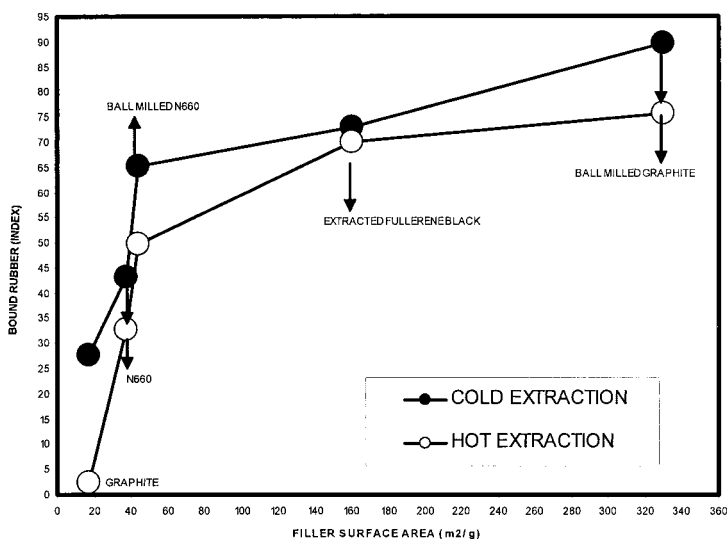


Fig. 2. Bound rubber versus filler surface area. Cold extraction refers to physical + chemical bound rubber. Hot extraction refers exclusively to chemically bound rubber.

Thus, the increased grafting is exclusively due to the changes in the morphology of the surface of carbon black, which involves the formation of free radicals and fullerene-like structures, but possible effect due to the increase in the surface area can be excluded in this specific case. For this reason we consider of extreme importance the result achieved with N660 carbon black as a demonstration that the fullerene-like structures contribute to the bound rubber phenomenon and hence to the overall reinforcement.

Another very interesting result in Fig. 1 refers to the extracted fullerene carbon black (EFCB). This black, by definition contains fullerene like structures as well as fullerenic structures, for instance giant unextractable fullerenes. The total bound rubber level achieved with EFCB is extremely high: 72.9% and after the hot solvent extraction remains practically unchanged at the 70% level. This means that all rubber adsorbed of EFCB is practically chemically bound on its surface.

Fig. 2 illustrates the same data of Fig. 1 as function of the carbon surface area. Obviously it can be observed an increase in total bound rubber by increasing the carbon black surface area. However, it can be observed again that the two N660 samples having more or less the same

surface area, display a significant different level of bound rubber and, most important, a different level of grafted rubber. The higher level is for the ball-milled sample, as expected. The other aspects emerging from Fig. 2 are the fact that the total bound rubber for pristine graphite sample is exclusively due to physical adsorption while for the ball milled graphite, the largest component of the total bound rubber is chemical in nature. The most astonishing result is with EFCB where practically the total bound rubber is coincident with the chemical bound rubber a result which has not been achieved with ball milled graphite having a much higher surface area.

Conclusions

The surface area of graphite can be increased dramatically by ball milling. Simultaneously the surface activity of the resulting carbon black appears dramatically higher than the starting graphite. This has been demonstrated by measurements of the bound rubber and the amount of chemically grafted rubber on the carbon surface. It is well documented that ball-milled graphite is rich in fullerene-like structures. Thus, the chemical grafting of natural rubber chains on the ball-milled graphite has been attributed to the formation of these kind of topological defects and to the general increase of the surface disorder.

If extracted fullerene carbon black (EFCB) is used in a bound rubber measurement with natural rubber, a very high level of bound rubber can be observed and simultaneously it has been demonstrated that all the bound rubber is chemically grafted on the EFCB surface while in general, with common carbon black, or with ball-milled graphite only a fraction of the rubber is chemically grafted on the surface and the other fraction is only physically adsorbed. Thus, again, the fullerene-like structures make the difference. EFCB is extremely rich in fullerene-like structures by definition and in fact all the bound rubber results fully grafted onto the EFCB surface.

Ball-milling of N660 carbon black under relatively mild conditions in order to create the fullerene-like structures without increasing significantly the surface area of the pristine sample, causes again a significant increase in the amount of the bound rubber and thus in the amount of the chemically grafted rubber fraction.

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