Abstract

The mechanical behavior of elastomeric materials is known to be rate-dependent and to exhibit hysteresis upon cyclic loading. Although these features of the rubbery constitutive response are well-recognized and important to its function, few models attempt to quantify these aspects of response perhaps due to the complex nature of the behavior and its apparent inconsistency with regard to current reasonably successful static models of rubber elasticity. In this paper a detailed experimental investigation probing the material response of carbon black filled Chloroprene rubber subjected to different time-dependent strain histories is presented. Some of the key observations from the experiments are: (1) both filled and unfilled elastomers show significant amounts of hysteresis during cyclic loading; (2) the amount of carbon black particles does not strongly influence the normalized amount of hysteresis; (3) both filled and unfilled elastomers are strain-rate dependent and the rate dependence is higher during the uploading than during the unloading; (4) at fixed strain, the stress is observed to approach the same equilibrium level with relaxation time whether loading or unloading. Based on the experimental data a new constitutive model has been developed. The foundation of the model is that the mechanical behavior can be decomposed into two parts: an equilibrium network corresponding to the state that is approached in long time stress relaxation tests; and a second network capturing the non-linear rate-dependent deviation from the equilibrium state. The time-dependence of the second network is further assumed to be governed by the reptational motion of molecules having the ability to significantly change conformation and thereby relaxing the overall stress state. By comparing the predictions from the proposed three-dimensional constitutive model with experimental data for uniaxial compression and plane strain compression we conclude that the constitutive model predicts rate-dependence and relaxation behavior well.
1 Introduction

The prediction of the mechanical behavior of elastomeric materials has been an active research area for many years. There have been numerous experimental studies addressing different characteristics of the elastomeric response. For example, it is well known that an elastomer undergoes significant softening during the first couple of load cycles and that the material response after that becomes repeatable [Mullins and Tobin, 1965, Harwood et al., 1965, Harwood and Payne, 1966a,b]. This phenomenon is often referred to as the Mullins effect. It is also well known that the stress in an elastomeric specimen after being subjected to a step in the applied strain will relax towards an equilibrium state (e.g. Ferry [1980]). This observation is often interpreted as an indication of the existence of a hyperelastic strain energy function for infinitely slow loading rates. A number of more intricate experiments have further shown that elastomers subjected to dynamic loading histories exhibit complicated time and temperature effects (e.g. Lion [1996], Hausler and Sayir [1995]).

Very recently, a number of constitutive models have been developed addressing different aspects of these observations. The proposed models can be broadly divided into two categories: equilibrium models and time-dependent models. Most of the early work [James and Guth, 1943, Treloar, 1975, Flory, 1977, Wall and Flory, 1951] was devoted to the prediction of the equilibrium response, but there has been a continuous effort in this field throughout the years. One of the more successful models for this problem is the 8-chain network model of [Arruda and Boyce, 1993b]. This model has been shown to successfully capture the equilibrium response under different loading conditions for many elastomers.

There exists significantly fewer models that attempt to predict the observed time and temperature dependence for general strain histories. Recently, there has been a renewed effort to understand and model these effects (e.g. Lion [1996], Hausler and Sayir [1995], Johnson et al. [1995], Dafalias [1991], Zdunek [1993]). Most of the proposed models, however, capture only a subset of the experimentally observed phenomena and are mainly phenomenologically based. One further complication of this general class of models is that they normally contain material dependent functionals that can be hard to experimentally determine for a new material.

In this paper, the large strain time-dependent behavior of elastomeric materials is studied. A detailed experimental investigation which probes the mechanical behavior of a set of Chloroprene rubbers containing a range of carbon black fillers under different loading conditions is presented; the results from the investigation are summarized in Section 2. The experimental data provide a foundation for the development of the micromechanism-inspired constitutive model presented in Section 3. The proposed model is evaluated by comparison with experimental data in Section 4.
2 Experiments

2.1 Procedure

In an effort to gain additional insight into the time-dependent behavior of elastomeric materials, experiments probing the mechanical behavior were conducted on a Chloroprene rubber with three different levels of carbon black and with two different levels of crosslinking density. Table 1 details the material compositions studied. In addition, a set of experiments were performed on an unfilled Nitrile rubber in an effort to assess whether the observed dependencies were filler-induced or general.

<table>
<thead>
<tr>
<th>Material</th>
<th>Carbon Black (Pph)</th>
<th>Cross link density (ETU/TMTD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroprene rubber</td>
<td>15</td>
<td>0.56/0.38</td>
</tr>
<tr>
<td>Chloroprene rubber</td>
<td>15</td>
<td>0.88/0.38</td>
</tr>
<tr>
<td>Chloroprene rubber</td>
<td>40</td>
<td>0.56/0.38</td>
</tr>
<tr>
<td>Chloroprene rubber</td>
<td>65</td>
<td>0.56/0.38</td>
</tr>
<tr>
<td>Chloroprene rubber</td>
<td>65</td>
<td>0.88/0.38</td>
</tr>
<tr>
<td>Nitrile rubber</td>
<td>0</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 1: Classification of the materials used in the experimental investigation. Filler particles: N600 carbon black. The crosslink density is specified by the curative levels used in the vulcanization (Pph Ethylene Thiourea (ETU) and Pph Tetramethyl Thiuram Disulfide (TMTD).)

The experiments were performed both in uniaxial compression of ASTM sized specimens (height and diameter were 13 mm and 28 mm, respectively) and in plane-strain compression (height and cross-sectional area of the specimens were 13 mm and 140 mm², respectively). The tests were conducted at room temperature using a computer controlled Instron servohydraulic uniaxial testing machine operated in strain control mode using an extensometer in order to eliminate the Instron load train compliance errors. The specimens were compressed between hardened steel compression platens which contained a spherical seat for improved alignment. Barrelling was prevented by inserting thin sheets of Teflon foil between the specimen surfaces and the compression platens, see Arruda and Boyce [1993a] for further details.

The specimens were subjected to load cycles consisting of a set of constant strain-rate segments probing strain-rate dependence during both up- and down-loading and relaxation behavior. All specimens were conditioned by 5-6 load cycles with increasing amplitude to a final strain of about -1 prior to testing to remove the influence of the Mullins effect Mullins and Tobin [1965] and to insure repeatability in the tests. An example of the Mullins effect is shown in Figure 1 for a Chloroprene rubber with 65 pph carbon black.
2.2 Results

Figure 2 shows the typical behavior of an elastomer subjected to load cycles with different final strains. The figure demonstrates the substantial amount of hysteresis that occurs at all levels of final strain. The data also provides a quantitative assessment of the repeatability of the tests and further show that the elastomer has no permanent set after one completed load cycle. The experiments have also shown that there is repeatability both between specimens of the same material and the same specimen between different tests. This repeatability indicates that no permanent damage is introduced in the material from the applied load cycles.

In Figure 3 is shown the strain rate dependence during uniaxial compression of a Chloroprene rubber with 15 pph carbon black. The graph indicates that the stress increases with increasing strain-rate during the uploading, and also the less well-documented characteristic that the strain-rate dependence during the unloading is weaker than during the uploading. Figures 4 and 5 show that both highly filled Chloroprene rubber and unfilled Nitrile rubber have the same qualitative behavior during uniaxial compression at different strain rates.

The strain rate dependence during the uploading for the Chloroprene rubber with 15 pph carbon black is summarized in Figure 6, and the corresponding results for the Nitrile rubber is shown in Figure 7. These two figures suggest that for a broad range of strain rates, the stress is proportional to the logarithm of the applied strain rate, and that the proportionality constant increases with strain.

The time-dependence of the material can also be probed with experiments of the type il-
Figure 2: Uniaxial compression to different final strains of a Chloroprene rubber with 15 pph carbon black. Strain rate $\dot{\varepsilon} = -0.01 \, \text{s}^{-1}$.

Figure 3: Uniaxial compression at different strain rates of a Chloroprene rubber with 15 pph carbon black.
Figure 4: Uniaxial compression at different strain rates of a Chloroprene rubber with 65 pph carbon black.

Figure 5: Uniaxial compression at different strain rates of Nitrile rubber.
Figure 6: Stress as a function of strain rate during the uploading of Chloroprene rubber with 15 pph carbon black.

Figure 7: Stress as a function of strain rate during the uploading of unfilled Nitrile rubber.
illustrated in the inset of Figure 8. In this experiment, the constant strain-rate loading was interrupted by relaxation segments both during the uploading and the unloading. The results from the test show that the stress decreases during the relaxation segments in the uploading, and that the stress in fact increases during the relaxation segments in the unloading (similar observations were recently made by Lion [1996].)

Figure 8: Stress relaxation test on a Chloroprene rubber with 15 pph carbon black. Strain rate $\dot{\epsilon} = -0.002 \text{ s}^{-1}$, relaxation time 120 s.

Figure 9 illustrates the dependence of the relaxation behavior on the prior strain rate. The graph shows that after 10 minutes relaxation the stress has significantly approached what appears to be an equilibrium state, and that this state is independent of the strain rates used in the preceding loading segments. The rates of approach towards this equilibrium state are shown in Figure 10, indicating that the rate of approach towards this equilibrium state is a decreasing function of time. The same qualitative relaxation behavior is exhibited by the Chloroprene rubber with 15 pph carbon black as is shown in Figures 11 and 12.

It has recently been argued Lion [1996] based on experimental data of this type that elastomers do not have one unique equilibrium state but that the behavior is characterized by “equilibrium hysteresis.” It is difficult to experimentally determine if this assumption is correct since, as is shown in Figure 12, the rate of approach towards equilibrium is a decreasing function of relaxation time. To determine whether the stress indeed approaches a unique level would require a relaxation time of length such that other undesirable degradation processes could come into play. Based on physical arguments (see Section 3.1.2), we have instead argued that the relaxation process is energy activated which implies the existence of an equilibrium locus that
Figure 9: Stress relaxation test on a Chloroprene rubber with 40 pph carbon black, the relaxation time is 10 minutes.

Figure 10: Stress relaxation test on a Chloroprene rubber with 40 pph carbon black, the relaxation time is 10 minutes.
Figure 11: Relaxation in stress as a function of relaxation time. Chloroprene rubber with 15 pph carbon black, strain rate $\dot{\epsilon} = -0.1$ s$^{-1}$, strain level $\epsilon = -0.6$.

Figure 12: Relaxation in stress as a function of relaxation time. Chloroprene rubber with 15 pph carbon black, strain rate $\dot{\epsilon} = -0.1$ s$^{-1}$, strain level $\epsilon = -0.6$. 
is only a function of the strain state, but this equilibrium state is only obtained in the limit of infinite relaxation times.

Experimental results for the different types of Chloroprene rubber that have been tested are summarized in Figure 13. This figure clearly demonstrates the strong correlation between the stiffness of the material and the volume fraction of carbon black filler particles. It is also shown that in comparing the particular carbon black content versus crosslink density effects, the influence of the volume fraction of carbon black particles is much stronger than on the crosslink densities that were tested.

![Stress-strain behavior of the different Chloroprene rubbers tested. Strain rate $\dot{\epsilon} = -0.01 \text{ s}^{-1}$. The labels 'high cross-link density' and 'low cross-link density' are indications of the curative levels used in the vulcanization, see Table 1.](image)

**Figure 13:** Stress-strain behavior of the different Chloroprene rubbers tested. Strain rate $\dot{\epsilon} = -0.01 \text{ s}^{-1}$. The labels ‘high cross-link density’ and ‘low cross-link density’ are indications of the curative levels used in the vulcanization, see Table 1.

In summary, the experimental investigation has shown that: (1) the material response becomes repeatable after the Mullins softening has been removed; (2) both filled and unfilled elastomers show significant amounts of hysteresis during cyclic loading, and this hysteresis is not related to the Mullins effect; (3) the carbon black particle content does not strongly influence the normalized amount of hysteresis (defined as dissipated energy divided by supplied energy during the loading phase); (4) depending on the filler contents, very little or no permanent set is observed after one load cycle; (5) both filled and unfilled elastomers are strain-rate dependent and the rate dependence is higher during the uploading than during the unloading; and finally, (6) at fixed strain, the stress is observed to approach the same equilibrium stress with relaxation time whether loading or unloading.
Constitutive Modeling

The experimental data presented in the previous section clearly demonstrated the complicated non-linear time-dependent behavior that is exhibited by rubber elastic materials. To address these observations, a simple micromechanism inspired model is developed that incorporates the time-dependent nature of elastomeric materials. The experimental observation that the mechanical behavior can be decomposed into two parts: an equilibrium response and a time-dependent deviation from equilibrium, suggests that the material can be modeled as two polymer networks acting in parallel, see Figure 14. The idea to decompose the total stress into an elastic and a history dependent component was proposed by Green and Tobolsky [1946], and the approach to model elastomers as two interacting networks has been used in different variations by Johnson and co-workers (1992, 1993 and 1995); Roland (1989); and Roland and Warzel (1990). In Figure 14, the first network \(A\) captures the equilibrium response of the material and the second network \(B\) captures the time-dependent deviation from the equilibrium state. Network \(A\) is a ‘perfect network’ and can be modeled by any of the classical models based on hyperelasticity. Network \(B\) is here modeled as a perfect network in series with a time-dependent element which acts to relieve the strain on the perfect network with time and capture the characteristics observed in the experimental investigation. The kinematics and the proposed micromechanism associated with this model are discussed in the next subsection.

![Figure 14: One dimensional rheological representation of the constitutive model.](image)

Finite Strain Kinematics and Constitutive Representation

The total deformation gradient \(F = \text{Grad} \, x = \nabla xx\) acts both on network \(A\) and network \(B\), \(i.e. \, F = F_A = F_B\). The deformation gradient on network \(B\) can further be decomposed into elastic and inelastic parts \(F_B = F^e_B F^p_B\) where the inelastic deformation gradient, \(F^p_B\), represents the configuration obtained by a complete virtual elastic unloading of network \(B\) to a stress free state, see Figure 15.
3.1.1 Kinematics and Constitutive Representation of Equilibrium Behavior (Element \((A)\))

By using the polar decomposition theorem the deformation gradient \(\mathbf{F}_A\) can be decomposed into stretch and rotation contributions:

\[
\mathbf{F}_A = \mathbf{R}_A \mathbf{U}_A = \mathbf{V}_A \mathbf{R}_A. \tag{1}
\]

The left stretch tensor \(\mathbf{V}_A\) is symmetric positive definite and can therefore be decomposed into its spectral representation

\[
\mathbf{V}_A = \mathbf{Q}_A \left[ \sum_{i=1}^{3} \lambda_i^{(A)} \mathbf{e}_i \otimes \mathbf{e}_i \right] \quad \mathbf{Q}_A^T = \sum_{i=1}^{3} \lambda_i^{(A)} \mathbf{l}_i^{(A)} \otimes \mathbf{l}_i^{(A)} \tag{2}
\]

where \(\mathbf{Q}_A\) is proper orthogonal. The stress in network \(A\) in a coordinate system oriented along the principal axes of \(\mathbf{V}_A\) can be obtained from a compressible\(^1\) version of the 8-chain network model of [Arruda and Boyce, 1993b] (see also Anand [1996])

\[
\sigma_i^{(A)} = C_R^{(A)} \sqrt{N^{(A)}} \left( \frac{\lambda_i^{(A)}}{\lambda_{\text{chain}}^{(A)}} \right)^2 - \left( \frac{\lambda_{\text{chain}}^{(A)}}{\lambda_{\text{chain}}^{(A)}} \right)^2 \mathcal{L}^{-1} \left( \frac{\lambda_{\text{chain}}^{(A)}}{\sqrt{N^{(A)}}} \right) + B \ln \left( \sqrt{I_3^{(A)}} \right) \tag{3}
\]

\(^1\)The network is modeled with a large finite bulk modulus for numerical convenience.
where
\[
C_R^{(A)} = \frac{n k T}{3},
\]
(4)
\[
\lambda_{chain}^{(A)} = \frac{1}{\sqrt{3}} \left[ \left( \lambda_1^{(A)} \right)^2 + \left( \lambda_2^{(A)} \right)^2 + \left( \lambda_3^{(A)} \right)^2 \right]^{1/2},
\]
(5)
\[
I_3^{(A)} = \left[ \lambda_1^{(A)} \lambda_2^{(A)} \lambda_3^{(A)} \right]^2,
\]
(6)
\[
\mathcal{L}(x) = \coth(x) - \frac{1}{x}.
\]
(7)

This model contains three material properties: the initial modulus, \( C_R^{(A)} \), the limiting network stretch, \( \sqrt{N^{(A)}} \), and the bulk modulus \( B \).

The total stress contribution from network \( A \) can therefore be written
\[
\mathbf{T}_A = \sum_{i=1}^{3} \sigma_i^{(A)} \mathbf{l}_i^{(A)} \otimes \mathbf{l}_i^{(A)}. \tag{8}
\]

3.1.2 Kinematics and Constitutive Representation of Time-Dependent Behavior (Element \((B)\))

The total velocity gradient of network \( B \), \( \mathbf{L}_B = \mathbf{\dot{F}}_B \mathbf{F}_B^{-1} \), can similarly be decomposed into elastic and inelastic components:
\[
\mathbf{L}_B = \mathbf{L}_e^B + \mathbf{F}_e^B \mathbf{L}_e^P \mathbf{F}_e^{-1}_B = \mathbf{L}_B^e + \mathbf{\dot{L}}_B^p
\]
(9)

where \( \mathbf{L}_B^p = \mathbf{\dot{F}}_B^p \mathbf{F}_B^{-1} \mathbf{F}_e \) and \( \mathbf{\dot{L}}_B^p = \mathbf{\dot{D}}_B^p + \mathbf{\dot{W}}_B^p \).

The unloading process relating the deformed state with the relaxed state is not uniquely defined since an arbitrary rigid body rotation of the relaxed configuration still leaves the relaxed configuration stress free. The unloaded configuration can be made unique in different ways [Boyce et al., 1989], one particularly convenient approach is to prescribe \( \mathbf{\dot{W}}_B^p = 0 \). This will, in general, result in elastic and plastic deformation gradients which both contain rotations. As for network \( A \), the left stretch tensor \( \mathbf{V}^e_B \) can be decomposed into
\[
\mathbf{V}^e_B = \mathbf{Q}^e_B \sum_{i=1}^{3} \lambda_i^{(Be)} \mathbf{e}_i \otimes \mathbf{e}_i \left( \mathbf{Q}^e_B \right)^T = \sum_{i=1}^{3} \lambda_i^{(Be)} \mathbf{l}_i^{(Be)} \otimes \mathbf{l}_i^{(Be)}. \tag{10}
\]

The stress acting on network \( B \) can now be obtained in the same manner as for network \( A \):
\[
\mathbf{T}_B = \sum_{i=1}^{3} \sigma_i^{(Be)} \mathbf{l}_i^{(Be)} \otimes \mathbf{l}_i^{(Be)}. \tag{11}
\]
where
\[
\sigma_i^{(Be)} = C_R^{(B)} \sqrt{N(B)} \left( \frac{\lambda_i^{(Be)}}{\lambda_{\text{chain}}} \right)^2 - \left( \frac{\lambda_i^{(Be)}}{\lambda_{\text{chain}}} \right)^2 L^{-1} \left( \frac{\lambda_i^{(Be)}}{\sqrt{N(B)}} \right) + B \ln \left( \sqrt{I_3^{(Be)}} \right). \tag{12}
\]

The total stress in the system then simply becomes \( T_A + T_B \).

The rate of shape change of network \( B \) can now be constitutively prescribed by

\[
\dot{D}_B^p = \dot{\gamma}_B N_B \tag{13}
\]

where \( N_B \) gives the direction of the driving stress state of the relaxed configuration and \( \dot{\gamma}_B \) is an effective creep rate. Noting that \( T_B \) is computed in the loaded configuration, the driving stress state on the relaxed configuration is then given by

\[
T_B^* = T_B, \quad \tag{14}
\]
\[
T_B' = T_B^* - \frac{1}{3} \text{tr} [T_B^*], \quad \tag{15}
\]

and the equivalent effective shear stress is

\[
\tau_B = \sqrt{\frac{1}{2} \text{tr} (T_B' T_B')}. \tag{16}
\]

The direction of the driving stress \( N_B \) can now be obtained from

\[
N_B = \frac{1}{\sqrt{2 \tau_B}} T_B'. \tag{17}
\]

As discussed above, the effective creep rate \( \dot{\gamma}_B \) of network \( B \) must be constitutively prescribed. Here, a micromechanism-inspired model is proposed on the assumption that the mechanism responsible for the time-dependent behavior is the reptation of macromolecules that are ‘elastically inactive’ (i.e. molecules that carry less load and have the capability to significantly change conformation during creep loading.) To illustrate this view consider first an over-simplified model with one free chain located in a network of chains as shown in Figure 16. If the network is deformed at a high enough rate then the free chain will also deform more or less affinely with the network. Hence the entropy of the free chain is decreased and the free chain contributes additional deformation resistance. If the applied strain is then held constant in the deformed state the free chain will slowly, by Brownian motion, return to a more relaxed configuration. The rate of return towards a relaxed configuration is given by the governing reptation motion of the free chain.

Let us now turn our attention to a more realistic situation in which free chains do not exist. In a real polymer network, however, there are almost always free chain-ends which behave as
the free chain described above. A reasonable extension to the free chain and free chain-end models is to consider also inactive chain segments such as \( A - B - C \) illustrated in Figure 17. Qualitatively, the same behavior is exhibited by the inactive chain segment in Figure 17 and

\[
\text{Figure 16: One free chain in a network.}
\]

the free chain in Figure 16. The loop \( A - B - C \) in Figure 17 undergoes Brownian motion and has an equilibrium position at a finite distance from the constraining chain \( DD' \). Hence, \( DD' \) behaves as an obstacle which imposes an energy barrier to the relaxation process. The relaxation towards equilibrium can therefore be considered to be energy activated.

To develop the constitutive equation for the time-dependent element consider a free chain-end of the type illustrated in Figure 18, but bear in mind that the presented arguments should also hold for the more general situation shown in Figure 17. The chain segment at \( B \) is constrained to travel back and forth along the constraining tube by Brownian motion in a combination of reptation motion and contour length fluctuations. Call the displacement of \( B \) along the tube \( u \). The average displacement of \( B \) can be shown by the theory of reptational motion of chain

\[
\text{Figure 17: Relaxation of inactive chain segments in a perfect network.}
\]
Figure 18: Relaxation of a chain end in a perfect network.
molecules Doi and Edwards [1986] to scale as \( \langle u \rangle = C_3\langle u^2 \rangle^{1/2} \equiv C_3\sqrt{\phi(t)} \). The effective length of the chain in a creep experiment can consequently be written

\[
l(t) = l_0 + C_3\sqrt{\phi(t)}
\]

where the mean square displacement of the chain segment \( \phi(t) \) has been derived Doi and Edwards [1986] by reptation dynamics considerations to scale as

\[
\phi(t) \propto \begin{cases} 
  t^{1/2}, & t \leq \tau_e \\
  t^{1/4}, & \tau_e \leq t \leq \tau_R \\
  t^{1/2}, & \tau_R \leq t \leq \tau_d \\
  t, & \tau_d \leq t 
\end{cases}
\]

where \( \tau_e \) is the time at which the tube constraint is first felt, \( \tau_R \) is the Rouse relaxation time, and \( \tau_d \) is the tube disengagement time. Equations (18) and (19) can be simplified to

\[
\lambda_{\text{chain}}^{BP}(t) = \frac{l(t)}{l_0} = 1 + C_4 t^{C_5} 
\]

where \( C_4 > 0 \) and \( C_5 \in [0.5, 1.0] \). Taking the time derivative of (20) gives

\[
\dot{\lambda}_{\text{chain}}^{BP} = C_4 C_5 t^{C_5-1}. 
\]

It is now possible to eliminate \( t \) between (20) and (21) giving

\[
\dot{\lambda}_{\text{chain}}^{BP} = C_6 \left[ \lambda_{\text{chain}}^{BP} - 1 \right]^{C_7} 
\]

where \( C_6 > 0 \) and \( C_7 \) is about -1. This equation shows how the effective creep rate depends on the chain stretch, where the chain stretch is correlated to the principal macroscopic stretch state by the 8-chain assumption Arruda and Boyce [1993b], i.e.

\[
\lambda_{\text{chain}}^{BP} = \sqrt{\frac{I_{\text{BP}}}{3}} = \sqrt{\frac{\left( \lambda_1^{BP} \right)^2 + \left( \lambda_2^{BP} \right)^2 + \left( \lambda_3^{BP} \right)^2}{3}}. 
\]

Equation (22) gives the creep rate at a constant stress level, but the creep rate also depends on the level of the applied stress. And as discussed above, this stress dependence is assumed to be energy activated. The microstructural connection to the activation parameters is complicated; it is possible, however, to use a generic expression of the form

\[
\dot{\gamma}_B = C_1 \left[ \lambda_{\text{chain}}^{BP} - 1 \right]^{C_2} \left( \frac{\tau_B}{\dot{\gamma}_B} \right)^m. 
\]
where $\tau_B$ is the effective stress measure introduced in Equation (16), and $\dot{\tau}_B$ is a material constant.

Note that in the proposed model the constants $\dot{C}_1 \equiv C_1/\dot{\tau}_B^m$ and $m$ are positive; and $C_2$ is a constant that is restricted by reptational dynamics to be in $[0, -1]$.

4 Results

The constitutive model presented in the previous section can now be compared with the experimental data from Section 2. It should be noted that although the proposed model is for an unfilled elastomer we have here also applied it to Chloroprene rubber with different filler contents. The reasoning for doing this is that the lowest filler content (15 pph) is sufficiently low that it can be argued that the fillers only affect the mean chain lengths and crosslink density, which in fact are input parameters to the model. To find out how well this approximation works from higher filler concentrations we have also applied the model to the Chloroprene rubber with 40 and 65 pph carbon black.

The material constants needed in the model can be obtained from, for example, two uniaxial compression experiments with different strain rates, see Appendix A. For the results presented in this section, the material constants were obtained from Figure 3 and given the following default values unless otherwise specified: $C_{R}^{(A)} = 0.2$ MPa, $C_{R}^{(B)}/C_{R}^{(A)} = 1.6$, $N^{(A)} = N^{(B)} = 8$, $B = 100$ MPa, $\dot{C}_1 = 7.0$ s$^{-1}$ (MPa)$^{-m}$, $C_2 = -1.0$, and $m = 4$.

The results from applying the proposed model to a uniaxial compression experiment with different final strain levels is shown in Figure 19 illustrating that the model provides good quantitative predictions of the stress-strain behavior and hysteresis. The prediction of the combined constant strain-rate and relaxation test of the type discussed in Section 2 is shown in Figures 20 and 21 for two very different strain rates. These two figures indicate that the model predicts the slow strain-rate data very well during both uploading and unloading. However, for very high strain rates, the behavior during loading is well predicted, but the departure from equilibrium during unloading is not well predicted. The reason for this is that the model predicts the same time-dependence during uploading and unloading, but as was discussed in Section 2, the Chloroprene rubber exhibits lower time-dependence during unloading. The physical reason for this difference between uploading and unloading is not clear and will be addressed in a future investigation. Also noticeable from Figure 21 is that even though the model predicts a significant amount of set after one load cycle, that deformation will be recovered with time causing no permanent set in a relaxed state.

The predicted rate of relaxation during both uploading and unloading at a strain rate of $\dot{\epsilon} = -0.1$ s$^{-1}$ and a strain of $\epsilon_{\text{relax}} = -0.6$ is shown in Figure 22. This figure shows that the predicted stress relaxation rate is in good agreement with the experimental data, also note how fast the relaxation rate decreases with relaxation time.
Figure 19: Stress-strain curves to different final strain levels, $\dot{\varepsilon} = -0.01 \text{ s}^{-1}$.

Figure 20: Stress relaxation behavior, Strain rate $\dot{\varepsilon} = -0.002 \text{ s}^{-1}$, 120 seconds relaxation.
Figure 21: Stress relaxation behavior, 30 seconds relaxation time. \( \dot{\epsilon} = -0.1 \text{ s}^{-1} \).

Figure 22: Stress relaxation during up-loading and down-loading, \( \dot{\epsilon} = -0.1 \text{ s}^{-1} \), \( \epsilon_{\text{relax}} = -0.6 \).
The proposed constitutive model is then applied to Nitrile rubber in Figure 23. The material constants used for the Nitrile rubber were: $C_R^{(A)} = 0.29 \text{ MPa}$, $C_R^{(B)}/C_R^{(A)} = 2.5$, $N^{(A)} = 6$, $N^{(B)} = 4$, $\hat{C}_1 = 7.0 \text{ s}^{-1}(\text{MPa})^{-m}$, $C_2 = -0.6$ and $m = 5$. The figure shows that the model gives reasonable predictions of the two very different strain rates used. In Figure 24 is shown the predicted behavior of a Chloroprene rubber with 65 pph carbon black in plane-strain compression when the model has been fitted to uniaxial data. The material constants used were: $C_R^{(A)} = 0.57 \text{ MPa}$, $C_R^{(B)}/C_R^{(A)} = 4$, $\hat{C}_1 = 0.4 \text{ s}^{-1}(\text{MPa})^{-m}$, $C_2 = -0.9$ and $m = 5$. The graph illustrates that the model can also give good predictions of plane strain loading.

And then, in Figure 25, is shown the results from applying the model to Chloroprene rubber with three different levels of carbon black. In this figure the material constants for the Chloroprene rubber with 15 and 65 pph carbon black were taken to be the same as used in Figures 19 and 24, respectively. The material constants for the Chloroprene rubber with 40 pph carbon black were taken to be $C_R^{(A)} = 0.36 \text{ MPa}$, $C_R^{(B)}/C_R^{(A)} = 2$, $\hat{C}_1 = 7.0 \text{ s}^{-1}(\text{MPa})^{-m}$, $C_2 = -1.0$ and $m = 4$. The figure shows that by determining appropriate material constants the constitutive model can give reasonable predictions also of elastomers with different volume fractions of carbon black particles.

5 Conclusions

In this paper a new micromechanism inspired constitutive model has been presented that allows for predictions of the large strain time-dependent behavior of elastomeric materials. The model
**Figure 24:** Comparison between predicted and experimentally determined uniaxial and plane-strain behavior, $\dot{\varepsilon} = -0.01$/s. Chloroprene rubber with 65 pph carbon black, ‘low cross-link density.’

**Figure 25:** Prediction of the stress-strain behavior of Chloroprene rubber filled with three different levels of carbon black. Strain rate $\dot{\varepsilon} = -0.01$ /s.
is based on the assumption that the behavior can be decomposed into two networks acting in parallel, one network captures the equilibrium state and the second network gives the time-dependent deviation from equilibrium. The time-dependence of the material is further assumed to be governed by the reptational motion of molecules that have sufficient freedom to change conformation during the loading. Furthermore, by incorporating these features into a large strain kinematics framework we get a constitutive model well suited for any arbitrary complex deformation and can be incorporated into finite element simulations.

The proposed model is then compared with experimental data for Chloroprene and Nitrile rubber subjected to different loading histories. In particular, it is shown that the model gives good quantitative agreement for different strain rates and relaxational behavior. It is further shown that it is possible to predict the behavior of particle filled elastomers by choosing appropriate effective material constants. A more direct approach to the prediction of the mechanical behavior of carbon black filled elastomers is currently in progress and will be the topic of a later report.

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A Determination of Material Constants

As discussed in Section 4, the material properties needed by the constitutive model are: the hyperelastic properties of network $A \{C_R^{(A)}, N^{(A)}, B\}$; the hyperelastic properties of network $B \{C_R^{(B)}, N^{(B)}, B\}$; and the properties of the time-dependent element $\{\hat{C}_1, C_2, m\}$. As an aid in determining these properties for a specific material the following procedure can be used.

1. The constants $C_R^{(A)}$ and $N^{(A)}$ can be determined from, for example, one uniaxial compression experiment. Let $\lambda_{lim}$ be the stretch at which the stress starts to increase without limit (see Figure 1), the value of $N^{(A)}$ can then be obtained from (3) and (4) giving

$$N^{(A)} = \frac{1}{3} \left[ \lambda_{lim}^2 + \frac{2}{\lambda_{lim}} \right].$$

Furthermore, if $(\sigma_{eq}, \lambda_{eq})$ is one point on the estimated equilibrium locus, then $C_R^{(A)}$ can be estimated from

$$C_R^{(A)} = \frac{\sigma_{eq}}{\lambda^2 - \frac{2}{\lambda}} \sqrt{\frac{\lambda^2 + 2/\lambda}{3N^{(A)}}} \left[ \mathcal{L}^{-1} \left( \sqrt{\frac{\lambda^2 + 2/\lambda}{3N^{(A)}}} \right) \right]^{-1}.$$
Definition of equilibrium locus and limiting stretch.

2. $C_R^{(B)}$ can be determined from the instantaneous unloading slope (i.e. tangent modules $E_t = dσ/dϵ$) at strain reversals

$$C_R^{(B)} = \frac{E_t}{3} \left[ 2λ^2 + \frac{1}{λ} \right]^{-1} - C_R^{(A)},$$

and $N^{(B)}$ can be taken to be equal to $N^{(A)}$.

3. The material constant $B$ is simply the bulk modulus of the material. If the bulk modulus is unknown and the material is almost incompressible, just take $B$ to be sufficiently large, for example $B ≈ 500C_R^{(A)}$. Note that the bulk modulus has little influence on the results reported here; however in loading situations where a rubber component is highly confined the bulk modulus is important.

4. The material constants $\{\hat{C}_1, C_2, m\}$ are restricted, based on physical arguments, such that $\hat{C}_1$ and $m$ are positive and $C_2 ∈ [-1, 0]$. Due to the coupled nature of these constants it is perhaps easiest to determine them by trial-and-error from a good initial guess. For a common elastomer take $\hat{C}_1 = 5 \text{ s}^{-1} \text{MPa}^{-m}$, $C_2 = -1$, and $m = 4$. By comparing the model predictions with experimental data for one additional uniaxial experiment at a different strain rate, it is a simple matter to adjust $\hat{C}_1$ to get the right strain-rate dependence.
References


