Theoretical Predictions of Stress-softening and residual strain effects in a reinforced multi-wall carbon nanotubes elastomer materials.

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RESUMEN
El efecto de ablandamiento y el de deformación residual en los elastómeros nanocompuestos son de gran importancia en muchas aplicaciones ingenieriles. Es esencial tener predicciones precisas del comportamiento mecánico de esos compuestos para la manufactura de nuevos productos basados en los desarrollos nanotecnológicos. En este artículo utilizamos un modelo no monotónico y un modelo de deformación residual para predecir ambos, el comportamiento mecánico de ablandamiento y la deformación residual para un BIMSM-MWNT (copolímero de isobutileno y paramethyl estireno con agregado de nanotubos de carbón de pared múltiple), para un hule natural (NR) reforzado con MWNT, y para un polibutadieno (PB) reforzado con partículas de negro de humo.

ABSTRACT
The stress-softened effect and the residual strain of reinforced nanocomposite elastomers are of great importance in many engineering applications. The accurate predictions of the mechanical behavior of these rubber-like composite materials are essential to manufacture new products based on nanotechnology developments. Here in this paper, we use a non-monotonous model and a residual strain model to predict both, the mechanical stress-softened behavior and the permanent set effects, for BIMSM-MWNT (brominated isobutylene and paramethylstyrene copolymer reinforced with multi-wall carbon nanotubes), natural rubber (NR-MWNT), and polybutadiene-carbon black (PB-CB) reinforced elastomers.

INTRODUCTION
The design of components of composite elastomeric materials reinforced with carbon nanotubes for biomedical devices and microdevices is a complex goal, involving the controlled mechanical behavior prediction, computational simulation, prototyping, machining and micromachining, improvement and quality.

In this article, we study stress-softening and residual strain effects since these phenomena occurs in materials that have many engineering applications (Ahir and Terentjev, 2005; Engel, 2006; Yuan, 2009; Oh, 2009; Zhang, 2011; Someya et. al., 2005; Yuan et. al., 2008; Sekitani et. al., 2009; Kim et. al., 2009).

In order to predict the physical behavior of these materials, constitutive models with an accurate prediction, easy implementation, and minimal number of parameters and economic computational time must be developed to represent physically the deformation process of elastomeric composites with carbon nanotubes (CNTs).

Reinforced Polymers
The combination of low volume fraction of CNTs suggests that CNTs are ideal candidates for high performance polymer composites (Shaffer and Sandler, 2006) since single wall carbon nanotubes (SWCNTs) have shown exceptional mechanical properties such as Young modulus and strength (Zhang and Shen, 2006; Yakobson, 1996; Demczyk et al., 2002). To model the behavior of a carbon nanotube reinforced polymeric material (CNRPs), Dikshit and co-workers applied a constitutive equations developed by Mulliken and Boyce for amorphous materials (Mulliken and Boyce, 2006) and assumed that SWCNT can be considered as a
homogeneous and isotropic materials represented by a cylindrical phase (Dikshit et al., 2008). Cantournet et al. (Cantournet et al., 2007) proposed a hyperelastic constitutive model for a MWNTs reinforced elastomer to describe the material behavior assuming that the strain energy of the elastomeric material can be computed by using the Arruda-Boyce model, which considers the material to be isotropic and isochoric (Arruda and Boyce, 1993; Bishoff et al., 2001), while the anisotropic strain energy function of the MWNT is “isotropized” by considering the average orientation of the MWNTs given with respect to the principal stretch directions, i.e. taking the azimuthal angle of 55º and this energy is computed by using the rule of mixtures. However, these models only predict the loading part of a cycle tension test. We recently studied in (Córdova et al., 2010) the influence of adding carbon nanotubes (CNTs) as fillers in rubberlike materials and modeled the Mullins effect for a MWNT reinforced elastomer (BIMSM-MWNT) with no preconditioning deformation. However this model does not consider permanent set effects.

**Softening Effect**

Mullins effect has been studied in the last decades by many researchers. See for instance, (Mullins, 1947; Mullins and Tobin, 1953; Bueche, 1961; Yokoyama, 1978; Harwood et al., 1965; Ogden and Rolixirgh, 1999; Beatty and Krishnaswamy, 2000; Elias Zúñiga, 2005; De Tommasi and Puglisi, 2006; De Tommasi et al. 2008) and references cited there in. Mullins effect shows a number of phenomena in loading and unloading tension test that can be summarized as follows: 1) loading and unloading paths of stress vs. strain tests differ substantially (hysteresis of energy), 2) under cyclic deformation with a fixed maximum strain, stress decreases with number of cycles (strain-softening or damage accumulation), 3) when stretching proceeds after several cycles of loading-unloading and strain exceeds the maximum strain under cyclic deformation, the stress–strain curve rapidly reaches that for a virgin specimen (strain-hardening) (Drozdov, 2009), and 4) after the material is stretched and released, the unload path does not reach the previous initial extension value of the loading path, this effect is known as permanent set or residual strain (Mullins, 1947). See Fig. 1.

The aim of this paper is to enhance our proposed material model (Córdova et al. 2010) by including permanent set effects based on the constitutive model developed in (Calva, 2008). At the end of the paper, we compare our enhance material model with experimental data obtained from three composite elastomers, two of them reinforced with carbon nanotubes and the other with carbon black (CB) particles.

**Experimental data, neat Silicone**

![Figure 1. Cyclic uniaxial tension test on a silicone elastomer sample at strain rate=0.02s⁻¹. Adapted from Montoya-Gómez et al., 2010.](image)

In the next section, we shall briefly review some basic concepts of continuum mechanics.

**BASIC CONCEPTS**

In this section, we review some kinematics relationships for finite deformations of incompressible, hyperelastic materials. First, let us consider a material particle at the place \( \mathbf{X} = X_k \mathbf{e}_k \) in an initially undeformed reference configuration of a body. When subjected to a prescribed deformation, the particle at \( \mathbf{X} \) moves to the place \( \mathbf{x} = x_k \mathbf{e}_k \) in the current configuration of the body in a common rectangular Cartesian frame \( \phi = 0 \); with origin at \( O \) and orthonormal basis \( \mathbf{e}_k \). An isochoric deformation is described by:

\[
\begin{align*}
\lambda_1 &= \lambda_1 X_1; \\
\lambda_2 &= \lambda_2 X_2; \\
\lambda_3 &= \lambda_3 X_3
\end{align*}
\]

(1)

in which \( \lambda_i, i = 1, 2 \) and 3, denote the principal stretches in \( \phi \). The Cauchy–Green deformation tensor \( \mathbf{B} = \mathbf{F}^T \mathbf{F} \) has the form:

\[
\mathbf{B} = \lambda_1^2 \mathbf{e}_{11} + \lambda_2^2 \mathbf{e}_{22} + \lambda_3^2 \mathbf{e}_{33}
\]

(2)
where \( \mathbf{e}_j = \mathbf{e}_j \otimes \mathbf{e}_k, \mathbf{e}_l \) are associated orthonormal principal directions, and \( \mathbf{F} \) is the usual deformation gradient. The magnitude of the strain at a material point \( \mathbf{X} \), also called the strain intensity and denoted by \( m \), is defined by \( m = \sqrt{\mathbf{B} \cdot \mathbf{B}} = tr \sqrt{\mathbf{B}^2} \) where \( tr \) denotes the trace operation. In the unstrained state \( \mathbf{F} = \mathbf{1} \), and the strain intensity \( m = \sqrt{3} \); otherwise \( m > \sqrt{3} \) for isochoric deformations (Beatty and Krishnaswamy, 2000).

The principal invariants \( I_k \) of \( \mathbf{B} \) are defined by:

\[
I_1 = tr \mathbf{B}, \quad I_2 = \frac{1}{2}[I_1^2 - tr \mathbf{B}^2], \quad I_3 = det \mathbf{B} = 1
\]

(3)

so the magnitude \( m \) of \( \mathbf{B} \) as a function of the invariants is given by:

\[
m = \sqrt{I_1^2 - 2I_2}, \quad m \geq \sqrt{3}
\]

(4)

Here \( m = \sqrt{3} \) when and only when \( \lambda = 1 \), the unstrained state. Also, for all deformations of an incompressible material, \( I_3 = 1 \).

To model the material stress-softening behavior, we may assume that microstructural material damage is characterized by a certain isotropic and non-monotonic increasing function \( F(m, M_{\text{max}}) \) that depends on the material strain intensity \( m \) and satisfies the conditions:

\[
0 < F(m, M) < 1; \quad F(M_{\text{max}}, M_{\text{max}}) = 1
\]

(5)

where \( M_{\text{max}} \), represents the maximum previous strain intensity at the point at which the material is unloaded from the virgin path. The softening function \( F(m, M_{\text{max}}) \) is determined by a constitutive equation that describes the evolution of microstructural change that begins immediately upon deformation from the natural, undistorted state of the virgin material. We assume that \( F(m, M_{\text{max}}) \) is a positive non-monotonic increasing function of the strain intensity on the interval \( m \in (\sqrt{3}, M) \). If we let \( m = M_{\text{max}} \) be the amount of stretch at the point at which the material is unloaded and fix the maximum previous strain intensity energy at \( m = M_{\text{max}} \) then, the stress-softened material response for subsequent unloading and loading again from an unstrained state, or from any other elastic point for which \( m = M_{\text{max}} \) is defined by the time independent constitutive equation

\[
\mathbf{\tau} = F(m; M_{\text{max}}) \mathbf{T}
\]

(6)

where \( \mathbf{\tau} \) denotes the Cauchy stress in the stress-softened material.

Based on the non-monotonic behavior of reinforced rubber-like materials (Diani et. al. 2009), we assume that the softening function has the form

\[
F(m, M) = e^{-\delta [(M-m)(m/M)\alpha]^\gamma}
\]

(7)

where \( \delta \) is a positive softening material parameter, \( \alpha \) and \( \gamma \) are a positive scaling constants chosen to best fit experimental data for a given rubber-like material. Substitution of Equation (7) into (6) gives:

\[
\mathbf{\tau} = e^{-\delta [(M-m)(m/M)\alpha]^\gamma} \mathbf{T}
\]

(8)

Notice that for our constitutive model given by Eq. (8), the ratios of the nontrivial physical stress components \( T_{ij} \) in the virgin material to the corresponding nontrivial physical components \( t_{ij} \) in the stress-softened material, for a given deformation state, are determined by the inverse of the softening function alone. That is, in accordance with Eq. (8), we have that:

\[
\frac{T_{ij}}{t_{ij}} = \frac{1}{e^{-\delta [(M-m)(m/M)\alpha]^\gamma}} \geq 1, \quad i, j = 1, 2, 3,
\]

(9)

no sum

The simple rule Eq. (9) provides a means to determine the softening parameters from experimental data as shown in Fig. 2. This is demonstrated by Gurtin and Francis in (Gurtin and Francis, 1981) for simple uniaxial tension data; however their results do not collapse to a single curve for all values of \( M \). Various hypothetical damage functions having properties similar to Eq. (7) have been introduced for analytical study, however these are not non-monotonic type. See (Gurtin and Francis, 1981; Ogden and Roxburgh, 1999; De Souza Neto, 1994; Johnson and Beatty 1993; Zuñiga and Beatty, 2002; Beatty and Krishnaswamy, 2000), and references cited there in.

**CANTOURNE MODEL**

In this section, we review the main features of Cantournet model and how the strain energy densities of the polymeric matrix and the volumetric fraction of carbon nanotubes can be computed.

According to Cantournet et. al., the strain energy density \( U_s \), of the MWNT-elastomer composite can be found by adding the strain energy density of the
elastomeric part $U_e$, to the strain energy density associated with the MWNT’s $U_{MWNT}$. They assumed that the strain energy density of the MWNT’s is giving by the following rule:

$$U_{MWNT} = \frac{(U_e - (1 - f)U_e)}{f}$$  \hspace{1cm} (10)

where $f$ is the volumetric fiber fraction. The elastomeric strain energy density $U_e$ is assumed to be given by the compressible version of the eight chain model (see, Bischoff et. al., 2001):

$$U_e = \left( \sqrt{N\lambda_{chain}} \beta + N\ln \frac{\beta}{\sinh \beta} - \frac{\sqrt{N\beta}}{3} \ln f \right) + \frac{1}{2}K_B(J - 1)^2$$  \hspace{1cm} (11)

where $N$ is the chain number of links, $\beta = \lambda^{-1/2} \lambda_{chain}$, $\lambda_{chain} = \sqrt{l_1/j}$, $\beta_0 = \lambda^{-1/2}(1/\sqrt{N})$, $\lambda^{-1} = \coth(\beta) - 1/\beta$, $J = \sqrt{l_3}$, $K_B$ is the material bulk modulus, and $l_1$ and $l_2$ are the first and third invariants of the left Cauchy-Green Tensor. Thus, the Cauchy stress due to the elastomeric matrix $T_e$, can be obtained by the following expression:

$$T_e = \frac{2}{f} \frac{\partial U_e}{\partial l_1} B + \frac{\partial U_e}{\partial f} I.$$  \hspace{1cm} (12)

This gives:

$$T_e = \mu_R \sqrt{N} \left( \frac{\beta}{\lambda_{chain}} B - \beta_0 I \right) + K_B(J - 1)I,$$  \hspace{1cm} (13)

where $B$ is the left Cauchy-Green deformation tensor and $\mu_R$ is the material shear Young Modulus. Notice that the second term becomes zero if the material is assumed to be incompressible i.e., $J = 1$.

Cantournet shows that the MWNT strain energy $U_{MWNT}$, can be expressed by an “isotropized” relation which is described by:

$$U_{MWNT} = A_1 (\lambda_{MWNT} - 1) + A_2 (\lambda_{MWNT} - 1)^2 - \frac{2A_1}{3} \ln f$$  \hspace{1cm} (14)

or in equivalent form by

$$U_{MWNT} = \frac{A_1}{3} (l_1 - 3) + \frac{A_2}{9} (l_1 - 3)^2 - \frac{2A_1}{3} \ln f$$  \hspace{1cm} (15)

where $A_1$ and $A_2$ are the “isotropized” parameters fitted from the $U_{MWNT}$ vs $(\lambda_{MWNT} - 1)$ data plots using the Cantournet et. al. procedure from uniaxial experimental tests.

Cantournet model states that the composite strain energy function is simply the sum of the contributions from the elastomer and from the MWNT. Thus, the Cauchy stress constitutive equation of the composite material is given by:

$$T_c = (1 - f) \frac{\mu_R \sqrt{N}}{3} \left( \frac{\beta}{\lambda_{chain}} B - \beta_0 I \right) + \frac{2}{3} f \left( A_1 + \frac{2A_2}{3} (l_1 - 3) \right) B + \frac{2A_1}{3} f I + K_B(J - 1)I,$$  \hspace{1cm} (16)

We first compute the strain energy density over the whole interval for each MWNT fraction. Then, we use the rule of mixtures given by Eq. (10) to compute the carbon nanotube strain energy density contribution. Next, the MWNT strain energy density can be expressed by the “isotropized” contribution that provides a framework for further reduction of their $U_{MWNT}$ energy density which is described by $U_{MWNT}$ vs $(\lambda_{MWNT}^2 - 1)$ curves. It is important to mention that in general the Cantournet model fits well for low volumetric MWNT fraction and for relative small deformations but tends to overestimate experimental data for high fractions of volumetric MWNT and large deformations.

**RESIDUAL STRAIN**

This section describes a method to predict analytically the permanent set phenomenon of rubberlike materials. The theory described here is based on pseudoeelasticity theory (Holzapfel et al., 1999) and considers an additional term that modifies the strain energy function to include description of the residual strain phenomenon.

To account for residual strains, Holzapfel et al. assumed a strain energy function $W$, of the form

$$W = W_0 (\lambda_1, \lambda_2, \lambda_3) + W_{rs} (\lambda_1, \lambda_2, \lambda_3, \xi_1, \xi_2, \xi_3) - p(J - 1)$$  \hspace{1cm} (17)
where the function $\hat{W}_0$ represents the energy associated with the primary loading path, $\hat{W}_{rs}$ is the function related to the material damage mechanism; $\xi_a, a = 1, 2, 3$ represent the discontinuous damage variables, $p$ is an arbitrary hydrostatic pressure and $J = \lambda_1 \lambda_2 \lambda_3 = 1$ due to the incompressibility condition.

$$\frac{\partial \hat{W}_{rs}}{\partial \xi_a} = 0$$  \hspace{1cm} (18)

Equation (17) will be used with Eq. (6) to derive the corresponding residual stress; thus, the stress softened material can be described by the following constitutive equation,

$$\tau = F(m, M) \textbf{T} = e^{-\delta(M-m)(m/M)^{1/3}} \left[ \textbf{T}_C + T_r \textbf{s} \right]$$  \hspace{1cm} (19)

where $\textbf{T}_C$ represents the virgin composite material stress which in the present work, will be represented by the Cantournet model; and the terms $T_{rs}$ is a discontinuous supplementary residual stress which is active in the unloading and reloading paths where $\lambda_a > \lambda_{a \text{ max}}, a = 1, 2, 3$, and becomes inactive in the primary loading path when $\lambda_a = \lambda_{a \text{ max}}, a = 1, 2, 3$. Here $\lambda_{a \text{ max}}$ represents the highest previous values of the principal stretches in the primary loading path. The form of the supplementary stress, for the principal directions, can be computed as the derivative of the damage mechanism with respect to the principal stretches:

$$T_{rs} = \lambda_a \frac{\partial \hat{W}_{rs}}{\partial \lambda_a}$$  \hspace{1cm} (20)

In this case, the damage energy density function given by (Calva, 2008) which depends on a positive scaling parameter $n$, is expressed as

$$\hat{W}_{rs} = \frac{3}{2} \sum_{a=1}^{n} \left[ \frac{\mu_c}{2C} \left( \lambda_a^n - \lambda_{a \text{ max}}^n \right)^2 - c_0 \right]$$  \hspace{1cm} (21)

Thus, we can determine the partial derivation of $\hat{W}_{rs}$ with respect to the principal stretches, i.e.

$$\frac{\partial \hat{W}_{rs}}{\partial \lambda_a} = n \frac{\mu_c}{C} \left( \lambda_a^n - \lambda_{a \text{ max}}^n \right) \lambda_a^{-1}$$  \hspace{1cm} (22)

where $C$ represents a material constant related to the damage mechanism, $c_0$ is an integration constant, and $n$ is a positive scaling parameter. Substitution of Eq. (22) into Eq. (20) yields the expression to compute the corresponding residual stresses:

$$T_{rs} = \frac{\mu_R}{C} \left( -n \lambda_a^n \lambda_{a \text{ max}}^n - \lambda_a^n \right) + 
\frac{n}{\lambda_a^n} \lambda_{a \text{ max}}^{-n} \left( \lambda_{a \text{ max}}^{-n} - \lambda_a^{-n} \right)$$  \hspace{1cm} (23)

Finally and by recalling Eq. (19), the stress-stretch constitutive material model that predicts softening and residual strain effects, for three dimensional state, is given by

$$\tau = \left[ (1-f) \frac{\mu_R}{3J} \sqrt{N} \left( \frac{\beta}{\lambda_{a \text{ chain}}} - \textbf{B} - \beta_0 \textbf{I} \right) + \frac{2}{3} f (A_1 + \frac{2A_2}{3} (I_1 - 3)) \textbf{B} + \frac{2A_1 f}{3} \textbf{I} + K_B (J - 1) \textbf{I} + \frac{\mu_R}{C} \left( -n \lambda_a^n \lambda_{a \text{ max}}^n - \lambda_a^n \right) \textbf{I} + \frac{n}{\lambda_a^n} \lambda_{a \text{ max}}^{-n} \left( \lambda_{a \text{ max}}^{-n} - \lambda_a^{-n} \right) \textbf{I} \right] e^{-\delta(M-m)(m/M)^{1/3}}$$  \hspace{1cm} (24)

NUMERICAL RESULTS

In this section, we compare experimental data obtained of three different reinforced elastomeric materials, BIMSM-MWNT (Cantournet et al.,...
natural rubber-MWNT (Nah et al., 2010), and PB-CB with theoretical predictions provided by Eq. (24). In this article, we performed uniaxial extension tests to obtain experimental data on samples of PB-CB materials. These samples were tested on a MTS Insight 2kN machine and using the ASTM D412-Rev A standard with Die C specimens.

First, we compare experimental data of elastomeric material called BIMSM-MWNT (Cantournet et al., 2007). Here, we choose the parameter values of $\alpha = \frac{1}{2}$, and $\gamma = 1$ in Eq. (24) and then we fitted the value of the softening parameter $\delta$ and the chain number of links $N = 200$ by following a procedure similar to the one described in (Cantournet et al., 2007). The shear modulus $\mu_R$, and the “isotropized” parameters, $A_1$ and $A_2$, for each volumetric fraction of MWNT are listed in Table 1. The damage parameter values for each volumetric fraction of MWNT’s, are summarized in Table 2. The residual strain parameters are fitted substituting Eq. (23) into Eq. (19) and summarized in Table 2.

**Table 1. Material parameter values of $A_1$, $A_2$, and $\mu_R$ for different weight fractions of MWNTs.**

<table>
<thead>
<tr>
<th>Weight Fraction</th>
<th>2.6% w</th>
<th>6.1% w</th>
<th>8.8% w</th>
<th>12.2% w</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$ (Mpa)</td>
<td>6.48</td>
<td>6.89</td>
<td>5.85</td>
<td>7.67</td>
</tr>
<tr>
<td>$A_2$ (Mpa)</td>
<td>2.58</td>
<td>3.10</td>
<td>2.42</td>
<td>3.10</td>
</tr>
<tr>
<td>$\mu_R$ (MPa)</td>
<td>0.642</td>
<td>0.671</td>
<td>0.695</td>
<td>0.770</td>
</tr>
</tbody>
</table>

We next use Eq. (24) and compute theoretical predictions by considering a volumetric fraction of 12.2% of MWNT. As we may see from Fig. 3, there is good agreement between experimental data and theoretical predictions mainly at low stretch values. We next used Eqs. (8) and (23) to compare this experimental data with theoretical predictions by plotting the ratio of the stress-softened $\tau_s$ with respect to the virgin stress $\tau_v$ versus the ratio of $(m-\sqrt{3})/(M-\sqrt{3})$ for the first two cycles, as illustrated in Fig. 4. We may conclude that theoretical predictions and experimental data agree well. Similar plots can be obtained by considering different volumetric fractions of MWNT. Table 3 and Table 4 summarize the root-mean-square error (RMSE) obtained in the first loading and unloading curves, respectively. Notice that for high volumetric fractions of MWNT, the RMSE between experimental data and theoretical predictions is relatively low mainly at low volumetric fractions. We may conclude that the modified Cantournet model tends to follow well data even for high volumetric fractions of MWCNT in the BIMSM-MWNT reinforced polymer.

**Table 2. Values for the damage parameter for different weight fractions of MWNTs.**

<table>
<thead>
<tr>
<th>Weight Fraction</th>
<th>0.0%</th>
<th>2.6%</th>
<th>6.1%</th>
<th>8.8%</th>
<th>12.2%</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta$</td>
<td>0.13</td>
<td>0.17</td>
<td>0.19</td>
<td>0.24</td>
<td>0.49</td>
</tr>
<tr>
<td>$N$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$C$</td>
<td>8.75</td>
<td>7.00</td>
<td>5.40</td>
<td>5.87</td>
<td>4.00</td>
</tr>
</tbody>
</table>

The maximum error $e$ has the value of 10.71 % for a weight fraction of 2.6%w, though the maximum RMSE is 0.054 for 12%w. This could be due to the
variations that the Cantournet model has over the loading path predictions as may be seen in Fig. 3.

In Fig. 5 is illustrated the variation of the softening parameter $\delta$ versus the weight fraction of MWCNT added to the polymeric matrix of the BISMS-MWNT reinforced polymer. As we may see from Fig. 5, as the weight fraction increases the softening parameter $\delta$ tends to increase by following a nonlinear behavior. Notice that if we fit the curve showed in Fig. 5, we may use the resulting equation to predict the value of $\delta$ at different weight fractions of MWCNT’s.

Table 3. RMSE at different weight fractions of MWCNT’s (loading path).

<table>
<thead>
<tr>
<th>% MWCNT</th>
<th>Percentage quadratic error, $e$</th>
<th>RMSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.6</td>
<td>10.71%</td>
<td>0.039</td>
</tr>
<tr>
<td>6.1</td>
<td>10.18%</td>
<td>0.048</td>
</tr>
<tr>
<td>8.8</td>
<td>10.67%</td>
<td>0.053</td>
</tr>
<tr>
<td>12.2</td>
<td>8.90%</td>
<td>0.054</td>
</tr>
</tbody>
</table>

Table 4. RMSE at different weight fractions of MWCNT’s (first unloading path).

<table>
<thead>
<tr>
<th>% MWCNT</th>
<th>Percentage quadratic error, $e$</th>
<th>RMSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.6</td>
<td>10.71%</td>
<td>0.042</td>
</tr>
<tr>
<td>6.1</td>
<td>10.18%</td>
<td>0.050</td>
</tr>
<tr>
<td>8.8</td>
<td>10.67%</td>
<td>0.054</td>
</tr>
<tr>
<td>12.2</td>
<td>7.99%</td>
<td>0.075</td>
</tr>
</tbody>
</table>

Figure 6 shows the variation of the residual strain parameter $C$ versus the volumetric fractions of MWCNT’s. As we may see, the values of $C$ tend to become lower at high volumetric fractions of MWCNT’s.

We next used uniaxial extension experimental data obtained from Nah. et al. (Nah. et. al., 2010) in reinforced natural rubber to assess the accuracy of our modified Cantournet model by using parameter values of: $\mu_R=3.36$ Mpa, $\delta = 0.35$, $C=4$, $n=1$, $\gamma = 1$, $\alpha = 0.5$, $A_1 = 137$ Mpa, $A_2 = 10.8$ Mpa. We may see from Fig. 7 that theoretical predictions underestimate experimental data at low strain values of 0.1 and overestimate data at strain values larger than 0.6. However, the qualitative and quantitative behavior exhibited by experimental data is well predicted from our modified Cantournet model given by Eq. (24). In this case, the computed RMSE is 0.68 and 0.56 for the loading and unloading paths respectively.

Finally, we used uniaxial extension experimental data obtained from samples of PBR-CB elastomer
This polymer was tested under the standard ASTM D412 Rev A. Some of the samples tested are shown in Fig. 8. Comparison of experimental data obtained at the constant strain rate of 0.3 s\(^{-1}\) and theoretical predictions are shown in Fig. 9 only for the second loading and unloading cycle. The estimated parameter values used were: \(\mu_R = 0.3815\) Mpa, \(N = 200\), \(\delta = 0.035\), \(C = 9\), \(n = 1\), \(\gamma = 0.5\), \(A_1 = 6.21\) Mpa, and \(A_2 = -0.25\) Mpa. As we may see from Fig. 9, there is good agreement between theoretical predictions and collected experimental data. It is important to mention that in this case, the maximum RMSE computed for the first three loading and unloading cycles was of 0.20258, as shown in Table 5.

**Table 5. RMSE values for the second and third loading and loading cycles.**

<table>
<thead>
<tr>
<th>Cycle 2</th>
<th>Cycle 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loading</td>
<td>Unloading</td>
</tr>
<tr>
<td>RMSE</td>
<td>0.143</td>
</tr>
<tr>
<td>MSE</td>
<td>0.020</td>
</tr>
<tr>
<td>Quadratic error, (e) (%)</td>
<td>19.63</td>
</tr>
<tr>
<td></td>
<td>10.61</td>
</tr>
</tbody>
</table>

**Figure 8. Specimens of PBR and PBR-CB respectively, submitted an uniaxial cycle tension test.**

**CONCLUSIONS**

Here in this paper, we have used a non-monotonous softening function and a permanent set function in an attempt to predict the mechanical stress-softened behavior of reinforced elastomers. It was shown that the assumptions made by Cantournet model to treat an anisotropic material as an equivalent “isotropized” material provides a simple model that can be used to predict the behavior of MWCNT reinforced polymers. The use of this model and the assumption that cyclic load induced non-monotonous material stress-softened behavior gives as a results a general constitutive equation that can be used to characterized the stress-softened and permanent set effects in reinforced polymeric materials with low mean square errors of less than 7% for a 12%w or less concentrations of weight fractions of a BIMSM-MWNT reinforced polymer. Moreover, the usage of Equations (19) and (24) to predict experimental data requires the determination of two macroscopic parameters \(\delta\) and \(\mu_R\) and of three “isotropized” micromechanics parameters, \(A_1\), \(A_2\), \(N\), and a phenomenological residual strain parameters \(C\). Here in all cases, we used the value of \(n = 1\) in Eq. (24). Finally, we may see that our phenomenological non-monotonous softening function described by the simple constitutive relation (7) herein applied to the BIMSM-MWNT, natural rubber and PBR-CB reinforced elastomers has shown to be remarkably accurate in modeling the corresponding experimental data for different loading and unloading cycles.

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