A Constitutive Model for Stress–Strain Response and Mullins Effect in Filled Elastomers

A. K. Mossi Idrissa,[1] S. Ahzi,[1] S. Patlazhan,[1,2] Y. Rémond,[1] D. Ruch[3]

[1]*Institut de Mécanique des Fluides et des Solides, Université de Strasbourg, 2 Rue Boussingault, 67000 Strasbourg, France*
[2]*Semenov Institute of Chemical Physics Russian Academy of Sciences, 4 Kosygin Street, 119991 Moscow, Russia*
[3]*Centre de Recherche Public Henri Tudor, 66 rue de Luxembourg, B.P. 144, L-4002 Esch-sur-Alzette, Luxembourg*

Received 30 November 2011; accepted 30 November 2011
DOI 10.1002/app.36596
Published online in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: In this work we propose a new constitutive theory to estimate the stress–strain response and the softening induced by the Mullins effect during the stretching of filled elastomers. In this study, we used the Mullins and Tobin concept where the filled elastomers are treated as composites with hard-domains and soft-domains and the softening is due to the hard domain transformation into soft domain during stretching. Gent strain energy is assumed to represent the behavior of the unfilled elastomers. This strain energy representation is then reformulated in order to consider fillers effect in the case of filled elastomers. The proposed approach takes into account the effect of the type of carbon-black filler and of its volume fraction on the mechanical response and microstructure evolution during stretching. The predicted results are compared to Mullins and Tobin experimental data, and good agreements are obtained. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: filled elastomers; Mullins'; effect; strain softening; Gent model; carbon black fillers; hard-to-soft transformation

INTRODUCTION

For many industrial applications, elastomers have been reinforced by different kind of fillers like carbon-black in order to improve the material mechanical properties such as stiffness, rupture energy, tear strength, tensile strength, cracking resistance, durability, owed to filler–filler and filler–elastomer's interactions. Filled and unfilled elastomers show differences in their stress–strain response under loading. Particularly, strain-induced stress softening phenomenon during cyclic tension, known as Mullins effect, is more pronounced in filled elastomers. For unfilled elastomers, Mullins[1] experimental data showed that previous stretching has relatively little effect on the stress–strain properties, this implies neglected softening. This phenomenon was observed at the first time by Bouasse and Carrière[2] and several subsequent authors' studies showed that the phenomenon does not have one single interpretation. Blanchard and Parkinson, and Bueche[3–5] suggested that increase in stiffness obtained in filled rubber to be a result of rubber-filler attachments providing additional restrictions on the cross-linked rubber network and Mullins effect resulted from the breakdown or loosing of links between the filler particles and the rubber chains. This idea was extended by other authors like Simo and Govindjee[6–8] by considering damage in the material network. On the basis of this idea of damage induced softening, Miehe and Keck[9] developed a constitutive model for material's behavior, and more recently others authors proposed a theory of network alteration for the Mullins effect.[10,11] They adopted the breakdown of links inside the material, which decreases molecular chain density and increases the average number of monomer segments in a molecular chain.

However, for Mullins and Tobin[12–14] a filled rubber is composed of two domains, one hard and one soft. During the application of stress, most deformation happens in the soft domain and the hard domain makes little contribution to the deformation and may be broken down to form soft domain by the application of stresses in excess of those previously applied. Hence, the soft domain volume increases with increased stretching. Mullins also showed that the samples of filled rubber, which were previously stretched have their stress–strain properties approach those of pure rubber due to the destruction of some substantially hard domain, which increased the stiffness.[1,14] In addition, it was also observed that filled rubbers recover partially or totally their original stiffness very slowly, after

Correspondence to: S. Ahzi (ahzi@unistra.fr).

several days at room temperature. This recovery is accelerated when the temperature is high.[4] Hard-domain and soft-domain concept was used by Johnson and Beatty.[15] They considered the hard-domain like clusters of molecular chains held together by short chain segments, entanglements, or intermolecular forces. Hence, during material stretching, chains are pulled from the clusters and hard-domain is transformed into soft domain. On the basis of the hard-to-soft transformation, Qi and Boyce[16] proposed a constitutive approach, based on a modified form of Miehe and Keck[9] for softening and the eight-chain model, to predict Mullins effect. Klüppel and Schramm[17] also proposed a generalized tube model for rubber elasticity and stress softening, which combines a non-Gaussian tube model of rubber elasticity with a damage model of stress-induced filler cluster breakdown. Other observations from Mullins, James and Green showed that, the softening is not identical in all directions and it is less in perpendicular direction of the stretch than in the stretch direction.[18,19]

In addition to filler particle volume fraction, a number of state variables influence the magnitude of the contributions of the effects to the mechanical response of filled elastomers: fillers size, type, and shape[20,21] or the fillers aggregate.[22,23] These are not generally included in most developed models. Here, the aim of this work is to develop a theory based on filled elastomers' microstructure evolution to explain softening phenomena. For this, we propose to extend the formulation of the Gent model for filled elastomers and we propose a new approach for the hard-to-soft transformation that includes fillers type.

MICROSTRUCTURE BEHAVIOR

Several authors[24–26] showed that filler volume concentration in filled rubber affect the material's microstructure, which can present particles in the following states: individual dispersion of primary particle with length scales 20—50 nm for small concentrations; their cluster gives birth to filler aggregate with length scales 100–200nm; and from filler aggregate clustering we obtain filler agglomerate, which can build a continuous network of particles, which is the percolation concentration.

The microstructure of elastomers reinforced by carbon black can be represented as a two-phase system composed of the soft- and hard-domains like in Mullins and Tobin[12] concept. Here, the volume of the hard domains includes total volume of the filler and the occluded matrix volume, which is formed in aggregates of the carbon black particles. The occluded volume is immobilized because of the close packing of the particles within the carbon black agglomerates and increases effectively the initial volume fraction, φ_h^0, of the hard-domain as $\varphi_h^0 = \varphi_{oc}^0 + \varphi_f^0$. The terms φ_f^0 and φ_{oc}^0 are the initial volume fractions of the filler and the occluded matrix, respectively. The soft-domain corresponds to the elastomeric matrix not occluded by the carbon black agglomerates. Its initial volume fraction is denoted by φ_s^0. The occluded volume does not contribute to the deformation of the composite until rupture of the agglomerates. Thus, the Mullins effect can be described as an evolution of the hard domain, which decreases because of the breaking up of the carbon black clusters during deformation processes. The released occluded matrix contributes to the deformation as an additional part of the elastomeric matrix. Hence, the transformation of hard- to soft-domain implies softening of the filled elastomers.

Medalia[27] showed that effective volume occupied by carbon black aggregates in a rubber can be obtained by: $\varphi_h^0 = \varphi_{oc}^0 + \varphi_f^0 = \varphi_f^0 q$ with $q = (1 + 0.02139\mathrm{DBP}_{\mathrm{Abs}})/1.46$. Here, the $\mathrm{DBP}_{\mathrm{Abs}}$ indicates the dibutyl-phtalate absorption (in $\mathrm{cm}^3/100$ g). We can therefore get the volume fraction of the occluded domain by:

$$\varphi_{oc}^0 = (q-1)\varphi_f^0 \tag{1}$$

In the nonstretched state ($\varepsilon = 0$), the material composition is defined by the following relationships:

$$\varphi_h^0 + \varphi_s^0 = 1, \qquad \varphi_h^0 = \varphi_{oc}^0 + \varphi_f^0, \qquad \varphi_{oc}^0 = (q-1)\varphi_f^0 \tag{2a}$$

During deformation, the composition evolution can be written in the following form:

$$\varphi_h + \varphi_s = 1, \qquad \varphi_h = \varphi_{oc} + \varphi_f, \qquad \varphi_s \geq \varphi_s^0, \qquad \varphi_h \leq \varphi_h^0 \tag{2b}$$

Here, φ_s, φ_h, φ_f, and φ_{oc} are soft, hard, particles, and occluded volume fractions, respectively, and φ_s^0, φ_h^0, φ_f^0, and φ_{oc}^0 are the corresponding initial values. We assume that the decrease of the hard domain in the filled elastomers is caused by the deformation during loading but not during unloading or reloading lower than previous loading. To describe the evolution of the hard-domain volume fraction as function of strain, we propose to use of the generalized model of Oshmyan et al.[29]:

$$\frac{d\varphi_h}{d\varepsilon} = -K_{\mathrm{hs}}\varphi_h + K_{\mathrm{sh}}\varphi_s \tag{3}$$

where K_{hs} and K_{sh} are phase transformation kinetic coefficients, which represent the transformation from

hard-to-soft and from soft-to-hard domains, respectively. These are defined by[29]:

$$\begin{cases} K_{\mathrm{hs}} = k_{\mathrm{hs}}^0 \exp\left(-\frac{U_{\mathrm{hs}}-\gamma\sigma_h}{kT}\right) = b_{\mathrm{hs}} \exp(\beta\sigma_h) \\ K_{\mathrm{sh}} = k_{\mathrm{sh}}^0 \exp\left(-\frac{U_{\mathrm{sh}}+\gamma\sigma_s}{kT}\right) = b_{\mathrm{sh}} \exp(-\beta\sigma_s) \end{cases} \qquad \beta = \frac{\gamma}{kT} \tag{4}$$

Here, σ_h, σ_s are respectively the stresses in the hard and soft domains, k is the Boltzmann constant, γ is the activation volume, T is the absolute temperature, U_{sh} and U_{hs} are the activation energies and b_{sh} and b_{hs} are preexponential coefficients. In our study, we assume that structural transition from soft- to hard-domain is neglected, which implies that $b_{\mathrm{sh}} = 0$. In fact, it is observed that several days are needed to recover very slowly the stiffness, which is decreased by the softening.[14]

Using the condition of $b_{\mathrm{sh}} = 0$, we obtain a simplification of eq. (3) in as follows:

$$\frac{d\varphi_h}{d\varepsilon} = -K_{\mathrm{hs}}\varphi_h \tag{5a}$$

After integration of eq. (5a) we get:

$$\varphi_h = \varphi_h^0 \exp(-K_{\mathrm{hs}}\varepsilon) \tag{5b}$$

The following expressions are also deduced:

$$\varepsilon \to 0 \Rightarrow \varphi_h \to \varphi_h^0 \tag{5c}$$

$$\varepsilon \to \infty \Rightarrow \varphi_h \to 0 \tag{5d}$$

The two last eqs. (5c) and (5d) show that hard domain volume fraction is bounded by upper and lower bound estimates. However, experimental conditions do not permit the transformation of the entire hard domains, particularly in the case of indestructible particles like carbon black. In this case, $\varphi_f = \varphi_f^0$, and only the occluded volume becomes soft.

Using eqs. (2b) and (5b), we obtain the soft domain evolution in the following form:

$$\varphi_s = 1 - \varphi_h^0 \exp(-K_{\mathrm{hs}}\varepsilon) \tag{6}$$

Equations (5b) and (6) describe the filled elastomers microstructure evolution during deformation and also explain the softening phenomena produced in the material. In the next part, filled elastomers' mechanical behaviors are treated with a reformulated form of Gent's strain energy, which takes into account fillers effect and microstructure evolution.

MECHANICAL BEHAVIOR

Gent model

Elastomers exhibit complex mechanical behaviors. For that, many constitutive models are built and are focused on one or more experimentally observed phenomena such as large strains, hysteresis, time dependent response, and stress-softening, or Mullins effect.[10,30–33] In these models, a strain energy W is used to characterize the material's mechanical behavior. Assuming isotropic and incompressible elastomers, the strain energy is generally given as function of the two first invariants of the left Cauchy-Green stretch tensor B.

$$W = W(I_1, I_2) \tag{7}$$

with

$$I_1 = trB,\ I_2 = \frac{1}{2}\left[trB^2 - (trB)^2\right]$$

The true stress tensor is defined by the differentiation of W with respect to B:

$$\sigma = -pI + 2B\frac{\partial W}{\partial B} = -pI + 2\left(\frac{\partial W}{\partial I_1} + I_1\frac{\partial W}{\partial I_2}\right)B - 2\frac{\partial W}{\partial I_2}B^2 \tag{8}$$

where p is the hydrostatic pressure.

In this work, we propose to extend the Gent model[31] for rubber networks to filled rubbers. The strain energy proposed by Gent[32] is given by:

$$W_G = -\frac{E}{6}J_m \ln\left[1 - \frac{J_1}{J_m}\right] = \frac{E}{6}J_m \ln\left[1 - \frac{J_1}{J_m}\right]^{-1} \tag{9}$$

Here, $J_1 = I_1 - 3$ and E is a modulus. Gent[32] showed that this energy results in stresses, which are closed to those given by Treloar's physically based model for rubbers and when J_1 approaches J_m the material reaches its fully extended state. This means that J_m corresponds to the limiting polymeric chain extensibility, which can be undergone by the material.

The Cauchy stress tensor associated to the Gent model is therefore given by:

$$\sigma = -pI + \frac{E}{3}\frac{J_m}{J_m - J_1}B \tag{10}$$

As shown by Boyce,[34] Chagnon et al.,[35] and Horgan and Saccomandi,[36] the parameters E and J_m in the Gent model are rather related to well-established parameters for elastomers deformation behavior, namely the rubbery modulus and the locking

stretch. To show this equivalence for the modulus E, Gent strain energy can be expressed in a series of polynomial form:

$$W_G = \frac{E}{6}\sum_{n=0}^{\infty}\frac{1}{n+1}\frac{J_1^{n+1}}{J_m^n} \tag{11a}$$

For small strains, the expression (11a) is reduced to the first term:

$$W_G = \frac{E}{6}J_1 = \frac{E}{6}(I_1 - 3) \tag{11b}$$

The equivalence of this eq. (11b) with the Neo-Hookean strain energy $W_{\mathrm{NH}} = \frac{\mu}{2}J_1 = \frac{\mu}{2}(I_1 - 3)$, which is valid in the range of small strains, implies:

$$E = 3\mu = 3n\theta k \tag{11c}$$

where n is the chain density, T is the absolute temperature, k is the Boltzmann constant, and μ the shear modulus (rubbery modulus).

The relation between the parameter J_m and the mechanical parameter N can be obtained by the use of the current chain stretch expression λ_{chain}[30] and its limiting value (locking stretch) at full stretch condition. The locking stretch is given by $\lambda_{\mathrm{chain}}^{\mathrm{lock}} = N^{1/2}$, where N is the number of statistical links in the chain between two chemical crosslinks. The chain stretch is given by:

$$\lambda_{\mathrm{chain}} = \frac{I_1^{1/2}}{\sqrt{3}} = \frac{(J_1+3)^{1/2}}{\sqrt{3}} \tag{12a}$$

At full stretch condition, the parameter J_1 tends to its limiting value J_m and equivalently the chain stretch tends to the locking one:

$$J_1 \to J_m \Rightarrow \lambda_{\mathrm{chain}} \to \lambda_{\mathrm{chain}}^{\mathrm{lock}} = N^{1/2} \tag{12b}$$

From eqs. (12a,b), we can therefore get:

$$\frac{(J_m+3)^{1/2}}{\sqrt{3}} = N^{1/2} \Rightarrow J_m = 3(N-1) \tag{12c}$$

Horgan and Saccomandi[36] and more recently Mossi-Idrissa et al.[37] showed that Gent model for incompressible rubbers is a very good qualitative and quantitative alternative to the comparatively complicated molecular models involving the inverse Langevin function.

Extension of the Gent model to filled rubber

Here, the filler particles effect will be studied in order to extend Gent strain energy to reinforced elastomers. Hence, the microstructure evolution, which happens during deformation, is introduced in the stress–strain relationship. One of the first and simplest estimation of the effective properties is that of Einstein[38,39] who derived the increase in viscosity caused by a suspension of spherical particles in a viscous fluid. Later Smallwood[22] applied the same approach, for filled solids with spherical filler particles at low-concentration, to predict the Young modulus.

$$E^e = E_m\left(1 + 2.5\varphi_f\right) \tag{13}$$

where φ_f is the volume concentration of filler and E_m is the elastic modulus of the matrix.

In this eq. (13), no account was taken of the interaction between neighboring filler particles. Guth and Gold[40,41] considered the interaction between pairs of particles by adding an extra term involving the square of the volume concentration, and proposed the following expression for the effective Young modulus:

$$E^e = E_m X \tag{14}$$

with $X = 1 + 2.5\varphi_f + 14.1\varphi_f^2$ is an amplified factor.

This equation shows that the modulus increases in reinforced elastomers because of the distortions introduced by the particles in the material network. Smallwood[22] also showed that for low-concentration of fillers, $\varphi_f < 0.1$, eq. (13) fitted the experimental elastic behavior lightly reinforced elastomers, but serious departures from the experiment results occurred higher fillers volume fractions. Guth[41] showed that the behavior of rubber containing carbon black, which consists essentially of spherical particles, conformed to eq. (14) up to volume fraction of about 0.3. We should note that there exist several other models for the estimation the effective properties in a composite materials such as the bounding estimates.[41–48]

The strain energy, W^*, of reinforced elastomers, which presents soft- and hard-domains is found from the stain energy of the deformable matrix, W_s, corresponding to the soft-domain (since the hard phase is assumed not to contribute to deformation). Hence:

$$\left.\begin{array}{l} W^* = \varphi_s W_s + \varphi_h W_h \\ \text{here} \quad \varepsilon_h = 0 \Rightarrow W_h = 0 \end{array}\right\} \Rightarrow W^* = \varphi_s W_s \tag{15}$$

Using Gent model for the soft domain, we obtain the following equation:

$$W_G^* = \varphi_s W_{\mathrm{GS}} = -\varphi_s \frac{E_m}{6} J_m \ln\left[1 - \frac{I_{1m} - 3}{J_m}\right] \tag{16}$$

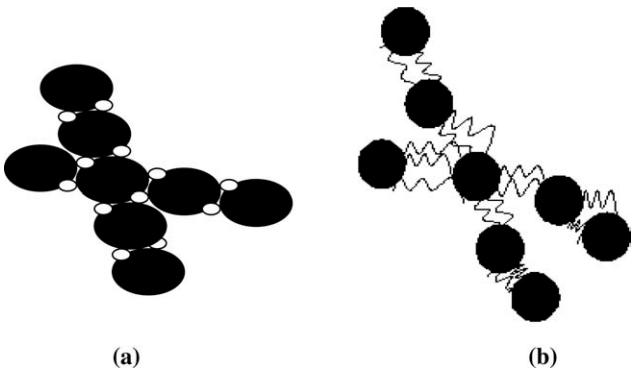

Figure 1 Schematic of the difference of the aggregate microstructure before (a) and after (b) deformation.

where W_{GS} is the Gent strain energy for the soft domain and I_{1m} is the average first invariant stretch of this domain.

In filled elastomers, the matrix is prevented from deforming uniformly by adhesion of the rubber to the surface of the particles and thus the overall apparent strain is less than the strains occurring locally. Mullins and Tobin[13] have proposed the notion of amplified strain to estimate the uniaxial strain in the matrix. This relation can be shown when the stress–strain relationship for the filled elastomer, $\sigma = E^e\varepsilon = E^e\ (\lambda - 1) = E_mX\ (\lambda - 1)$, and unfilled elastomers, $\sigma = E_m\ (\Lambda - 1)$, is considered for the same average stress. The amplified stretch expression is therefore deduced as $\Lambda = X(\lambda - 1) + 1$ where λ is the apparent macroscopic axial stretch in the filled rubber. In the work of Govindjee and Simo,[7] they proposed amplifying the total deformation gradient in order to obtain the relation between the volume average strain quantities and the matrix quantities. This can be written in the following form:

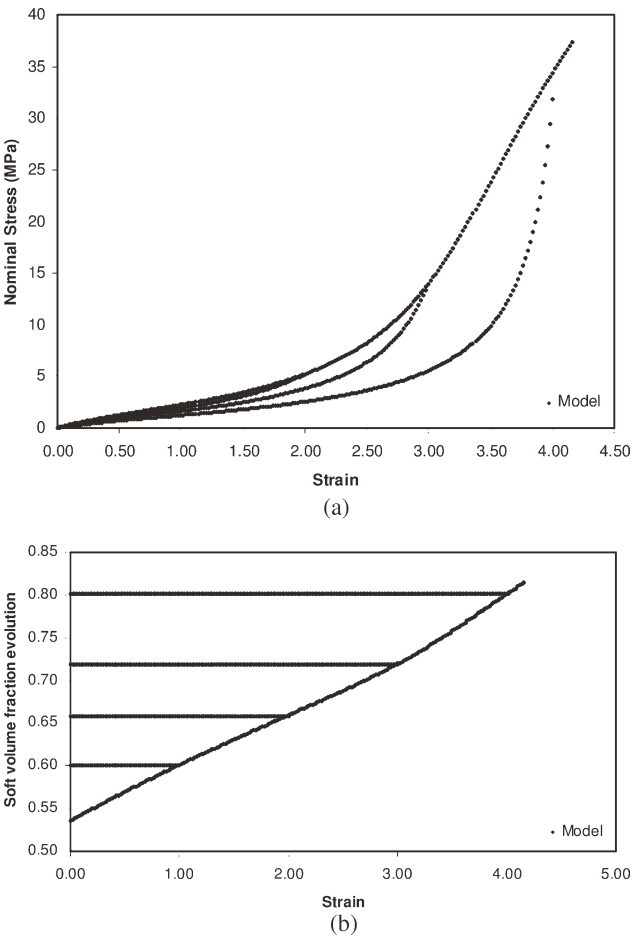

Figure 2 (a) Loading-unloading-reloading cyclic response predicted the new constitutive model. The material parameters: $b_{hs} = 0.15\ s^{-1}$, $\varphi_f = 0.19$, $\beta = 2.10^{-3}$, $E = 1$ MPa, $J_m = 60$, $DBP_{Abs} = 120\ cm^3/100$ g. (b) Soft volume fraction evolution for the new constitutive model during stretching represented in Figure 2(a).

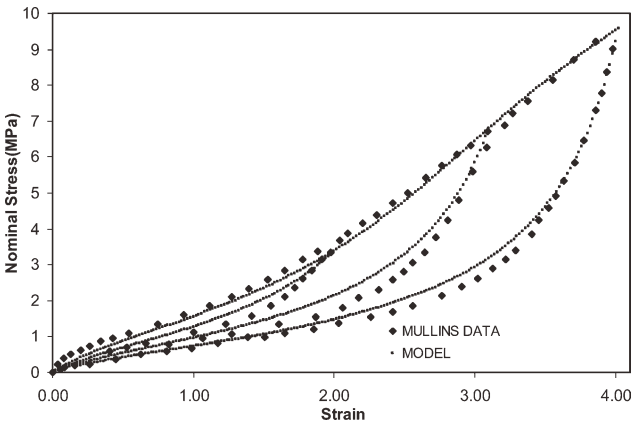

Figure 3 Model prediction compared to Mullins and Tobin experimental results where the elastomer is GRS filled with carbon black S301. The material parameters: $b_{hs} = 0.18\ s^{-1}$, $\varphi_f = 0.2$, $\beta = 9.10^{-3}\ MPa^{-1}$, $E = 0.7$ MPa, $J_m = 56$, $DBP_{Abs} = 113\ cm^3/100$ g.

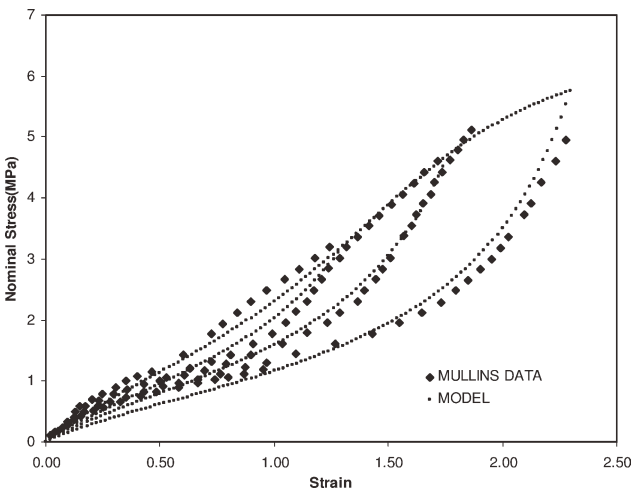

Figure 4 Model prediction compared to Mullins and Tobin experimental results where the elastomer is the natural rubber filled with carbon black S301. The material parameters: $b_{hs} = 0.18\ s^{-1}$, $\varphi_f = 0.19$, $\beta = 4.10^{-2}\ MPa^{-1}$, $E = 0.9$ MPa, $J_m = 28$, $DBP_{Abs} = 113\ cm^3/100$ g.

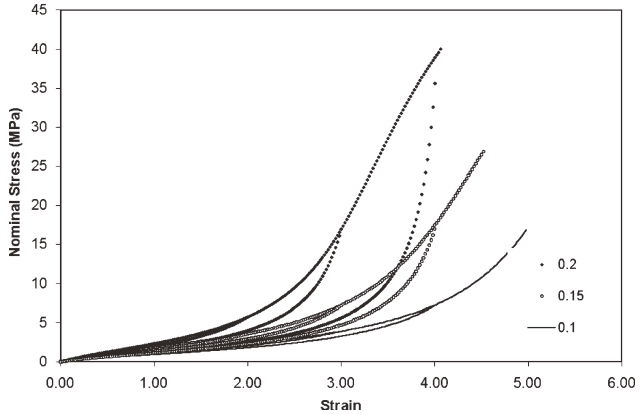

Figure 5 Prediction of the effect of the filler volume fraction on the stress–strain response. The material parameters: $b_{hs} = 0.15\ s^{-1}$, $\beta = 2.10^{-3}\ MPa^{-1}$, $E = 1$ MPa, $J_m = 60$, $DBP_{Abs} = 120\ cm^3/100$ g.

$F_m = (F - \varphi_f R)/(1 - \varphi_f)$ with $F = RU$. Here, F and F_m are respectively the volume average and matrix deformation gradients, R is the rotation tensor, and U the right stretching tensor. As in the work of Bergstrom and Boyce,[49] we propose to use the amplification of the first invariant stretch I_1, which corresponds to Mullins and Tobin stretch amplification with an extension to a general three-dimensional deformation state:

$$I_{1m} = X(I_1 - 3) + 3 \tag{17}$$

where I_1 is the average first invariant stretch of the composite material. Using eq. (17) in the reinforced elastomers strain energy of eq. (16), we can deduce our proposed extension of the gent strain energy to filled elastomers:

$$W_G^* = -\varphi_s \frac{E_m}{6} J_m \ln\left[1 - \frac{X(I_1 - 3)}{J_m}\right] \tag{18}$$

On the basis of eqs. (13) and (14), the following expression for the amplification factor X was derived[16]: $X = 1 + 3.5(1 - \varphi_s) + 18(1 - \varphi_s)^2$.

From the proposed extension of Gent strain energy for filled elastomers [eq. (18)], we get the corresponding Cauchy stress tensor:

$$\sigma_G^* = -pI + \varphi_s \frac{E_m X}{3} \frac{J_m}{J_m - X(I_1 - 3)} B \tag{19}$$

In summary, the proposed constitutive model for stress–strain behavior of filled elastomers can be summarized by the following constitutive relations:

$$\sigma_G^* = -pI + \varphi_s \frac{E_m X}{3} \frac{J_m}{J_m - X(I_1 - 3)} B \tag{20a}$$

$$X = 1 + 3.5(1 - \varphi_s) + 18(1 - \varphi_s)^2 \tag{20b}$$

$$\varphi_s = 1 - \varphi_h^0 \exp(-K_{hs}\varepsilon) \tag{20c}$$

$$\varphi_h^0 = \varphi_f^0(1 + 0.022139\mathrm{DBP}_{Abs})/1.46 \tag{20d}$$

RESULTS AND DISCUSSION

Equation (20) which represent the constitutive model are used to predict the stress–strain response of filled elastomers including soft-domain evolution. In the first application, we simulated loading unloading under uniaxial tension. The predicted stress–strain response is shown in Figure 2(a) and the corresponding evolution of the soft phase volume fraction is shown in Figure 2(b). The selected material parameters are also shown in these figures. In Figure 2(a), the stress–strain behavior with cyclic loading and unloading. The first cyclic shows loading until $\varepsilon = 2$ and unloading to $\varepsilon = 0$; in the second cyclic, we have reloading until $\varepsilon = 3$ and unloading to $\varepsilon = 0$ and the third cyclic corresponds to reloading until $\varepsilon = 4$ and also unloading to $\varepsilon = 0$. To validate this model, it is compared to Mullins and Tobin[11] vulcanized materials' data for GRS and natural rubbers filled with carbon black S301 with DBP absorption equal to 113 $cm^3/100$ g.[50] This comparison is reported on Figure 3 for filled GRS and Figure 4 for filled natural rubber. These comparisons show a fairly good agreement between the model predictions and the experimental stress–strain response. In our model, the two parameters that characterize the filler particles in the composite are filler volume fraction and DBP absorption. In Figure 5, the effect of the volume fraction is shown by changing its value, 0.1, 0.15, and 0.20. As expected, we can observe in this Figure 5 that the higher filler volume

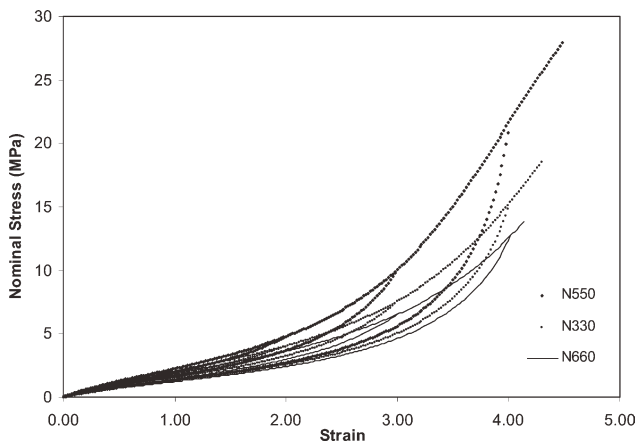

Figure 6 Prediction of the effect of the type of carbon black on the stress–strain response. The material parameters: $b_{hs} = 0.15\ s^{-1}$, $\varphi_f = 0.20$, $\beta = 2.10^{-3}\ MPa^{-1}$, $E = 1$ MPa, $J_m = 75$, $N660/DBP_{Abs} = 91\ cm^3/100$ g, $N330/DBP_{Abs} = 101\ cm^3/100$ g, $N550/DBP_{Abs} = 120\ cm^3/100$ g.

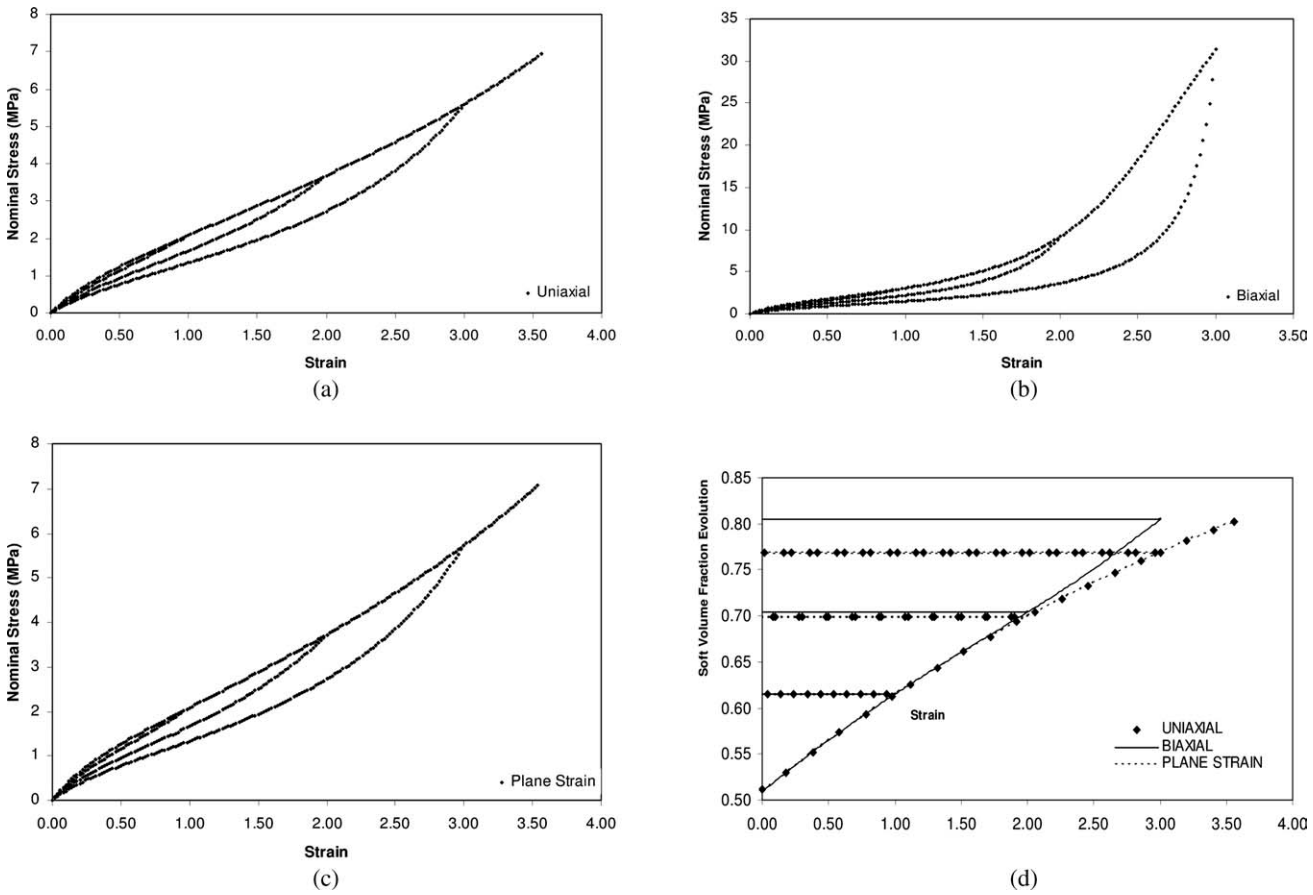

Figure 7 (a) Prediction of the stress strain response for loading-unloading-reloading under uniaxial tension. The material parameters: $b_{hs} = 0.24\ s^{-1}$, $\varphi_f = 0.2$, $\beta = 2.10^{-3}\ MPa^{-1}$, $E = 1$ MPa, $J_m = 75$, $DBP_{Abs} = 120\ cm^3/100$ g. (b) Prediction of the stress–strain response for loading-unloading-reloading under equi-biaxial tension. The material parameters: $b_{hs} = 0.24\ s^{-1}$, $\varphi_f = 0.2$, $\beta = 2.10^{-3}\ MPa^{-1}$, $E = 1$ MPa, $J_m = 75$, $DBP_{Abs} = 120\ cm^3/100$ g. (c) Prediction of the stress–strain response for loading-unloading-reloading under plane strlain tension. The material parameters: $b_{hs} = 0.24\ s^{-1}$, $\varphi_f = 0.2$, $\beta = 2.10^{-3}\ MPa^{-1}$, $E = 1$ MPa, $J_m = 75$, $DBP_{Abs} = 120\ cm^3/100$ g. (d) Predicted evolution of the soft phase volume fraction for the loading cases in Figure 7(a–c).

fraction leads to a stiffer stress–strain response. In Figure 6, three types of carbon black (N660/DBP_{Abs} = 91, N550/DBP_{Abs} = 120, N330/DBP_{Abs} = 101) are used for the same filler volume fraction. In this figure, the type of the carbon black affects the stress–strain response. Stiffer response is obtained for carbon black with higher DBP, which means higher volume fraction of the hard domain (higher agglomeration with increased occluded phase).

To verify our model's ability to correctly predict the stress–strain response under different cyclic states of deformation, Figures 7(a–c) are the predicted results for uniaxial tension where the chains extend in one direction ($\lambda_1 = \lambda$, $\lambda_2 = \lambda^{-1/2}$, $\lambda_3 = \lambda^{-1/2}$), equi-biaxial tension, which offers two principal tensile stretching ($\lambda_1 = \lambda$, $\lambda_2 = \lambda$, $\lambda_3 = \lambda^{-2}$) and plane strain tension ($\lambda_1 = \lambda$, $\lambda_2 = 1$, $\lambda_3 = \lambda^{-1}$). The corresponding soft-domains volume fraction evolutions are shown in Figure 7(d). Our predicted stress–strain response under different cyclic stretching conditions is in accord with the results obtained by Qi and Boyce.[16]

CONCLUSION

In this article, the combination of the extended Gent model with a new kinematic model for phase transformation lead to a simple and original approach that correctly predicts the stress–strain behavior of filled elastomers, which takes into account Mullins effect (softening effect). The proposed model takes into account the type of carbon black via the DBP absorption. Although neglected in this article, the proposed model has the ability to predict stiffness increase, which happens slowly by setting b_{sh} different from zero. This is not possible with damage theories based only on the breakdown of elastomers links of Govindjee and Simo[7] or Marckmann et al.[10] The constitutive model gives a fairly good agreement with experimental data in the literature and also proves its ability to be applicable to different states of deformation. Our approach can also be easily implemented in computational codes such as FEM for three-dimensional simulations. The 3D nature of our approach can be justified

by the assumption of isotropic softening and by the predictive capability of our approach under multiaxial loading.

The interest of the new model is that we propose a new approach based on combining the Gent model for stress–strain relation with a new model for hard-to-soft phase transformation. We note that the Gent model does not involve the complex Langevin function, which is used in the 8-chain model. We believe that our new approach is a predictive approach that is much simpler for numerical implementation such as in FEM codes.

REFERENCES

1. Mullins, L. J Rubber Res 1947, 16, 275.
2. Bouasse, H.; Carrière, Z. Ann Fac Sci de Toulouse 1903, 5, 257.
3. Blanchard, A. F.; Parkinson, D. Ind Eng Chem 1952, 44, 799.
4. Bueche, F. J Appl Polym Sci 1960, 4, 107.
5. Bueche, F. J. Appl Polym Sci 1961, 5, 271.
6. Simo, J. Comput Methods Appl Mech Eng 1987, 60, 153.
7. Govindjee, S.; Simo, J. J Mech Phys Solids 1991, 39, 87.
8. Govindjee, S.; Simo, J. J Mech Phys Solids 1992, 40, 213.
9. Miehe, C.; Keck, J. J Mech Phys Solids 2000, 48, 323.
10. Marckmann, G.; Verron, E.; Gornet, L.; Chagnon, G.; Charrier, P.; Fort, P. J Mech Phys Solids 2002, 50, 2011.
11. Chagnon, G.; Verron, E.; Marckmann, G.; Gornet, L. Int J Solids Struct 2006, 43, 6817.
12. Mullins, L.; Tobin, N. R. Rubber Chem Technol 1957, 30, 555.
13. Mullins, L.; Tobin, N. R. J Appl Sci 1965, 9, 2993.
14. Mullins, L. Rubber Chem Technol 1969, 42, 339.
15. Johnson, M. A.; Beatty, M. F. Continuum Mech Thermodyn 1993, 5, 301.
16. Qi, H. J.; Boyce, M. C. J Mech Phys Solids 2004, 52, 2187.
17. Klüppel, M.; Schramm, J. Macromol Theor Simul 2000, 9, 742.
18. Mullins, L. Rubber Chem Technol 1948, 21, 281.
19. James, A. G.; Green, A. J Appl Polym Sci 1975, 19, 2319.
20. Harwood, J. A. C.; Mullins, L. J Appl Polym Sci 1965, 9, 3011.
21. Mullins, L. Rubber Chem Technol 1950, 23, 239.
22. Smallwood, H. M. J Appl Phys 1944, 15, 758.
23. Meinecke, E. A.; Taftaf, M. I. Rubber Chem Technol 1988, 61, 534.
24. Morozov, I.; Lauke, B.; Heinrich, G. Comput Mater Sci 2010, 47, 817.
25. Heinrich, G.; Klüppel, M.; Viglis, T. A. Curr Opin Solid State Mater Sci 2002, 6, 195.
26. Vilgis, T. A.; Heinrich, G.; Klüppel, M. Reinforcement of Polymer Nano-Composites; Cambridge University Press: Cambridge, 2009.
27. Medalia, A. I. J Colloid Interface Sci 1970, 32, 115.
28. Harwood, J. A. C.; Payne, A. R. J. Appl Polym Sci 1966, 10, 315.
29. Oshmyan, V. G.; Patlazhan, S. A.; Remond, Y. Polym Sci 2006, 48, 1004.
30. Arruda, E. M.; Boyce, M. C. J Mech Phys Solids 1993, 41, 389.
31. Hart-Smith, L. J App Phys 1966, 17, 608.
32. Gent, A. N. Rubber Chem Technol 1996, 69, 59.
33. Qi, H. J.; Boyce, M. C. Mech Mater 2005, 37, 817.
34. Boyce, M. C. Rubber Chem Technol 1996, 69, 781.
35. Chagnon, G.; Marckmann, G.; Verron, E. Rubber Chem Technol 2004, 77, 724.
36. Horgan, C. O.; Saccomandi, G. J Elasticity 2002, 68, 167.
37. Mossi Idrissa, A. K.; Ahzi, S.; Rémond, Y.; Gracio, J. Eng. Mater. Technol 2011, 133, 030905.
38. Einstein, A. Ann Physik (Leipzig) 1906, 19, 289.
39. Einstein, A. Ann Physik (Leipzig) 1911, 34, 591.
40. Guth, E.; Gold, O. Phys Rev 1938, 53, 322.
41. Guth, E. J Appl Phys 1945, 16, 20.
42. Vand, V. J Phys Colloid Chem 1948, 52, 277.
43. Simha, R. J Phys Chem 1940, 44, 25.
44. Budiansky, B. J Mech Phys Solids 1965, 13, 223.
45. Mori, T.; Tanaka, K. Acta Metall 1973, 21, 571.
46. Suquet, P. In Continuum Micromechanics; Suquet, P., Ed.; Springer-Wien: New York, 1997.
47. Voigt, W. Wied Ann 1889, 38, 573.
48. Reuss, A. Z. Angew Math Mech 1929, 9, 49.
49. Bergstrom, J.; Boyce, M. C. Rubber Chem Technol 1999, 72, 633.
50. Roychoudhury, A.; De, P. P. J Appl Polym Sci 1993, 50, 181.