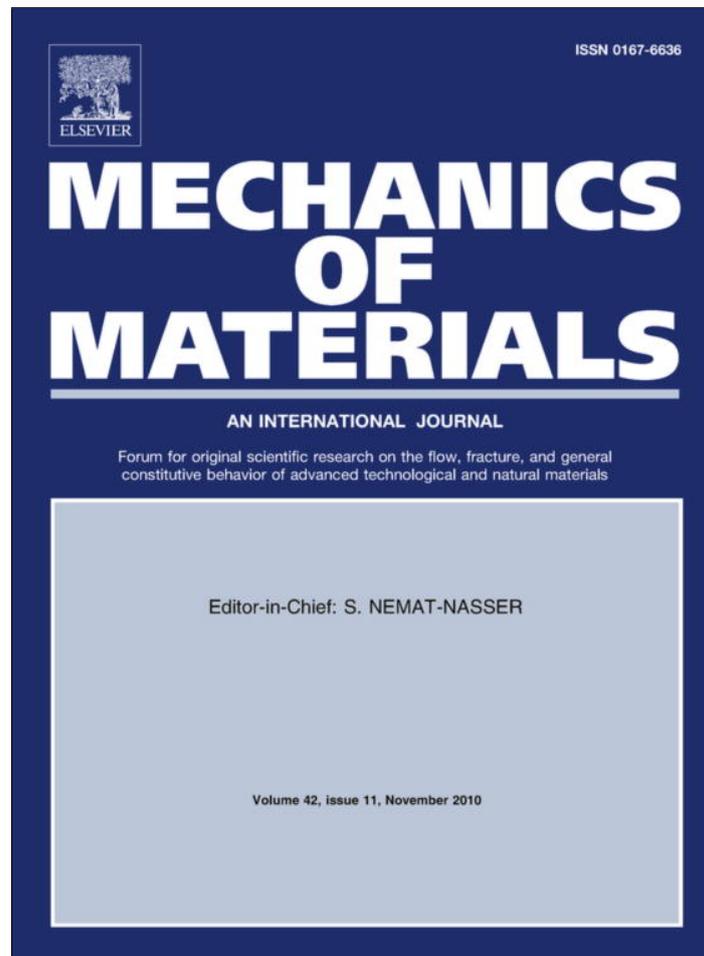


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# A simple analogy between carbon black reinforced rubbers and random three-dimensional open-cell solids

Agathe Robisson\*

Schlumberger Doll Research, 1 Hampshire Street, Cambridge, MA 02139, USA

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## ABSTRACT

We propose to analyze carbon black filled elastomers as random three-dimensional cellular solids where bending arms are made of carbon black clusters coated with bound rubber, and where the matrix is the free rubber. Both phases are co-continuous. This work aims at presenting a simple but lacking physical model that integrates the to-date understanding of rubber reinforcement and can describe the complex small strain mechanical behavior that results from adding a colloidal filler such as carbon black or silica to a rubber. This analogy is able to capture the composite modulus changes with filler content, temperature and strain, through the description of the volume fraction of the bending arms composing the skeleton. Indeed, the modulus decreases with strain as the bending arms are breaking apart (analogy with filler network breaking apart through des-agglomeration process) and decreases with temperature as the bending arms are getting thinner (analogy with the adsorbed layer of rubber on filler disappearing with rising temperature).

Experimental data involving a hydrogenated nitrile butadiene rubber (HNBR) filled with N330 carbon black and resulting from a systematic study of strain and temperature influences, agree well with the model.

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## 1. Introduction

Technical rubbers used in dynamic applications (tire, damping components) or in high temperature applications (automotive o-rings, oilfield) can experience temperatures far above room temperature. Their chemical behavior has been an important focus of both manufacturing companies and end-users, but their mechanical behavior has been far less studied and understood at those temperatures, even though a significant decrease of mechanical properties is observed. Indeed, some industrial elastomers exhibit a drop in small strain modulus of more than 50% when temperature increases from 20 °C to 150 °C, and this decrease was found to be highly dependent on the nature and the quantity of reinforcing fillers present in the elastomer.

The reinforcing effect of carbon blacks has been mostly studied at room temperature and has been reported to be dependent on the filler loading (Guth, 1945) and the physical nature of the carbon black (Medalia, 1970). More specifically, it is highly correlated to the specific surface area of the filler (Rehner, 1943; Göritz et al., 1999), to the filler aggregate structure and agglomeration (Payne, 1962; Payne and Whittaker, 1971; Medalia, 1974; Mele et al., 2002; Heinrich and Klüppel, 2002), and the filler surface properties (Heckman, 1964; Dannenberg, 1986; Göritz et al., 1999). Networking or percolation of filler has been largely studied through electrical conductivity measurement: Changes of orders of magnitude occur around percolation threshold (Medalia, 1986).

The interactions between rubber and filler, driving property changes in the polymer close to the rubber filler or trapped within the aggregates, has also largely been discussed, introducing the concepts of “bound rubber” and “occluded rubber”. Occluded rubber is the immobilized

\* Tel.: +1 617 768 2203; fax: +1 617 768 2384.

E-mail address: [agathe.robisson@gmail.com](mailto:agathe.robisson@gmail.com)

rubber within aggregates. Bound rubber is the rubber modified (“immobilized” or “insolubilized”) by vicinity of filler (Stickney and Falb, 1964; Dessewffy, 1962; Meissner, 1974; Wolff et al., 1993).

The filler reinforcement is also affected by strain, and the decrease in modulus has been attributed both to the breakdown of filler aggregate network (Payne and Whittaker, 1971) and the decrease of bound rubber content due to the modification of the adsorption/desorption equilibrium with strain (Maier and Göritz, 1996). The effect of temperature has also been related to those two phenomena: the breakdown of filler network due to thermal expansion (Payne and Whittaker, 1971) and the decrease of bound rubber thickness following Arrhenius law (Dessewffy, 1962; Maier and Göritz, 1996; Guy et al., 2009).

In this paper, we discuss and model those specific effects considering the filled elastomer as a random three-dimensional open-cell solid where bending arms are made of carbon blacks clusters coated with bound rubber, and where the free rubber is the matrix. The analogy between cellular solids and filled rubbers comes after (Witten et al., 1993; Lin and Lee, 1996 and Kluppel et al., 1997) work that involved the characterization of both the complex mechanical and electrical behaviors of such composites.

## 2. Mechanical model

### 2.1. Analogy between carbon-black filled rubbers and open cell three-dimensional solids

The open-cell solid based model is inspired by the now accepted physical representation of filled rubber, where carbon black fillers surrounded by bound rubber form a percolated network, i.e. continuous phase, inside the matrix (Mele et al., 2002; Leblanc, 2002). Our high resolution scanning electron microscope (SEM) microstructure observations agree with this physical picture, Figs. 1 and 2. We observe a rubber sample comprising 28 vol.% of N330 carbon black (70 phr) and surprisingly, the sample looks like a granular material, where “grain” size varies between 50

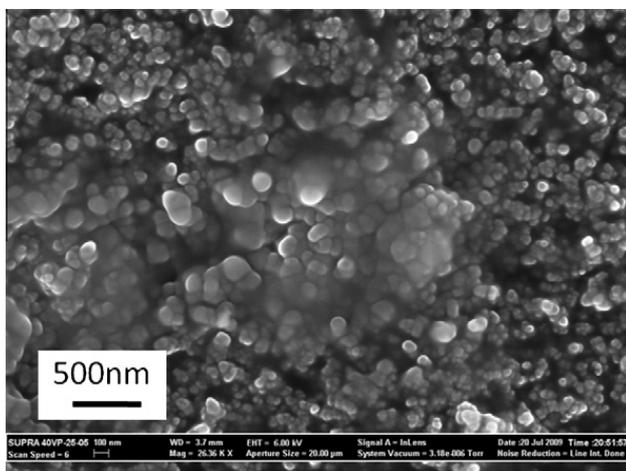


Fig. 1. SEM picture, HNBR rubber filled with 28% N330 carbon black (0.28 CB), HNBR sample surfaces were prepared at  $-50^{\circ}\text{C}$  using a microtome.

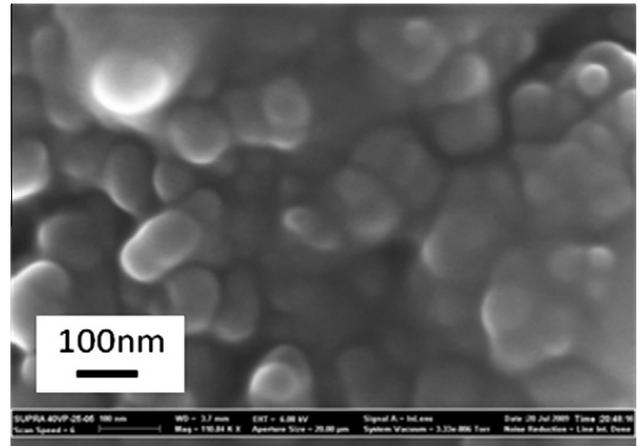


Fig. 2. SEM picture, HNBR rubber filled with 28% N330 carbon black (0.28 CB), HNBR samples surfaces were prepared at  $-50^{\circ}\text{C}$  using a microtome.

and 200 nm. The soft appearance of the grain surface tends to suggest all “grains” are covered with rubber. They also seem connected to each other through this same smooth matter, i.e. rubber. We assimilate the “grains” to carbon black aggregates coated with rubber. It appears the microtome knife did not break apart those aggregates, but instead cut the rubber matrix in between aggregates, showing that those aggregates would form agglomerates through filler-rubber-filler contacts and not through direct filler-filler contacts.

In our analogy between filled rubbers and open-cell solids, the connected “grains” (or aggregates) would form the skeleton of the solid. Indeed, the small strain modulus of filled rubbers is mainly governed by the filler agglomerates (carbon black aggregates coated with adsorbed rubber and bonded to each other through the adsorbed rubber layer) to the same extent that the modulus of cellular solids is governed by the modulus of the skeleton material. The general empirical relationship between the cellular solid reduced density ( $\frac{\rho}{\rho_s}$ ) and its modulus is (Gibson and Ashby, 1988):

$$E = C E_s \cdot \left(\frac{\rho}{\rho_s}\right)^n \quad (1)$$

$E_s$  is the Young’s modulus of the material composing the skeleton.  $C$  and  $n$  are constants and depend on the microstructure.

This equation can also be written as a function of the volume fraction  $\Phi$  of the material composing the skeleton.

$$E = C E_s \cdot \Phi^n \quad (2)$$

The volume fraction of filler is also raised to the power in the widely used Guth and Gold model (1938) to take into account the interactions between particles. The squared power was insufficient to model rubber with more than 10% of filler, and Guth introduced a shape factor  $f$ , associated with the formation of rodlike filler particles. In Fig. 3, we compare results from the Guth and Gold equations to our experimental results (described later), plotting the reinforcement as a function of filler content. The non-linearity of the reinforcement with carbon black content

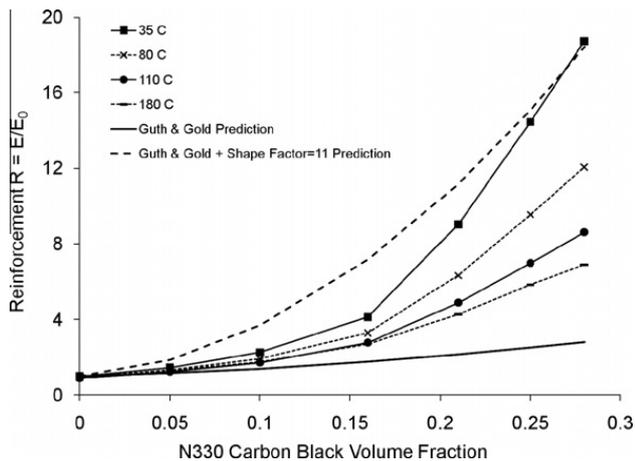


Fig. 3. Carbon black content dependence of reinforcement ( $R = E'/E_0$ ) for HNBR rubber filled with N330 carbon black at different temperatures – experimental data's and Guth and Gold model predictions (1938).

is not properly captured. Medalia (1974), on the other side, associated the stiffening to the fraction of rubber that does not deform, the “occluded” rubber, i.e. the rubber trapped within the aggregates. He introduced an effective filler fraction, rather than a pure carbon black filler fraction, to model this stiffening. Other authors (Meissner, 1974; Guth, 1945) mention a rubber fraction that would participate in the stiffening as well: the fraction of rubber that is adsorbed on the surface of the filler, the “bound rubber”.

2.2. Open-cell solid skeleton: influence of the adsorbed rubber phase

The rubber adsorbed phase, or bound rubber, has been largely described and discussed. Smit (1966) measured a shift in loss modulus peak that he attributed to an adsorbed rubber layer and approximates the thickness to be a minimum of 2 nm. Heinrich and Klüppel (2002) mention a glassy phase that greatly contributes to the stiffness of the carbon black cluster arms. Mele et al. (2002) consider this additional phase in their model and are able to predict viscoelastic behavior of silica filled SBR. Electrical conductivity studies showed that around and above percolation, conductivity seems to be limited by the conduction through rubber between aggregates (Meier et al., 2007). The gap size was found to be between 2 and 5 nm and to be independent of carbon black concentration.

Practically, bound rubber can be measured using the solvent method: it is the portion of rubber that cannot be removed when the raw rubber is put in a good solvent (Dessewffy, 1962). Using this method, the bound rubber phase was measured to be proportional to carbon black content (Villars, 1956; Dessewffy, 1962), and dependent on filler type, polymer gum, polymer molecular weight, mixing time and energy, and uncured compound storage time (Leblanc, 2002). The layer thickness was described as 4–8 nm for 17 different carbon blacks (Wolff et al., 1993).

Bound rubber was also characterized by nuclear magnetic resonance (NMR) through the measure of change in mobility of polymer segment chains around fillers. Kauf-

man et al. (1971) studied bound rubber/carbon black samples after extraction of the rubber matrix by a good solvent in temperature. By analyzing this residue (carbon black + bound rubber), they measured that 14% of the bound rubber chains were completely immobilized, and the remaining chains were still constrained compared to the chains in the pure rubber. They also showed that this mobility restriction was temperature dependant. Leu et al. (2004) identified with similar techniques the immobile layer and the constrained layer, with a total thickness between 2 and 4 nm.

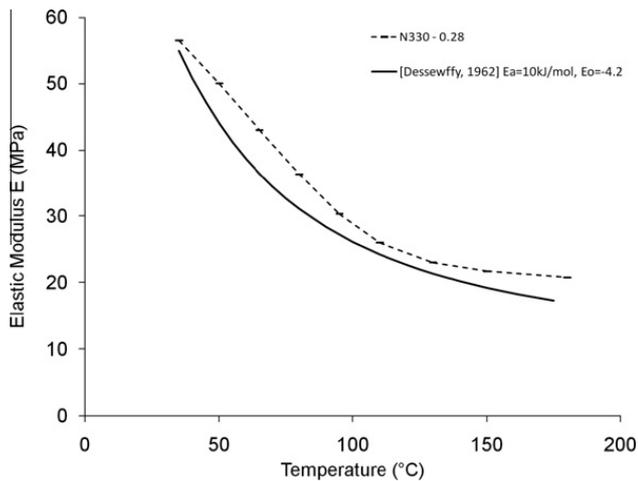
Following these published results, as well as our microstructural observations (SEM, Figs. 1 and 2, and Atomic Force Microscopy (AFM) (Qu et al., submitted for publication)), we assume that the skeleton that constitutes the continuous stiff phase in the open-cell foam is made of carbon black (CB) aggregates coated with bound rubber (BR), and connected through bound rubber. The effective skeleton volume fraction  $\Phi_{eff}$  can therefore be described as

$$\Phi = \Phi_{eff} = \Phi_{CB} + \Phi_{BR} \tag{3}$$

The temperature dependence of the filled rubber small strain modulus is mainly related to this adsorbed rubber phase. Physically, the bound rubber results from equilibrium between adsorption and desorption of polymer chains on carbon blacks and the process is thermally activated (Göritz et al., 1996). Practically, it can be measured as a function of temperature using the solvent method, and the fraction that does not dissolve was found to decrease when the temperature of the solvent exposure increased, following a Maxwell–Boltzmann distribution (Dessewffy, 1962; Wolff et al., 1993; Göritz et al., 1999).

$$\ln(\Phi_{BR}) = E_0 + \frac{E_a}{RT} \tag{4}$$

where  $E_0$  is a constant and  $E_a$  is the adsorption energy. Similarly, Heinrich and Klüppel (2002) describe the softening of filled rubbers with temperature as related to the change in bending–twisting modulus of the aggregate’s arms that happens when the adsorbed rubber changes from glassy to rubbery phase. Payne argues that the modulus dependence to temperature is induced by the network breakdown due to strain caused by thermal expansion (1962). In this paper, we assume that the softening is related to the change in geometry of the skeleton, and the change can be caused either by the decrease in diameter of the skeleton arms when the bound rubber desorbs, or the decrease in effective contacts between aggregates when bound rubber desorbs from filler surface, breaking agglomerates apart. The effective reinforcing fraction therefore decreases with temperature following the Arrhenius Equation. Fig. 4 illustrates the fitting of the Arrhenius equation on experimental results for a highly filled rubber sample. The identified adsorption energy is 10 kJ/mol. This value is comparable to values obtained by Dessewffy (1962) from measurements on different carbon black filled natural rubbers exposed to benzene between 20 °C and 90 °C, and where adsorption energy were calculated between 7.5 and 17.6 kJ/mol (resp. 0.08 eV and 0.18 eV). Göritz et al. (1999) mentioned very similar values of 17.6 kJ/mol (0.18 eV) for SBR (styrene butadiene rubber)



**Fig. 4.** Elastic modulus as a function of temperature for HNBR rubber filled with N330 carbon black,  $\Phi_{CB} = 0.28$  – experimental data and prediction using Dessewffy equation (1962).

and 14.6 kJ/mol (0.15 eV) for NR (natural rubber). [Guy et al. \(2009\)](#) found an activation energy for silica filled sSBR of 8–12 kJ/mol.

Following this idea, we propose the equation below to describe bound rubber: the bound rubber phase content  $\Phi_{BR}$  is proportional to carbon black volume fraction  $\Phi_{CB}$  and follows an Arrhenius temperature behavior:

$$\Phi_{BR} = B\Phi_{CB} \exp\left(\frac{E_a}{RT}\right) \quad (5)$$

The effective skeleton (reinforcing phase) volume fraction is then

$$\Phi_{eff} = \Phi_{CB} \cdot \left(1 + B \exp\frac{E_a}{RT}\right) \quad (6)$$

### 2.3. Open-cell solid skeleton: influence of the strain

Filled rubbers exhibit an elastic modulus drop not only with temperature but also with strain. Payne attributed this modulus decrease to the breakdown of the three dimensional agglomerates of carbon blacks (1962). Strain is not only responsible for breaking down the filler network but also for decreasing the bound rubber content. [Leblanc \(2002\)](#) and [Maier and Göritz \(1996\)](#) mention that the complex adsorption/desorption process taking place at the particle surface, described above, was also dependent on strain. [Kraus \(1984\)](#) proposed a model following Payne's interpretation and wrote the excess storage modulus of the agglomeration network ( $E' - E'_\infty$ ) as a function of the number of effective contacts at zero deformation  $N_0$  and the number of surviving filler/filler contact  $N$  and at strain amplitude  $\varepsilon_0$ .

$$\frac{E' - E'_\infty}{E'_0 - E'_\infty} = \frac{N}{N_0} = \frac{1}{1 + \left(\frac{\varepsilon_0}{\varepsilon_C}\right)^{2m}} \quad (7)$$

$E'_0$  is the “zero-amplitude” storage modulus value,  $E'_\infty$  is the high amplitude storage modulus value,  $\varepsilon_C$  is the characteristic strain,  $m$  is a constant.

In this model, we use our cellular solid analogy and consider that the backbone of the foam gets disrupted by strain the same way the number of effective contacts decreases with strain in the Kraus model. The disruption occurs both by the decreased effective contact between aggregates and the bound rubber desorption. The effective reinforcing filler fraction therefore decreases with strain following:

$$\Phi_{eff} \propto \frac{1}{1 + \left(\frac{\varepsilon}{\varepsilon_C}\right)^m} \quad (8)$$

Finally, the effective skeleton volume fraction depends on strain and temperature following:

$$\Phi_{eff} = \Phi_{CB} \cdot \left(1 + B \exp\frac{E_a}{RT}\right) \cdot \frac{1}{1 + \left(\frac{\varepsilon}{\varepsilon_C}\right)^m} \quad (9)$$

Referring back to Eq. (2), the elastic modulus of the cellular solid composed by carbon black clusters coated with bound rubber follows:

$$E = E_S \cdot \Phi_{eff}^n \quad (10)$$

Where  $E_S$  is the Young's elastic modulus of the material composing the skeleton, and  $n$  is a constant depending on the cell structure.

### 2.4. Open-cell solid skeleton: influence of the “free” rubber matrix

The cellular solid is also filled with rubber matrix, i.e. the “free” rubber. In order to take this filling into account, we propose here the simple composite parallel model (upper bound) ([Willemse et al., 1999](#)), where  $E_M$  is the modulus of the rubber matrix.

$$E = \Phi_{eff}^n E_S + (1 - \Phi_{eff}) E_M \quad (11)$$

This choice was made out of simplicity but can be improved considering that the two phases (reinforcement and matrix) are interconnected and co-continuous.

### 2.5. Proposed open-cell solid model to represent carbon-black filled elastomers

Finally, the model can be written as

$$E = \Phi_{eff}^n E_S + (1 - \Phi_{eff}) E_M \quad (12)$$

with  $\Phi_{eff} = \Phi_{CB} \cdot \left(1 + B \exp\frac{E_a}{RT}\right) \cdot \frac{1}{1 + \left(\frac{\varepsilon}{\varepsilon_C}\right)^m}$

$E_S$  is the modulus of material composed by carbon black aggregates coated with bound rubber,  $E_M$  is the Young's modulus of the matrix (free rubber),  $n$  is the cellular solid exponent,  $\Phi_{CB}$  is the volume fraction of carbon black,  $\varepsilon_C$  is the characteristic strain for backbone breakdown,  $E_a$  is the filler networking energy (or adsorption energy),  $B$  is the filler networking energy constant, and  $m$  is the strain exponent constant.  $R$  the gas constant ( $8.31 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ).

This model allows us to explain small strain modulus change with strain (des-agglomeration process: clusters are breaking apart), temperature (bending arms are getting

thinner, therefore more flexible, and less connected, as bound rubber disappears) and carbon black content (relative density of the cellular solid increases with carbon black).

### 3. Model identification on experimental data set and discussion

This theoretical model was assessed by comparison against preliminary data set.

A systematic study of the influence of temperature, strain amplitude and carbon black content was conducted on a hydrogenated nitrile butadiene rubber (HNBR) compound. HNBR was filled with N330 carbon black content varying between 0 phr (parts per weight = parts for hundred of rubber) and 70 phr. The material also contains plasticizer for processing and is sulfur cured, but all ingredients besides filler content are constant. Summary of tested formulations is shown in Table 1. The glass transition temperature of the material has been measured by differential scanning calorimetry equal to  $-26 \pm 1$  °C and is independent of filler content.

All mechanical tests were performed using a Dynamic Mechanical Analysis (DMA) testing setup (Q800 from TA Instrument), using parallelepipedic samples under uniaxial tensile cyclic loading at 5 Hz. Both storage modulus, or elastic modulus,  $E'$ , and loss modulus  $E''$ , were recorded; this study focuses on the elastic modulus  $E'$  which we refer to as  $E$  (Heinrich and Klüppel, 2002). Note that the loss factor  $\tan\delta(=E''/E')$  is typically 0.1 at small strains and never greater than 0.3. The loss modulus is then less than a tenth of the norm of the complex modulus and we neglect it in this work. Temperature sweep tests were run at constant double strain amplitude (DSA) (0.001 = 0.1%) and sweeping temperature between 35 °C and 180 °C. Strain sweep tests were run between 0.0002 (0.02%) and 0.2 (20%) double strain amplitude, at four different temperatures, 35 °C, 80 °C, 100 °C and 150 °C. In all tests, the modulus values are averaged after 3 cycles (softening or “Mullins” effect is therefore not taken into account). The error is estimated to be mainly due to dimension measurements and equal to  $\pm 5\%$ . Tests are described in a previous communication (Chartier and Robisson, 2009).

Those tests were used to identify our constitutive equation. There are six constants to identify: the filler adsorption (or filler networking) energy  $E_a$ , the skeleton modulus  $E_s$ , the cell exponent  $n$ , the filler adsorption energy constant  $B$ , the critical strain  $\varepsilon_c$ , the strain exponent

$m$ . Those constants were identified using a Matlab routine using all tests.  $E_M$  is the Young's modulus of the matrix (free rubber), i.e. the Young's modulus of the unfilled rubber sample.

The initial set of parameter input for the optimization was approximated from previous literature and experimental results, and is shown Table 2.

The constants resulting from identification are shown in Table 3 and the comparison between the experiments and the modeling in Figs. 5–10. The typical Payne effect is represented: The modulus of filled samples is constant at very low strain, up to 0.1%, and then decreases. This effect is higher for higher filler content samples and for lower temperatures. The drop in filled samples modulus with temperature is also correctly captured. The unfilled rubber sample has a quasi-constant modulus with temperature, around 3 MPa, and filled rubber exhibits a drop in modulus with temperature as well as the obvious increased modulus with increased carbon black content.

The identified adsorption energy is close to the values identified by Dessewffy (1962) and Göritz et al. (1999) and Guy et al. (2009) using solvent method and are within the range of Van des Waals interactions. Note that activation energies related to glass transition are much higher than those values. For example, Cervený et al. (2000) calculated the activation energy for the glass transition of an SBR (styrene butadiene rubber) and found a value of 294 kJ/mol.

The modulus of the material composing the skeleton (carbon black coated with bound rubber) is 214 MPa. This value is of the right order of magnitude, between pure rubber (3 MPa) and carbon black (1 GPa), but cannot be given a simple physical meaning. Also, for simplicity, we considered this value constant with temperature, although it would most likely vary as the fraction of rubber in the skeleton decreases with temperature.

From the above results, using the values of effective reinforcement content, we can calculate the thickness of bound rubber around fillers assuming they are spherical and perfectly dispersed (no interference). Fig. 11 illustrates the results considering fillers with 42 nm diameter (approximate dimension of a single carbon black particle) and 80 nm (approximate size for N330 CB aggregate) as a function of temperature. Considering the structure effect (aggregates are not spherical) and the interference between fillers, bound rubber thickness should be in between those two curves. The thickness would be between 5 and

**Table 1**

Carbon black contents of HNBR-carbon black composite samples.

Sample name	Carbon black content (phr)	Carbon black volume fraction $\Phi_{CB}$
N330-0	0	0
N330-0.05	10	0.05
N330-0.10	20	0.10
N330-0.16	35	0.16
N330-0.21	50	0.21
N330-0.25	60	0.25
N330-0.28	70	0.28

**Table 2**

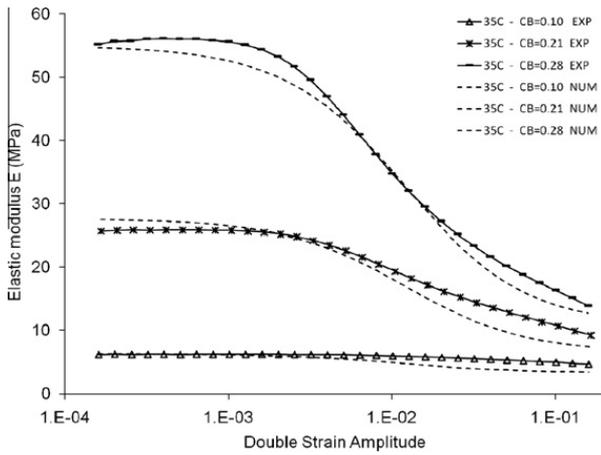
Initial set of parameters for model identification.

$E_a$ (J/mol)	$E_s$ (MPa)	$n$	$B$	$\varepsilon_c$	$m$
10000	100	3.5	0.1	0.02	2

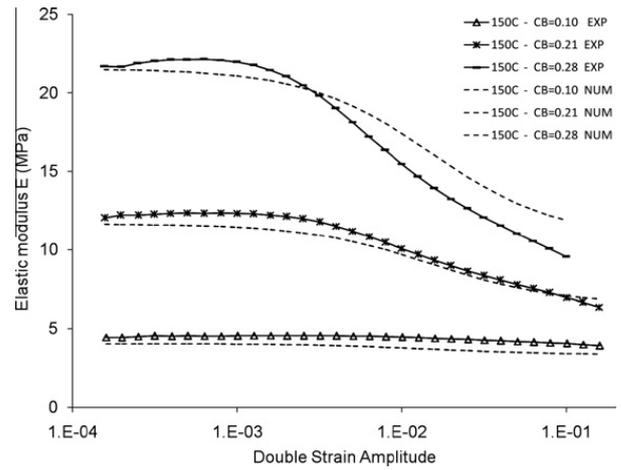
**Table 3**

Fit parameter on proposed model.

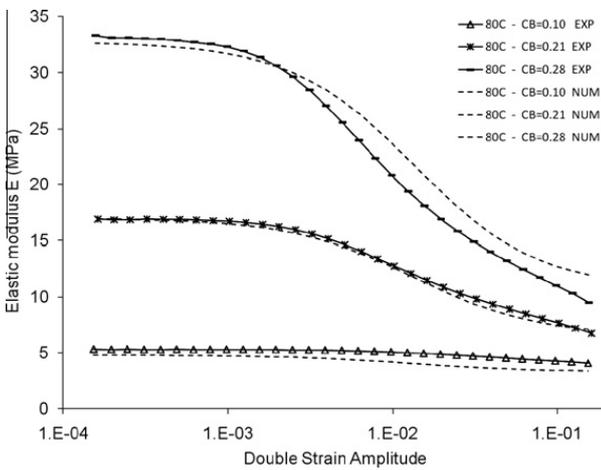
$E_a$ (J/mol)	$E_s$ (MPa)	$n$	$B$	$\varepsilon_c$	$m$
9497	214	2.52	0.03	0.02	1.13



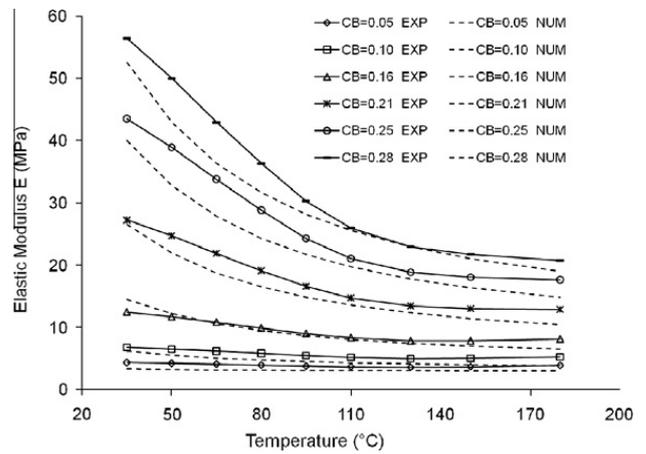
**Fig. 5.** Model identification result – elastic modulus as a function of DSA,  $T = 35\text{ }^{\circ}\text{C}$ , dotted lines are experimental data, dashed lines result from numerical simulation.



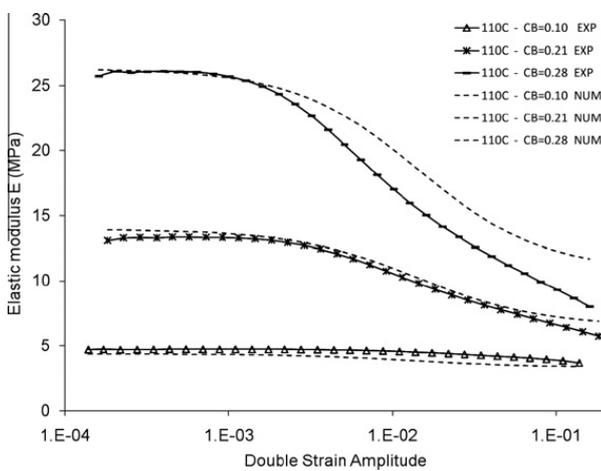
**Fig. 8.** Model identification result – elastic modulus as a function of DSA,  $T = 150\text{ }^{\circ}\text{C}$ , dotted lines are experimental data, dashed lines result from numerical simulation.



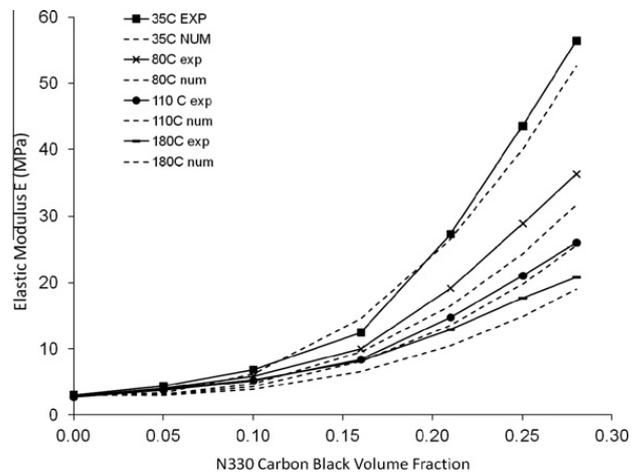
**Fig. 6.** Model identification result – elastic modulus as a function of DSA,  $T = 80\text{ }^{\circ}\text{C}$ , dotted lines are experimental data, dashed lines result from numerical simulation.



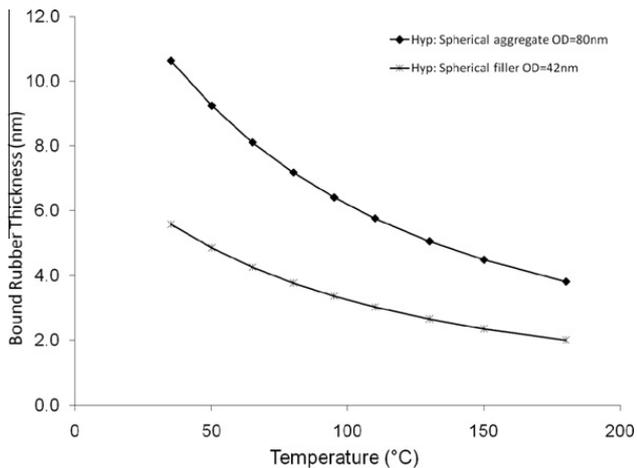
**Fig. 9.** Model identification result – elastic modulus as a function of temperature, dotted lines are experimental data, dashed lines result from numerical simulation.



**Fig. 7.** Model identification result – elastic modulus as a function of DSA,  $T = 110\text{ }^{\circ}\text{C}$ , dotted lines are experimental data, dashed lines result from numerical simulation.



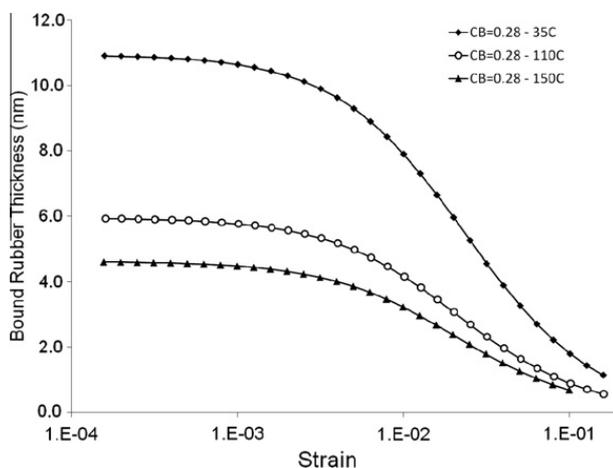
**Fig. 10.** Model identification result – elastic modulus as a function of carbon black content, dotted lines are experimental data, dashed lines are result of numerical simulation.



**Fig. 11.** Bound rubber thickness calculation using the open – cell solid model and assuming fillers are spherical.

11 nm at room temperature and between 2 and 4 nm at 180 °C. Those values are close to the bound rubber content measured using solvent methods: 4–8 nm in (Wolff et al., 1993), order of nm (Litvinov and Steeman, 1999). The dependence of bound rubber thickness on the filler dimension physically indicates the influence of the interfacial area per unit volume. Indeed, the larger the surface area, the smaller the particle size and the higher the reinforcing ability of the filler. In other words, if we use our analogy to the cellular solid, the modulus of the foam is dependant not only on the pore volume fraction, but also on the pore size.

Shown Fig. 12 is the bound rubber decrease when strain increases from 0.01% to 10%, calculated using the same method. The thickness decreases from 11 to 1 nm at 35 °C when strain increases from 0.01% to 10%. This decrease is thickness is overestimated, as the assumption of percolated network of filler is not correct anymore. In this case, the effective skeleton fraction is decreased not only due to decrease in bound rubber but also to the aggregate–aggregate contact disruption, i.e. some fillers do not contribute to the reinforcement anymore.



**Fig. 12.** Bound rubber thickness calculation using the open – cell solid model and assuming fillers are spherical.

#### 4. Conclusion

This work focuses on mechanical behavior of filled rubber at temperatures far above the ambient and strains between 0% and 10%. We propose a model that relies on an analogy between these materials and random three-dimensional open-cell solids. In this analogy, aggregates of fillers, coated with a layer of adsorbed rubber and connected to each other, form the skeleton of the cellular solid. The free rubber matrix fills the pores and both phases are co-continuous. The model successfully captures the effect of filler content, temperature and strain on the small strain modulus of filled rubbers. It requires the identification of six constants. Two of them, the adsorption, or networking, energy and the critical strain can be identified from literature reviews and have strong physical meaning.

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