Simplified Modeling Calculations to Enlighten the Mechanical Properties (Modulus) of Carbon Black Filled Diene Rubber Compounds

Jean L. Leblanc

UPMC—Paris-Sorbonne Universités, Polymer Rheology and Processing, 60, rue Auber, F-94408 Vitry-sur-Seine, France

ABSTRACT: A simplified model is developed to calculate the modulus of carbon black filled rubber compounds by using standard characterization data of the filler, its volume fraction and only one fitting parameter: the number of junctions between neighboring carbon black aggregates. The model is based on three hypotheses with respect to (1) the optimal dispersion of aggregate, (2) the pure physical nature of rubber—carbon black interactions, and (3) the possibility to describe aggregates essentially in terms of specific surface area and structure, both accessible through standard characterization methods. Average rubber—filler interactions are introduced through micromechanical considerations. The model is probed by using dynamic strain sweep test results on two series of carbon filled compounds, one on the basis of SBR1500 Emulsion Styrene-Butadiene Rubber, the other on RSS3 Natural Rubber. It is found that the number of junctions is decreasing with increasing strain amplitude, thus, offering a clear explanation for the well known dynamic strain softening effect. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 599–607, 2011

Key words: carbon black; rubber; modulus; model; calculation

INTRODUCTION

Without reinforcing filler, rubbers would have received no application of industrial importance, key developments like automotive and aircraft tires would have remained in limbo and our world would have evolved along a totally different path. The discovery of rubber reinforcement by finely dispersed carbon black (CB) particles in Silvertown, UK in 1907 is thus the perfect example of a key engineering development, whose complex scientific issues still challenge an overall understanding despite a century of active research works.[1] What is well established today is that carbon black aggregates are the reinforcing entities, that such aggregates develop complex interactions with rubber chains and that the reinforcing effect is essentially physical, with very little role, if any, played by rubber and/or carbon black chemistry. Despite the complexity of the problem, some progress was made at the eve of this century so that workable theoretical models are now available to somewhat enlighten the likely origin of reinforcement by carbon black.

Theoretical models are useful if they allow calculations to be made whatever the complexity of the problem considered. The easier the calculation, the more convincing the model, and the more significant the information obtained through calculation. But as a map is not the land, a theoretical model is only a simplification of reality, useful only if the simplification is based on clear reasonning. Filled rubber compounds belong to the class of so-called complex polymer systems whose many issues essentially derive from three basic aspects: (1) an heterogeneous nature, i.e., several phases can be identified, (2) at least one phase exhibits a viscoelastic character, i.e., it has a macromolecular nature, and (3) strong interactions spontaneously develop between the various phases.[2] A number of materials, either of natural origin or of industrial importance, or both, meet this definition and carbon black filled rubber compounds are particularly interesting with respect to the role they play in a number of invaluable applications. At first glance, filled rubber compounds challenge any modeling attempt owing to their complexity, since the most basic formulations do contain more than ten ingredients. By focusing on the rubber and the carbon black, it is however possible to somewhat reduce this complexity to the main tractable components, i.e., the matrix and the dispersed filler. Then, providing a few, justified approximations are considered, it is feasible to develop simple modeling calculations. The objectives of this article are to show that, starting from a suitable geometrical description of carbon black aggregates, easy-to-measure properties do

Correspondence to: J. L. Leblanc (jean.leblanc@ifoca.com)

indeed document such a description so that certain mechanical properties of CB filled rubber compounds can be calculated and compared with experimental data.

Complexity of carbon black filled rubber compounds

Rubber compounds are complex formulations with many ingredients that, from a rheological point of view, can be seen as belonging to three main classes: (1) elastomer(s), i.e., the viscoelastic matrix; (2) fine solid particles, i.e., filler(s) and solid chemicals, e.g., Zinc Oxide; (3) low viscosity materials, i.e., processing oil, waxes and plasticizers, liquid or rubber soluble chemicals. The two former classes play the main role but elements from the third class may significantly affect either the flow properties of the matrix or/and the interactions between the matrix and the dispersed solid phase. It is now well established, whereas not fully understood that a fine structure, so-called morphology, spontaneously develops in CB filled rubber compounds and not only affects the flow properties but also is deeply rooted in the mechanical properties of the vulcanizate.

In what carbon black filled compounds are concerned, it has been well demonstrated that the aggregate is the reinforcing element of any CB grade and the ultimate dispersed element at the end of an optimal mixing procedure. CB aggregates are three-dimensional structures that form through coalescence of roughly spherical elementary particles during the burning/quenching steps of the fabrication process. Aggregates are strongly asymmetrical and at best suiting an ellipsoidal envelope whose long axis is in the 100–200 nm range. However, within a given CB grade, coexist a large variety of aggregate shapes, from spheroidal to ellipsoidal, linear, and branched objects.[3] Generally, the smaller the elementary particles and the more complex the structure of the aggregate, the more reinforcing the carbon black. Practically, carbon blacks are characterized through either adsorption or absorption techniques using simple chemicals. Two such techniques are cetyltrimethylammonium bromide CTAB adsorption (result in m^2/g of carbon black) for assessing the specific surface area and dibutylphthalate DBP absorption (results in cm^3 of absorbed DBP per 100g of filler) for structure assessment. Both techniques are standard methods, respectively, ASTM D3765[4] and ASTM D2414[5] (or ASTM D3493[6] if the carbon black sample is "crushed" before adding drop wise DPB).

Modeling carbon black filled rubber compounds

Owing to their inherent complexity and the various effects at play, deriving an effective model for the mechanical properties of CB filled compounds is at first glance a very challenging task. Indeed, would one want to take into account all the peculiar compounding aspects and the specificities of CB reinforcement, excessively complex mathematical relationships should be developed, and their use would require large computer facilities. In the author's opinion, such an approach is relatively vain because it is possible to simplify the problem by focusing on the matrix, on the carbon black and on the interactions between both, owing to a few reasonable hypotheses, well backed-up by experimental observations. The real challenge is however to develop a model whose all parameters have a physical meaning and are easily assessed through simple available techniques. Would the model allow easy calculations, then it will have a high value, from an engineering point of view.

The following hypotheses are drawn:

1. In a rubber compounds, carbon black aggregates are optimally dispersed so that their spatial arrangement within the rubber matrix complies with simple geometrical descriptions;
2. Rubber–carbon black interactions are essentially physical so that they have no permanent character and are therefore depending of the strain state;
3. Carbon black aggregates can essentially be described in terms of specific surface area and structure, both accessible through standard characterization methods.

To develop a reasonable model to relate mechanical properties (for instance the modulus) of rubber compounds to their intrinsic elements, one will proceed in three steps: first to describe the reinforcing element, i.e., the aggregate, with respect to grade characterization results from standard methods, second to adequately consider an ideal state of filler dispersion, with respect to a simple geometrical description, and third to introduce average rubber–filler interactions with respect to micromechanical considerations.

Modeling the carbon black aggregate

An aggregate is a complex assembly of a number of elementary particles, and within a given CB grade, different aggregate shapes coexist, even if more reinforcing grades tend to contain more open aggregates. Therefore, when one intends to use CB characterization data to describe a given grade, one implicitly considers an hypothetical average aggregate, typical of that grade. The effective volume of an aggregate cannot be directly assessed with any precision and Medalia suggested to consider this quantity as equivalent
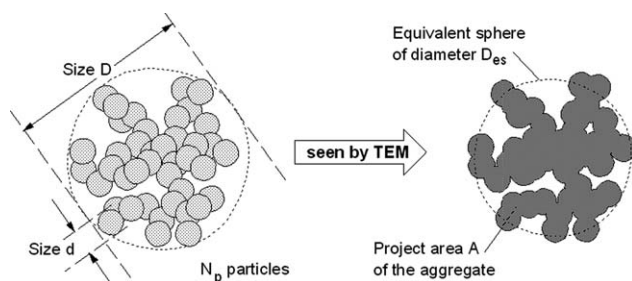
Figure 1 Concept of equivalent sphere for a single Carbon Black aggregate.

to that of a sphere of the same (mean) projected area as the aggregate (see Fig. 1). Obviously the volume of solid carbon within an aggregate is the product of the number of particles N_p times the volume of an elementary particle (assumed to be spherical) of average diameter d. It follows that the measured projected area (a two dimensional quantity) of an aggregate is related to the projected area of its calculated equivalent sphere (a three dimensional quantity) through a scaling law. Medalia et al. performed a so-called "*floc simulation*" to establish the following equality[7,8]:

$$N_p = \left(\frac{A}{A_p}\right)^{1/\varepsilon} \qquad (1)$$

where A is the measured projected area, N_p is the number of elementary particle of projected area A_p and ε a scaling exponent equal to 0.847. Note that in the original publications by Medalia et al., $\varepsilon = 0.87$ but it is a misprint as demonstrated in.[9]

The solid volume V_s of an aggregate is thus the volume of an elementary particle (of diameter d) times the number of particles, so that:

$$V_s = N_p \frac{\pi\ d^3}{6} = \left(\frac{4\ A}{\pi\ d^2}\right)^{1/\varepsilon} \frac{\pi\ d^3}{6} \qquad (2)$$

Modeling the state of dispersion

Let us consider a given mass M_{CB} of carbon black. The number of aggregates Na_{CB} in those M_{CB} grams of carbon black is :

$$Na_{CB} = \frac{M_{CB}}{V_s\ \rho_{CB}} \qquad (3)$$

where ρ_{CB} is the specific gravity of the carbon black.

As discussed above, a CB filler rubber compound can be considered as a soft three-dimensional network in which aggregates act as "anchoring knots" for elastomer chains. One part of the rubber consequently plays a particular role in connecting carbon black aggregates, in other words, in making "junctions" between them,

as suggested by Ouyang et al.[10,11] (with however a number of misprints and unit inconsistencies in their published equations). It is clear that the average inter-aggregate distance is the central argument in this approach, as used in the following development.

At the end point of the so-called "crushed" dibu-tylphtalate adsorption test (ASTM D3493) all the aggregates of the M_{CB} grams of carbon black sample are likely exhibiting the most compact arrangement in the DBP matrix. It follows that, with respect to the overall volume of the DBP + Carbon Black mixture, the filler volume fraction is maximum and given by :
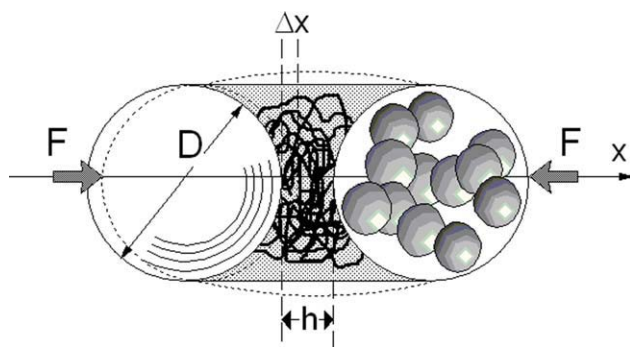
$$\Phi_{maxCDBP} = \frac{\frac{M_{CB}}{\rho_{CB}}}{\frac{M_{CB}}{\rho_{CB}} + cDBP \times M_{CB}} \qquad (4)$$

where cDBP it the crushed DBP adsorption number (cm^3 DBP/100 g of filler). The number of junctions (or contact) points is $Na_{CB}\left(\frac{\varsigma}{2}\right)$ if ς is the average number of contact points between neighboring aggregates. In the DBP + Carbon Black mixture, all aggregates are in contact and the oil fills the micro pores between them. One can hardly consider that carbon black aggregates are dispersed in dibutylph-talate but, if one makes the (strong) hypothesis that in a rubber compound, dispersed aggregates keep the same compact arrangement as in DBP, except that the distance between neighboring aggregates is expanded by an average distance h_{gap}, then one has defined what can be called an optimal state of dispersion, from a three-dimensional point of view.

To proceed further, one has to consider a suitable three-dimensional arrangement of the optimally dispersed aggregates so that the quantity h_{gap} can be conveniently identified. Let us consider a cubic arrangement for the sake of simplicity (Fig. 2), it comes that the carbon black volume fraction is given by:
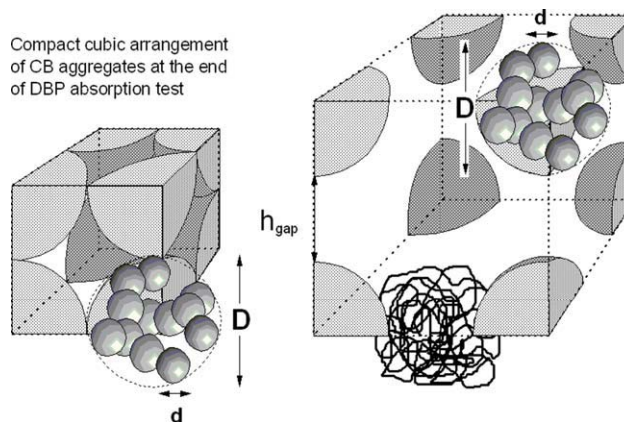
Figure 2 Dispersed in a CB matrix, aggregates keep the same arrangement as at the end of DBP absorption test but interaggregate distance is widened by a distance h_{gap}. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 3 Micro-mechanical interactions between two Carbon Black aggregates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\Phi_{CB} = \frac{\frac{M_{CB}}{\rho}}{\left(\left(\frac{M_{CB}}{\rho_{CB}} + CDBP \cdot M_{CB}\right)^{1/3} + h_{gap} \cdot \left(Na_{CB} \cdot \frac{\varsigma}{2}\right)^{1/3}\right)^3}$$

(5)

In the rubber compound, the maximum carbon black volume fraction is thus lower than in the mixture with DBP because rubber chains move apart neighboring aggregates by the distance h_{gap}. An expression can then be derived for the junction distance, i.e.,:

$$h_{gap} = \left(\frac{3\varsigma}{\pi N_p}\right)^{-\frac{1}{3}} d \left(\sqrt[3]{\frac{1}{\Phi_{CB}}} - \sqrt[3]{\frac{1}{\Phi_{max}}}\right)$$

(6)

where ς is the average number of contact points between neighboring aggregates, N_p the number of elementary particles of diameter d in an aggregate, Φ_{CB} and Φ_{max} respectively, the filler volume fraction and the maximum packing fraction of the carbon black grade in the compound. If one considers that an aggregate consists of a simple assembly of touching elementary particles, one has the following relationship between the specific surface area S_{sp} (in m^2/g) and the elementary particles diameter d: $S_{sp} = \frac{6}{d \rho_{CB}}$. The above equation can consequently be rewritten as:

$$h_{gap} = \left(\frac{3\varsigma}{\pi N_p}\right)^{-\frac{1}{3}} \frac{6}{\rho_{CB} S_{sp}} \left(\sqrt[3]{\frac{1}{\Phi_{CB}}} - \sqrt[3]{\frac{1}{\Phi_{max}}}\right)$$

(7)

So, according to this approach, in a given compound, the junction gap h_{gap} is inversely proportional to the specific surface area of the carbon black, as measured for instance by the adsorption of Cetyltrimethylammonium Bromide CTAB (ASTM D3765). In addition, higher structure blacks will give shorter junction gap because Φ_{max} would be smaller. To readily use eq. (7), one needs characterization

data on carbon black, namely the specific area, the (average) number of particle per aggregate and the number of junction per aggregate. Characterization data are available from various sources (see for instance[9]) and Np can be estimated with the empirical equation developed by Medalia, i.e.:

$$N_p = [1.333 \cdot (1 + DBPa \cdot \rho_{CB} \cdot 0.0115)]^{\frac{2}{3\epsilon - 2}}$$

(8)

where DPBa stands for dibutylphtalate absorption number ($cm^3/100g$ filler) and ρ_{CB} is the specific gravity of the carbon black, generally taken as $\approx$ 1.86 g/cm^3

Modeling the average rubber—carbon black interactions

The above considerations imply that the more reinforcing the carbon black the smaller the junction gap width. A diene rubber with a molecular weight in the 200,000–400,000 g/mol range has a random coil diameter in the 20–40 nm range. It means that for reinforcing carbon black grades, one macromolecule only can establish a junction between two neighboring aggregates. For less or no reinforcing grades, the junction will always involve entangled rubber chains with, as a consequence, lower reinforcing effects. It is accepted today that interactions between (diene) rubbers and carbon black have essentially a physical nature, likely due to topological constraints exerted by the (hard) surface of CB particles on (soft) rubber segments, as explicitly developed in.[12]

The micro-mechanical interactions between two neighbor aggregates and the local rubber matrix can be considered by suitably adapting the analysis made by Gent et al.[13,14] of the behavior of a rubber volume bonded between two rigid spheres (see Fig. 3). When a compressive (or a tensile) force F provokes a small displacement Δx of one sphere with respect to the other, there is a compression (or tensile) stiffness that consists of two parts: (1) the rubber layer compressed (or stretched) between the two spheres, (2) the restraints at the bonded surfaces of the spheres. Gent and Park developed a theoretical equation, which can be approximated by the simple following equality:

$$\frac{F}{E_0 \cdot D \cdot \Delta x} \approx \alpha \cdot \frac{\pi}{8} \cdot \left(\frac{h}{D}\right)^{-\beta}$$

(9)

where E_0 is the modulus of the rubber, D the diameter of the spheres, h the initial gap, $\alpha \approx 1.22$ and $\beta \approx 0.96$. This equation essentially predicts an inverse dependence of the stiffness upon the ratio h/D for relatively large separation, i.e., in a layer thickness range down to one-tenth of the sphere radius.

If one considers a volume V of filled compound, the overall number of carbon black aggregates is $\frac{N}{V} = \Phi_{CB} \cdot \rho_{CB} \cdot \frac{Na_{CB}}{M_{CB}}$, where M_{CB} is the mass of carbon black that corresponds to the volume fraction Φ_{CB}. With respect to eq. (2), it follows that in a cross-sectional area of the sample (i.e., $\left[\sqrt[3]{V}\right]^2$), the number of aggregates is :

$$\left(\frac{N}{V}\right)^{2/3} = \left(\frac{6\,\Phi_{CB}}{\pi\,N_p}\right)^{2/3} \cdot \frac{1}{d^2} \tag{10}$$

When the sample is stretched (of compressed) along one axis by a strain ΔX, there will be $\left(\frac{N}{V}\right)^{2/3}$ junction gaps contributing to the stress, in addition to the response of the unfilled rubber fraction. With respect to eq. (9), the junction gaps contribute to a force over the cross section $V^{2/3}$ and, because obviously $\Delta X = \Delta x \cdot (N/V)^{1/3}$, the network junction contributes to the modulus by a quantity:

$$\frac{F_J}{\Delta X} = \left(\frac{N}{V}\right)^{1/3} \cdot E_0 \cdot D_{es} \cdot \alpha \cdot \frac{\pi}{8}\left(\frac{h_{gap}}{D_{es}}\right)^{-\beta} \tag{11}$$

where D_{es} is the equivalent sphere diameter of an aggregate, in agreement with Medalia's views. When expressing D_{es} in terms of number of elementary particles and substituting eqs. (7) and (10) into eq. (11), it comes :

$$\frac{F_J}{\Delta X} = E_0 \cdot \alpha \cdot \frac{\pi}{8}$$
$$\cdot \left(\frac{6\,\Phi_{CB}}{\pi\,N_p}\right)^{\frac{1+\beta}{3}} \cdot N_p^{\frac{\varepsilon(\beta+1)}{2}} \cdot \left(\frac{\zeta}{2}\right)^{\frac{\beta}{3}} \cdot \left[1 - \left(\frac{\Phi_{CB}}{\Phi_{max}}\right)^{\frac{1}{3}}\right]^{-\beta} \tag{12}$$

However, over the cross section, there is also a contribution from the rubber matrix alone, whose associated stiffness can be estimated as :

$$\frac{F_R}{\Delta X} = E_0 \cdot \left(1 - \Phi_{CB}^{2/3}\right) \tag{13}$$

so that the final equation to calculate the modulus of a carbon black filled rubber compound is:

$$E_{cpd} = E_0 \left\{ \alpha \cdot \frac{\pi}{8} \cdot \left(\frac{6\,\Phi_{CB}}{\pi}\,N_p\right)^{\frac{1+\beta}{3}} \cdot N_p^{\frac{\varepsilon(\beta+1)}{2}} \right.$$
$$\left. \cdot \left(\frac{\zeta}{2}\right)^{\frac{\beta}{3}} \left[1 - \left(\frac{\Phi_{CB}}{\Phi_{max}}\right)^{\frac{1}{3}}\right]^{-\beta} + 1 - \Phi_{CB}^{2/3} \right\} \tag{14}$$

All parameters in eq. (14) are physically identified and all but one can be derived either from the formulation (e.g., Φ_{CB}) or from standard characterization methods for carbon black (e.g., Φ_{max}, eq. (4),

and N_p, eq. (8). Only ς, the average number of contact points, must either be guessed or extracted from experimental data, as demonstrated below. Note that eq. (14) explicitly considers tensile moduli but one can expect that the model is valid for other strain mode, e.g., shearing, because the ratio E_{cpd}/E_0 is essentially the same as the ratio G_{cpd}/G_0.

EXPERIMENTAL

A series of emulsion Styrene-Butadiene Rubber (Buna SE 1500, Lanxess, Germany) compounds with N330 carbon black level ranging from 0 to 50 phr but no curatives[*] were prepared in a Haake Rheocord 90 laboratory mixer, equipped with a 300 cm³ chamber and Banbury type rotors. Rotors rate was 40 RPM, fill factor 0.7 and a dead-weight of 5 kg was used to close the chamber. The highest carbon black loaded batch ($\Phi_{CB} = 0.1836$) corresponds approximately to an ASTM standard formulation (ASTM D3185-06 - « Evaluation of SBR (Styrene-Butadiene rubber) including mixtures with oil),[15] with a lower oil level however, and a reinforced protective system to ensure a better temperature and ageing stability. All batches were mixed for the same time (5.5 min.) so that the overall mixing energy ranged from 423.6 MJ/m³ (unfilled compound) up to 732.5 MJ/m³ (50 phr black filled compound); temperatures at the end of the mixing operations were in the 110 to 124°C range (respectively, unfilled and 50 phr black filled compounds). A similar series of Natural Rubber compounds[+] were prepared with Ribbed Smoked Sheet RSS3, as commercially available in France. The same mixer, mixing conditions and procedure were used but RSS3 was separately premasticated in a 1.5 L Banbury mixer for 3 min (ME ≈ 630 MJ/m³), dumped, sheeted-off and stored for 24 h at room temperature before preparing compounds. To ensure that all rubber-filler interactions were completed,[16] all compounds were stored under dark cover at room temperature for one month before performing rheological tests.

Complex modulus at 100°C, 0.5 Hz were measured with a Rubber Process Analyzer RPA® 2000 (Alpha Technologies, now a division of Dynisco LLC, Franklin, MA), using a strain sweep test protocol. This test procedure consists in performing

[*]Buna SBR SE 1500: 100 phr (part per hundred rubber); N330 carbon black: variable; Napthenic oil: 5 phr; Zinc Oxide: 5 phr; Stearic Acid: 3 phr; Trimethylquinoline, polymerized: 2 phr; N-isopropyl-N'-phenyl-p-phenylene diamine: 1 phr

RSS3: 100 phr; N330 carbon black: variable; Napthenic oil: 5 phr; Zinc Oxide: 5 phr; Stearic Acid: 3 phr; Trimethylquinoline, polymerized: 2 phr; N-isopropyl-N'-phenyl-p-phenylene diamine: 1 phr

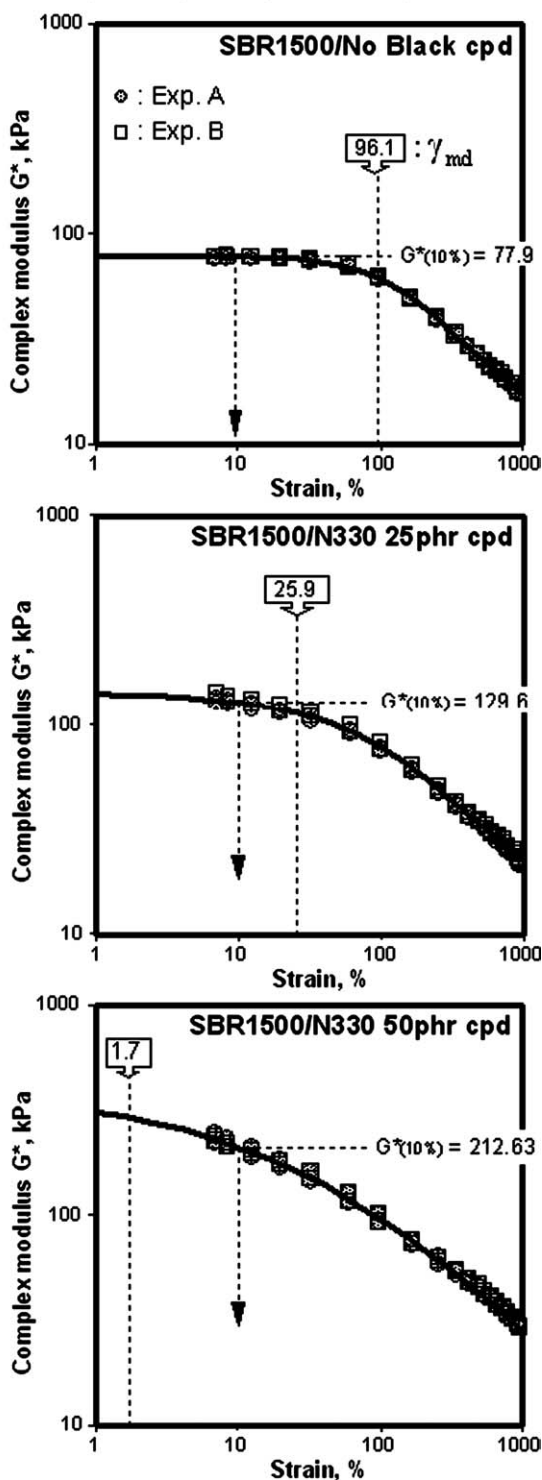**RPA-FT; 100°C; 0.5Hz; tests a&b, runs 1&2**

Figure 4 RPA strain sweep tests (100°C; 0.5 Hz) on SBR compounds; typical results and fitting with Eq. 15.

experiments (at fixed frequency and temperature) through two subsequent runs separated by a resting period of 2 min. The experimental strain amplitude window is 0.5 to 68°. At least two samples of the same compound are tested (more if results reveal material heterogeneity), in such a manner that,

through inversion of the strain sequences (i.e., run 1 and run 2), sample fatigue effects are detected, if any. Differences are indeed expected between runs 1 and 2 for materials exhibiting strain memory effects, either permanent or at least not fully dampened after the 2 min resting period. No significant strain history effect were observed with all the samples tested, so that results from runs 1 and 2 were merged and fitted using the following equation:

$$G^*(\gamma) = G_f^* + \left[\frac{G_0^* - G_f^*}{1 + \left(\frac{\gamma}{\gamma_{md}} \right)^B} \right] \quad (15)$$

where G_0^* is the modulus in the linear region, G_f^* the final modulus, γ_{md} the strain for the mid-modulus value, i.e., $(G_0^* + G_f^*)/2$, to be reached, and B a parameter related to the strain sensitivity of the material.

Figure 4 shows typical results on SBR compounds. As can be seen eq. (15) perfectly fits experimental data and is thus a very convenient manner to pertinently summarize a large number of measured data through a reduced set of significant parameters. Similar observations are made with NR compounds. Experimental data in terms of eq. (15) parameters are given in Tables I and II.

As can be seen, the fitting is excellent with respect to standard (i.e., mean square) deviation values that are always higher than 0.99. These data precisely document the effect of compounding ingredients, namely carbon black on complex modulus. eq. (15) gives either the so-called linear complex modulus G_0^*, readily an extrapolation to zero strain of the measured data, or any recalculated $G^*(\gamma)$ value within the experimental window, i.e., 6.98 to 949.46%. When the tested material exhibits a linear viscoelastic behavior within the RPA experimental window, G_0^* appears less an extrapolated value than a truly measured material property, as it is readily the case up to around 25 phr Carbon Black. When the material shows a nonlinear behavior in the experimental windows, then caution must be taken in discussing G_0^* results. A few negative values for G_f^* are reported in Tables I and II. They have obviously no physical meaning and are mere artifacts of the nonlinear fitting algorithm. In fact G_f^* are mathematical values at infinite strain and are therefore purely hypothetical. While necessary for the goodness of the fit, such data are not considered as relevant in terms of material properties.

Calculating complex dynamic modulus of filled compounds

To use eq. (14) to calculate G* modulus one needs essentially standard (ASTM) characterization data for Carbon Black, i.e., DPB (ASTM D2414-09a) and

TABLE I
Strain Sweep Tests at 100°C, 0.5 Hz Tests on SBR1500 Carbon Black Filled Compounds

Sample	SBR-00	SBR-05	SBR-10	SBR-15	SBR-25	SBR-30	SBR-33	SBR-35	SBR-40	SBR-50
N330 loading	no black	5phr	10phr	15phr	25phr	30phr	33phr	35phr	40phr	50phr
Φ_{black}	0.0000	0.0220	0.0431	0.0632	0.1011	0.1189	0.1293	0.1360	0.1525	0.1836
G_0^*, kPa	78.7	88.5	99.2	114.1	143.7	163.3	173.5	194.3	234.9	363.7
G_f^*, kPa	12.3	11.4	10.7	9.7	5.9	3.7	2.6	1.9	−1.5	−3.9
γ_{md}	200.0	181.8	163.9	137.0	108.7	90.1	80.6	67.1	48.1	18.5
B	1.50	1.33	1.22	1.07	0.91	0.83	0.8	0.75	0.68	0.59
r^2	0.9999	0.9999	0.9999	0.9998	0.9999	0.9999	0.9999	0.9999	0.9999	0.9998
$G_{(10\%)}^*$, kPa	77.95	86.92	96.36	108.07	129.62	141.13	146.19	157.25	174.14	212.63

Results in terms of fit parameters of eq. (15); note that negative G_f^* values have no physical meaning but result from the non-linear fitting process.

cDBP (ASTM D3493 - 09) absorption data and an appropriate value for the number of junctions ς. For N330 carbon black, eq. (4) yields $\Phi_{max} = 0.382$ with cDBP = 0.87 cm^3/g and eq. (8) gives the number of particles/aggregate $N_p = 209$ with DBP = 1.02 cm^3/g. Figure 5 shows the comparison of experimental data with results obtained with eq. (14) either for the (linear) complex modulus G_0^* or a value within the experimental window, here G*(10%). The curve drawn using the well-known Guth and Gold model [i.e., $G^* (\Phi) = G^* (0) \times (1 + 2.5 \Phi + 14.1 \Phi^2)$] is shown for comparison. The number of junctions ς was obtained by fitting the data with eq. (14), using a nonlinear algorithm (i.e., Marquardt-Levenberg). As can be seen, using $\varsigma = 3.16$, a good agreement is seen between experimental and calculated data for the (linear) complex modulus G_0^*, but $\varsigma = 0.99$ must be used for a good (in fact better) agreement with G*(10%). It must be noted however that G_0^* is an extrapolated value [through nonlinear fitting of experimental results with eq. (15)], and therefore relatively uncertain in the case of the highly loaded compounds. Considering recalculated values, e.g., G*(10%), within the experimental strain window allows to consider unambiguous modulus values that perfectly meet the model.

Figure 6 shows the same demonstration in the case of filled Natural Rubber compounds. The (linear) complex modulus G_0^* data call for the same comments but lower values for the number of junctions must be used as the strain amplitude increases.

The decrease of dynamic moduli, either the complex G* or the elastic G′ modulus, upon increasing strain amplitude at constant frequency and temperature is a typical nonlinear viscoelastic property of polymer materials. Already observable with unfilled rubbers, this so-called dynamic strain softening (DSS) effect is enlarged by the presence of fillers, particularly reinforcing ones like carbon black. Various physical interpretations have been offered for the DSS effect, all calling to local mechanisms that generally involve interactions either between filler particles, or between particles and polymer matrix, or a combination of both (see[9] for an extended discussion). With unfilled materials, the DDS effect is weaker but readily observed (see Fig. 4 above) and in such cases a convincing explanation is the nonaffinity of the deformation, which essentially means that macromolecular entanglements move with respect to a coordinate system embedded in the material.

Equation (14) can be seen as the product of the modulus of the unfilled system (i.e., E_0) times a

TABLE II
**Strain Sweep Tests at 100°C, 0.5 Hz Tests on RSS3 Carbon Black Filled Compounds**

Sample :	RSS3–00	RSS3–05	RSS3–10	RSS3–15	RSS3–25	RSS3–30	RSS3–33	RSS3–35	RSS3–40	RSS3–50
N330 loading :	no black	5phr	10phr	15phr	25phr	30phr	33phr	35phr	40phr	50phr
Φ_{black}	0.0000	0.0220	0.0431	0.0632	0.1011	0.1189	0.1293	0.1360	0.1525	0.1836
G_0^*, kPa	109.3	115.2	128.7	133.4	137.2	183.9	194.9	201.5	236.9	366.1
G_f^*, kPa	11.7	10.0	8.9	8.7	9.7	4.3	2.8	1.8	−1.6	−11.1
γ_{md}	150.4	137.9	124.1	117.5	117.8	82.2	74.5	70.1	55.7	27.0
B	1.57	1.41	1.30	1.24	1.30	1.00	0.95	0.91	0.83	0.67
r^2	0.9935	0.9980	0.9985	0.9962	0.9973	0.9985	0.9983	0.9981	0.9989	0.9961
$G_{(10\%)}^*$, kPa	107.97	112.67	124.28	127.74	132.21	164.39	170.09	172.49	190.69	237.99

Results in terms of fit parameters of eq. (15); note that negative G_f^* values have no physical meaning but result from the non-linear fitting process
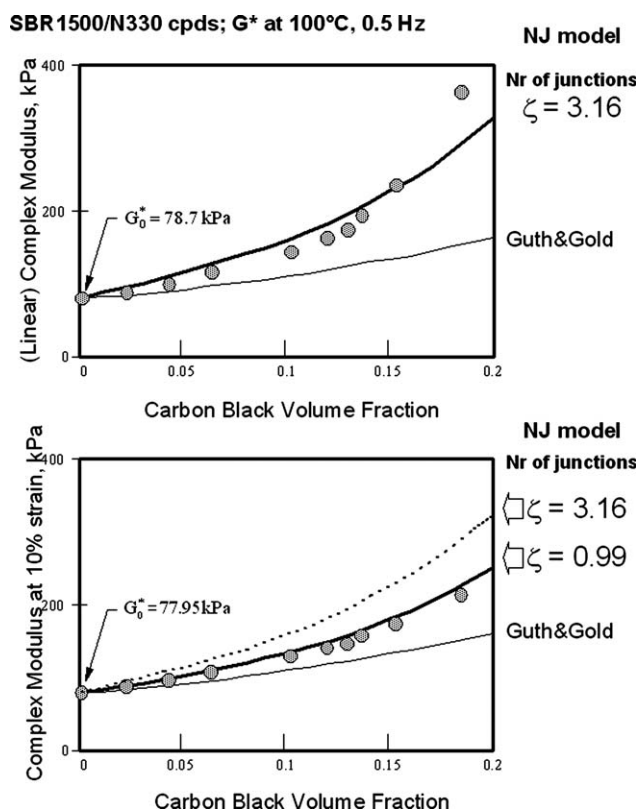
Figure 5 Calculating the complex modulus of N330 filled SBR1500 compounds.

term accounting for the effect of CB aggregates. It follows that in the application of eq. (14) to experimental data, the DSS effect on the unfilled matrix is de facto incorporated in the modulus values at zero CB loading. Consequently how the number of junction ς varies with increasing strain amplitude might be considered as an explanation for the enhanced DSS effect with filled systems. Figure 7 compares the variation of ς for the two studied systems. As can be seen, at a given strain amplitude, the number of junction is significantly differing for SBR and NR compounds, the former having about three times more junctions than the latter. Such an observation is conform with the stronger filler-rubber interactions in the case of Natural Rubber and hence a lower number of junctions to achieve the same (relative) level of reinforcement. One also sees that the decrease of ς with strain amplitude is a behavior common to both systems and particularly important as soon as the strain is larger than 1%. Because rubber - carbon black interactions are essentially physical in the case of diene elastomers, the decrease of junctions with higher strain amplitude is generally reversible providing the CB loading is not excessive, as readily demonstrated by the superimposition of run 1 and run 2 strain sweep data (see Fig. 4). The DSS effect of (uncured) CB filled systems can thus be assigned to a progressive
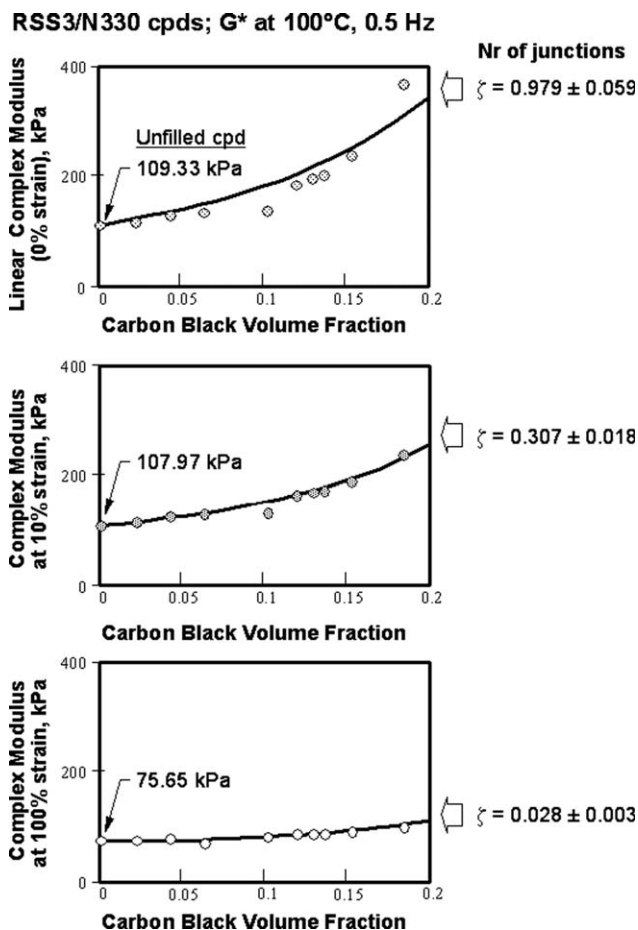
Figure 6 Calculating the complex modulus of N330 filled RSS3 compounds.

and temporary detachment of rubber segments, physically anchored on aggregate surfaces. This
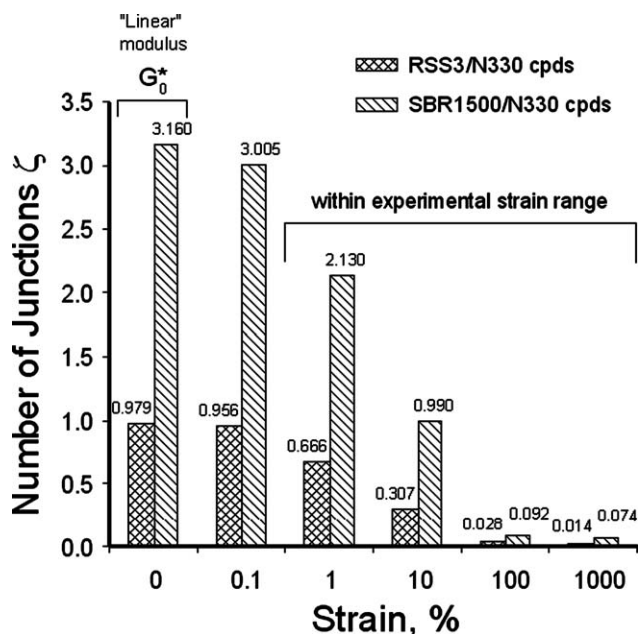
Figure 7 Variation of the number of junctions with increasing strain amplitude.

conclusion is an unexpected benefit of the modeling approach.

CONCLUSIONS

Carbon Black filled rubber compounds are very complex systems but it is possible to somewhat reduce this complexity to the main tractable components, i.e., the matrix and the dispersed filler. With respect to a few, justified approximations, a simple model was developed to readily calculate modulus, by using only CB standard characterization data, CB volume fraction and only one adjustable parameter, the number of junctions per aggregate. The model was successfully probed with two series of CB filled compounds, using SBR1500 and RSS3 as rubber matrix materials and the usual compounding ingredients. Through a comparison of experimental data and calculation results, it was found that the (guessed) number of junctions must decrease with increasing strain amplitude to meet the dynamic strain softening effect, as observed during strain sweep experiment. Unexpectedly thus, the proposed model is offering an explanation for the DSS effect.

NOMENCLATURE

A	Measured projected area of an aggregate (m^2)
B	Strain sensitivity parameter (strain sweep experiment)
cDBP	Crushed DBP adsorption number $(cm^3$ DBP/100 g of filler) [ASTM D3493 - 09]
D	Diameter an elementary particle in a CB aggregate (m)
D	Diameter of enveloping sphere of an aggregate (m)
D_{es}	Equivalent sphere diameter of an aggregate
DPB	adibutylphtalate absorption number (cm3/100g filler) [ASTM D2414–09a]
E_0	Modulus of rubber matrix (kPa)
E_{cpd}	Modulus of rubber compound (kPa)
G_0^*	(Extrapolated) Modulus in the linear region, kPa (strain sweep experiment)
G_f^*	Final modulus at infinite strain, kPa (strain sweep experiment)
h_{gap}	Average distance between neighboring

	aggregates (m)
M_{CB}	Mass of a carbon black sample (g)
N_p	Number of elementary particle of projected area A_p (m^2)
Na_{CB}	Number of aggregates in M_{CB} grams of carbon black
S_{sp}	Specific surface area of carbon black (m^2/g)
V_s	Solid volume of an aggregate (m^3)
$\alpha \approx 1.22$	Prefactor
$\beta \approx 0.96$	Scaling exponent
ϵ	Scaling exponent (0.847)
γ_{md}	Strain for the mid-modulus value, i.e., $(G_0^* + G_f^*)/2$ (strain sweep experiment)
ρ_{CB}	Specific gravity of the carbon black ($\approx$ 1.86 g/cm^3.)
ς	Average number of contact points between neighboring aggregates
Φ_{CB}	Carbon black volume fraction
Φ_{max}	Maximum packing fraction of carbon black in compound

References

1. Gent, A. N. In Current Topics on Elastomer Research; Bhowmik, A. K., Ed.; CRC Press, Taylor & Francis Group: Florida, 2008; Chapter 1, pp 3–20.
2. Leblanc, J. L. Prog Polym Sci 2002, 27, 627.
3. Herd, C. R.; McDonald, G. C.; Hess, W. M. Rubb Chem Technol 1992, 65, 107.
4. ASTM D3765-99. Standard Test Method for Carbon Black-CTAB (Cetyltrimethylammonium Bromide) Surface Area. ASTM International: West Conshohocken, PA, 2003; DOI: 10.1520/D3765-99, Available at: www.astm.org.
5. ASTM D2414-09a. Standard Test Method for Carbon Black-Oil Absorption Number (OAN). ASTM International: West Conshohocken, PA, 2003; DOI: 10.1520/D3765-99, Available at: www.astm.org.
6. ASTM D3493-09. Standard Test Method for Carbon Black-Oil Absorption Number of Compressed Sample (COAN). ASTM International: West Conshohocken, PA, 2003; DOI: 10.1520/ D3765-99, Available at: www.astm.org.
7. Medalia, A. I. J Colloid Inter Sci 1967, 24, 393.
8. Medalia, A. I.; Heckman, F. A. Carbon 1969, 7, 567.
9. Leblanc, J. L. Filled Polymers : Science and Industrial Applications; CRC Press: Taylor & Francis Group, Florida, 2010; Chapter 4, Section 4.1.4.
10. Ouyang, G. B.; N. Tokita, M.;. J Wang. Hysteresis mechanisms for carbon black filled vulcanizates - a network junction theory for carbon black reinforcement. ACS, Rubb Div Mtg, Cleveland, Ohio; Oct. 17–20, 1995; paper 108.
11. Ouyang, G. B. Kautch Gummi Kunstst 2006, 59, 332.
12. Leblanc, J. L. J Appl Polym Sci 2000, 78, 1541.
13. Gent, A. N.; Park, B. Rubb Chem Technol 1986, 59, 77.
14. Gent, A. N.; Hwang, Y. C. Rubb Chem Technol 1988, 61, 630.