THERMO-MECHANICS OF ELASTOMERS UNDERGOING SCISSION
AND CROSS-LINKING AT HIGH TEMPERATURES

Alan Wineman, Alan Jones, Department of Mechanical Engineering
John Shaw, Department of Aerospace Engineering
University of Michigan, Ann Arbor, MI 48109, USA

ABSTRACT The elastomeric materials used in tires are frequently subjected to severe thermal, chemical and mechanical stress conditions. These conditions produce significant changes in material properties that affect their service life. The prediction of service life has become an increasingly important part of the engineering design process, and there is a need for a robust life prediction model.

There are many physical factors which affect the durability of an elastomeric material, such as deformation, conversion of mechanical energy to heat due to dissipative effects, heat transfer within the component, and changes in material properties due to changes in microstructure. The goal of this work is the development of a thermo-mechanics model that incorporates these factors.

This paper focuses on the effect of high temperatures on an elastomeric component. There are two sources of temperature rise, a hot environment and internal heating due to mechanical loading such as occurs during cyclic loading. Internal mechanical heating can lead to a substantial temperatures occurring within the component. When the temperature of the material becomes sufficiently high, macromolecules undergo time dependent scission, recoil and may cross link to form new networks with new reference configurations. This process can affect the stiffness of the material system, induce anisotropy and lead to permanent set.

A constitutive theory is presented that accounts for this temperature dependent microstructural change on the mechanical response. It is based on experimental results and is motivated by the two network theory of Tobolsky. The theory is applicable for large deformation and varying temperature histories. An example is presented which illustrates the implications of scission and re-crosslinking.

Key Words: scission, crosslinking, multi-network theory, constitutive equation
Introduction

Elastomeric materials are frequently used under severe thermal, chemical and mechanical stress conditions. These conditions produce changes in mechanical properties that cause failure. There is clearly a need for a model that can account for these changes in the service life prediction of elastomeric components.

Many physical factors affect the durability of an elastomeric component, such as large deformation, conversion of mechanical energy to heat due to dissipative effects, heat transfer within the component, and changes in material properties due to microstructural changes. The goal of this research program is the development of a thermo-mechanical model that incorporates these factors. Important steps are being taken towards the development of a realistic and accurate life and durability prediction model through theoretical and experimental studies of rubber under thermo-mechanical loading. Initial results can be found in the article by Wineman, Jones and Shaw [1] and some recent results are presented here.

The current focus is on the role of heating on the durability of an elastomeric component. There are two sources of heating of elastomeric components. First, components are often used in hot environments, such as in the engine compartment of an automobile, where they may operate in temperatures over 100°C. Second, internal mechanical heating, such as occurs during cyclic loading, can lead to a substantial temperature rise within the component. This is illustrated by an experiment as shown in Figure 1. A bushing at Tenneco Automotive Corporation was tested. The outer sleeve of the bushing was supported in a fixed housing and its center was connected to a movable post. The bushing design includes an air gap, which affects its compliance under displacements in the horizontal direction in the figure. The post was given a 1000 N vertical pre-load and then subjected to sinusoidally oscillating displacements in the vertical direction with respect to the figure. The displacement amplitude was 2 mm and the frequency was 10 Hertz. The initial bushing temperature was about 70°F. The temperature rise in the bushing was measured with a thermal imaging camera. As can be seen, after 2.5 minutes the temperature of the lower part of the bushing increased to 86°F. Since rubber is a poor heat conductor and bushings normally undergo oscillations for long periods of time, there can be significant temperature rises within the bushing while it
is in operation. Regardless of the mechanism of heating, there can be significant degradation of the elastomer when its temperature becomes sufficiently high. Therefore, there is a need for a constitutive model of the thermo-mechanical response of an elastomer as it degrades at high temperatures. This model, along with the equations of thermo-mechanics, would be used in a computational code to determine the stresses, deformation, temperatures and material property changes in an elastomeric component in typical applications.

Section 2 contains a discussion of experimental results from the literature that characterize the process of degradation of rubber at elevated temperatures and a simple thermo-mechanical model that has been proposed to model this process. These results apply to fixed uniaxial extension and constant temperature. Section 3 contains results from our experimental program that are used to guide the development of a constitutive equation for large deformation and time dependent temperatures. This constitutive equation is described in Sections 4 and 5. A numerical example is presented in Section 6 that shows the interaction of the spatial variation of temperature, scission and deformation.

Experimental Background
In the experiments conducted by Tobolsky [2], a rubber strip at room temperature was subjected to a fixed uniaxial stretch and then held at a higher fixed temperature for some time interval. At temperatures above $T_{cr}$, (say 100°C), called the chemorheological temperature, the stress decreased with time. At the end of a specified time interval, the stress was removed and the specimen was returned to its original temperature. The specimen was also observed to have a permanent stretch. Tests were carried out for different applied stretches, temperatures and time intervals. The decrease in tensile stress with time and the permanent stretch were measured. The data were analyzed assuming neo-Hookean behavior, for which the relation between tensile (Cauchy) stress $\sigma(t)$ and uniaxial stretch ratio $\alpha$ is

$$\sigma(t) = 2n(t)kT(\alpha^2 - 1),$$

(1)
where $T$ is the absolute temperature, $k$ is the Boltzmann constant and $n(t)$ is the current cross link density. The decrease in $n(t)$ was attributed to scission of molecular network cross links which is reflected in a decrease of crosslink density $n(t)$. The permanent stretch was attributed to a new network that formed in the stretched state (healing). The stress–stretch relation for the system consisting of the two networks was assumed to be

$$\begin{align*}
\sigma(t) &= 2n_1kT\left(\hat{l}^2 \frac{1}{\hat{l}}\right) + 2n_2kT \hat{l}^2 \hat{\ell} \hat{l}^2 - \hat{l}^2 \hat{\ell} \hat{l}^2
\end{align*},$$

where $\hat{l}$ is the stretch ratio of the original network held at the high temperature, $n_1$ is the cross link density of the original network at the end of the test and $n_2$ is the cross link density of the new network. Equation (2) expresses the assumptions that (i) the stresses in the networks can be added, (ii) each network acts as an incompressible isotropic neo-Hookean elastic material and (iii) the new network is formed stress free at the stretch ratio $\hat{l}$ of the original network. Tobolsky’s data suggested that $n_1$ and $n_2$ are independent of the stretch ratio $\hat{l}$ for $\hat{l} < 3$ to 4. This was supported by the results of Scanlan and Watson [3]. It was also assumed (Tobolsky [2] and Tobolsky, Prettyman and Dillon [4]) that all broken cross-links re-formed to produce a new network in a stress free state. In other words, there was conservation of crosslinks, $n_1 + n_2 = n(0)$, which is referred to hereafter as complete healing.

Neubert and Saunders [5] carried out tests similar to those of Tobolsky, but for a pure shear deformation. They measured permanent biaxial stretch upon removal of stress and reduction of the temperature to its original value, and found that predictions based on the assumption of neo-Hookean response led to inaccurate predictions of permanent set. They modified Tobolsky’s assumption (ii) by assuming the rubber could be described as a Mooney-Rivlin material, and showed that this model led to better agreement with measured permanent biaxial stretch. Fong and Zapas [6] later proposed using the Rivlin-Saunders model to determine the permanent biaxial stretch.
Several important results can be deduced from Equation (2). First, there is permanent stretch \( l_R \) on removal of stress and \( 1 < l_R < \hat{l} \). Second, an expression for the response relative to the permanent stretch state (Berry, Scanlan and Watson [7]) can be shown to have the same form as in equation (1) but the modulus has been reduced from that of the original neo-Hookean network \( 2n(0)kT \) and depends on the cross-link densities of the networks and the stretch ratio \( \hat{l} \). Details can be found in the article by Wineman, Jones and Shaw [1].

This simple model shows that permanent set and modified mechanical response are consequences of scission and re-crosslinking. These, in turn, depend on the temperature and time held at that temperature. Although both networks in the model are neo-Hookean, the results of Neubert and Saunders [5] suggest that there will be permanent set and modified mechanical response for other assumed network models. Moreover, the material will exhibit induced anisotropy relative to the permanent set. (Greene, Smith and Ciferri [8]).

These changes in the response of an elastomeric component have important implications for its operational life. A component can fail when its properties have changed to such an extent that it no longer meets the design specifications. Clearly, there is a need for a model that can be used to predict how long a component will meet these specifications, and which can also be used in numerical simulations.

**Experimental Results**

Representative results from our experimental program are presented here. Uniaxial extension experiments were performed on an EnduraTEC ER32 pneumatic tension-torsion machine having a capacity of 2800 lb in tension and 1350 in-lb in torsion. A custom-built thermal chamber enclosed the test section. It has a \( \pm 0.5^\circ \text{C} \) spatial variation of temperature in the range \( 20^\circ \text{C} \leq 150^\circ \text{C} \). Low thermal mass grips were also custom-built. Grip and specimen temperatures were measured using exposed junction K-type thermocouples. Stretch was measured directly from the specimen test section through a window in the thermal chamber using a laser extensometer with a 1 micron resolution (Electric Instrument Research, Irwin, PA). The extensometer produced a
planar laser sheet, avoiding parallax problems through the chamber window. A programmable control system was developed which allowed stretch control, force control or mixed stretch-force control. Data was acquired using Labview software on a Macintosh G3. Uniaxial specimens were 0.5 in. by 2 in. strips cut from commercial grade 0.08 in. thick rubber sheets provided by Tenneco Automotive Corporation.

Uniaxial extension experiments were carried out at a number of fixed stretches and fixed temperatures. Since the tensile force $F(t)$ and Cauchy tensile stress $\sigma(t)$ on a specimen of cross-sectional area $A_o$ are related by $F(t) = \sigma(t)A_o\ell$, it follows that $F(t)/F(0) = \sigma(t)/\sigma(0)$. Figure 2 shows plots of $F(t)/F(0)$ vs. time carried out at a fixed stretch of $\ell = 2$ at various temperatures. The tests were carried out to 10,000 minutes but data for only the first 200 minutes is shown. At 95° C, $F(t)/F(0)$ relaxes to a value of 0.2 after 4500 min and to 0.1 after 9000 min. The time for this relaxation to occur is seen to decrease significantly as the temperature increases. Figure 3 shows plots of $F(t)/F(0)$ vs. time for numerous stretches carried out at 125° C. As can be seen, the relaxation has little dependence on stretch. These results are in agreement with Tobolsky’s conclusion that $F(t)/F(0)$ is independent of the stretch.

Three room temperature stress–stretch plots are shown in Figure 4. The plot labeled ‘virgin material’ shows the response of the rubber before there is any thermally induced degradation. After the initial stress-stretch plot was carried out the specimen was held at $\ell = 1.5$ and $T = 125^\circ$ C for 120 min. The specimen was returned to room temperature, the stress was removed and the stress-stretch plot labeled ‘after 120 min’ was measured. Another specimen was held at $\ell = 1.5$ and $T = 125^\circ$ C for 1558 min, after which it was returned to room temperature, the stress was removed and the stress-stretch plot labeled ‘after 1558 min’ was measured. Figure 4 shows that permanent stretch increases and the material softens with the time held at $T = 125^\circ$ C. This response demonstrates the softening as a result of scission and re-crosslinking.

The development of permanent stretch was also studied by the method of intermittent force release from a specified stretch. A specimen was held at a stretch of $\ell = 1.75$ at $T = 125^\circ$ C for 60 minutes, after which the force was removed. The specimen reached a permanent stretch. This cycle was repeated several times. Figure 5 shows that
the permanent stretch increased with time during scission based force relaxation. Figure 6a shows an experimental temperature history. Figure 6b shows the actual relaxation and the relaxation constructed using the data in Figure 2 by a method described later. This method gives a quite satisfactory approximation to the measured response.

Figure 7a shows both the measured response and that predicted by a constitutive equation presented in the next section to a two step stretch history at \( T = 125^\circ C \). A step stretch of \( \bar{l} = 1.5 \) was initially applied until \( F(t)/F(0) \) reduced to 0.5 and then the stretch was increased to \( \bar{l} = 2 \). The force calculated from the model over predicts the measured force response, possibly due to the assumption that both networks are neo-Hookean. As can be seen in Figure 7b, if the predicted force is reduced by a constant value, the rates of relaxation coincide.

The preceding results were obtained under stretch control conditions. Figure 8 shows results of a creep experiment under force control at constant engineering stress at \( T = 125^\circ C \). As the stress is rapidly increased to \( \bar{\sigma}_E = 58 \) psi, the stretch rises immediately to \( \bar{l} = 1.14 \). The stretch continues to increase to about \( \bar{l} = 1.58 \) after 300 minutes.

**Constitutive Equation**

The experiments of Tobolsky were carried out for uniaxial tests at a fixed stretch and constant temperature and led to Equation (2). The ideas inherent in this equation and the experimental results presented in the previous section are now used as a foundation for a proposed constitutive framework for the three dimensional response of rubber subjected to arbitrary homogeneous deformation and temperature histories. For further discussion of the constitutive equation presented here, see Wineman and Min [9].

Consider a rubbery material in a stress free reference configuration at a temperature \( T_0 \). It is assumed that there is a range of deformations and temperatures in which the material response can be treated as incompressible, isotropic and nonlinearly elastic. If \( \mathbf{x} \) is the position at current time \( t \) of a particle located at \( \mathbf{X} \) in the reference configuration, the deformation gradient is \( \mathbf{F} = \partial \mathbf{x} / \partial \mathbf{X} \). The left Cauchy-Green tensor is defined as \( \mathbf{B} = \mathbf{FF}^T \). The Cauchy stress \( \bar{\sigma} \) is given by
\[ \square = \p^{(1)} \mathbf{I} + \square^{(1)}(\mathbf{B}, T) = \p^{(1)} \mathbf{I} + 2 \frac{\partial W^{(1)}}{\partial I_1} \mathbf{B} \square 2 \frac{\partial W^{(1)}}{\partial I_2} \mathbf{B} \square, \]

where \( \p^{(1)} \), an arbitrary hydrostatic pressure, arises from the constraint that deformations are isochoric, \( I_1, I_2 \) are invariants of \( \mathbf{B} \) and \( W^{(1)}(I_1, I_2, T) \) is the strain energy density associated with the original material. In Equation (3), \( \square, \mathbf{B}, T \) depend on the current time \( t \), which is omitted from the notation for brevity.

The experimental work of Tobolsky as well as that presented in the previous section suggests the onset of scission corresponds to a temperature \( T_{cr} \) called the chemorheological temperature. For temperatures \( T < T_{cr} \), no scission occurs. All of the material is in its original state and the total stress is given by Equation (3). For temperatures \( T > T_{cr} \), scission of the original microstructural network occurs continuously in time. Let \( b^{(1)} \) denote the volume fraction of the original network remaining at time \( t \). \( b^{(1)} \) can depend on deformation, temperature history and time. This dependence is denoted by \( b^{(1)} = b^{(1)}[\mathbf{B}, T(s)]_{s=0}^{t} \), where the notation \( T(s)|_{s=0}^{t} \) indicates dependence on all values of temperature from time \( s = 0 \) to time \( s = t \). \( b^{(1)} = 1 \) at \( t = 0 \) and \( b^{(1)} \) monotonically decreases with \( t \). Tobolsky’s experiments indicated that \( b^{(1)} \) does not depend on the stretch provided that it is less than 3 to 4. This was supported by the results of Scanlan and Watson [3] and the results shown in Figure 3. For the sake of simplicity it is assumed that \( b^{(1)} \) does not depend on the deformation, i.e. \( b^{(1)} = b^{(1)}[T(s)|_{0}^{t}]. \)

Now consider an intermediate time \( \hat{t} \) \( [0,t] \) and the corresponding deformed configuration of the original material. Due to the formation of new crosslinks, a network is formed in the interval from \( \hat{t} \) to \( \hat{t} + d\hat{t} \) whose reference configuration is the configuration of the original material at time \( \hat{t} \). As suggested by Tobolsky [2] and Tobolsky. Prettyman and Dillon [4], (assumption (iii) of the Experimental Background section), this is assumed to be an unstressed configuration for the newly formed network. Under subsequent deformation, the motion of the newly formed network coincides with
the motion of the original network. Stress arises in this newly formed network due to its deformation relative to its unstressed configuration at time $\hat{t}$. At the later time $t$, the material formed at earlier time $\hat{t}$ has the relative deformation gradient $\hat{F} = \partial x / \partial \hat{x}$, where $\hat{x}$ is the position of the particle in the configuration corresponding to time $\hat{t}$ and $x$ is its position at time $t$.

For simplicity in presentation, the new network is assumed to respond as an incompressible isotropic nonlinear elastic material with temperature dependence. The left Cauchy-Green tensor $\hat{B} = \hat{F} \hat{F}^T$ is introduced for deformations of this network. The Cauchy stress $\sigma^{(2)}(t)$ at time $t$ in the network formed at time $\hat{t}$ is then given by

$$\sigma^{(2)} = \sigma^{(2)}(p) + \sigma^{(2)}(B, T) = \sigma^{(2)}(p) + 2 \frac{\partial W^{(2)}(\hat{B})}{\partial I_1} \hat{B} \left( \frac{\partial W^{(2)}(\hat{B})}{\partial I_2} \right) \hat{B}^T I,$$

where $\sigma^{(2)}(p)$ arises from the constraint that deformations are isochoric and $I_1, I_2$ are invariants of $\hat{B}$. $W^{(2)}(I_1, I_2, T)$ is the strain energy density associated with the newly formed network and can differ from that associated with the original network.

Let $a(\hat{t})$ be a scalar-valued function that gives the rate at which volume fraction of new network is formed at time $\hat{t}$. Thus, $a(\hat{t}) > 0$ and $a(\hat{t}) d\hat{t}$ is interpreted as the volume fraction of original material that has reformed during the time interval from $\hat{t}$ to $\hat{t} + d\hat{t}$. Since this new network is at a temperature $T > T_{cr}$, it is assumed that it also undergoes scission. Let $b^{(2)}(t, \hat{t})$ denote the volume fraction of the network formed at time $\hat{t}$ that is remaining at time $t$. The properties of $b^{(2)}$ are similar to those of $b^{(1)}$. $b^{(2)}(\hat{t}, \hat{t}) = 1$ and $b^{(2)}(t, \hat{t})$ monotonically decreases with $t$ for fixed $\hat{t}$. It is assumed that $b^{(2)}(t, \hat{t})$ is independent of the deformation of the new network and depends on the temperature history from the time it forms, i.e. $b^{(2)} = b^{(2)}(s) \mathbb{I}_{\hat{t}, t}$. The volume fraction of crosslinks at time $t$ in the network that was formed at time $\hat{t}$ is $a(\hat{t}) b^{(2)}(t, \hat{t}) d\hat{t}$. 
a(\hat{t}), b^{(1)}(t), b^{(2)}(t,\hat{t}) describe the kinetics of scission and re-crosslinking and hence are material properties of a particular rubber. They are continuous functions of time and vary according to the following conditions:

\[ t = 0 \quad \text{In the reference configuration at temperature } T_o < T_{cr}, \]
\[ b^{(1)} = 1, \quad a = 0, \]
\[ t > 0 \quad \text{When } T < T_{cr}, \]
\[ \frac{db^{(1)}}{dt} = 0, \quad a = 0, \quad \frac{db^{(2)}}{dt} = 0 \]  \hspace{1cm} (5)
\[ t > 0 \quad \text{When } T > T_{cr}, \]
\[ \frac{db^{(1)}}{dt} < 0, \quad a > 0, \quad \frac{db^{(2)}}{dt} < 0 \]

The total current stress in the material is taken as the superposition of the contribution from the remaining original network and stress in the new networks (assumption (i) of Section 2). Thus,

\[ \mathbf{\sigma} = \mathbf{pI} + 2b^{(1)} \mathbf{B} \frac{\partial W^{(1)}}{\partial I_1} \mathbf{B} \mathbf{I} + 2a(\hat{t})b^{(2)}(t,\hat{t}) \mathbf{B} \frac{\partial W^{(2)}}{\partial I_1} \mathbf{B} \mathbf{I} \hat{\mathbf{t}} \]  \hspace{1cm} (6)

where \( b^{(1)}, \mathbf{B}, T, \mathbf{\sigma} \) are evaluated at the current time \( t \). This generalizes Tobolsky’s assumption (i). Since \( \mathbf{\hat{B}} = \mathbf{I} \) in an undeformed newly formed network, it follows from Equation (4) that its stress has the form \( q\mathbf{I} \). This can be absorbed into the term \( \mathbf{pI} \) in Equation (6), which represents a superposed hydrostatic stress. The undeformed new network does not contribute to the stress and can be interpreted as stress free. This generalizes Tobolsky’s assumption (iii). Although Tobolsky assumed the response of the original and newly formed networks to be neo-Hookean, Neubert and Saunders [5] and Fong and Zapas [6] considered other possibilities. Thus, \( W^{(1)}(I_1, I_2, T) \) and \( W^{(2)}(\mathbf{\hat{I}}_1, \mathbf{\hat{I}}_2, T) \) are unspecified. This generalizes Tobolsky’s assumption (ii).

It is assumed that the rate of formation of new networks is related to the rate of scission of the original network by,
\[
a(t) = \frac{\text{db}(t)}{dt},
\]

(7)

where \( [0,1] \) is a scalar parameter that depends on the particular system being considered. Tobolsky’s assumption of network conservation corresponds to complete healing or \( h = 1 \). Complete scission, by contrast, occurs with no new network formation and can be modeled with \( h = 0 \). Available experimental work does not address whether a time lag exists between scission and cross-linking. Accordingly, in the absence of experimental data on this point, any time lag between scission and cross-linking is neglected.

It is useful to illustrate the forms taken by Equation (6) for some simple deformations. The relation between tensile stress \( \square \) and axial stretch \( \hat{\square} \) for uniaxial extension is

\[
\begin{align*}
\square &= 2b^{(1)} \left[ T(s) \right]_{t}^{\hat{t}} \left[ \frac{1}{\hat{I}_1} \frac{\partial W^{(1)}}{\partial I_1} + \frac{1}{\hat{I}_2} \frac{\partial W^{(1)}}{\partial I_2} \right] \\
&
+ 2 \left[ a(\hat{t})b^{(2)} \right] \left[ T(s) \right]_{t}^{\hat{t}} \left[ \frac{1}{(\hat{t})^2} \frac{\partial W^{(2)}}{\partial \hat{I}_1} \frac{\partial I^2}{\partial \hat{I}_1} + \frac{1}{(\hat{t})^2} \frac{\partial W^{(2)}}{\partial \hat{I}_2} \frac{\partial I^2}{\partial \hat{I}_2} \right] \hat{t}
\end{align*}
\]

(8)

where

\[
\begin{align*}
I_1 &= \square^2 + 2/\square \\
I_2 &= 2\square + \hat{\square}^2
\end{align*}
\]

(9)

\[
\begin{align*}
\hat{I}_1 &= \square^2/(\hat{t})^2 + 2\hat{\square}/(\hat{t}) \\
\hat{I}_2 &= 2\square/(\hat{t}) + \hat{\square}^2/\hat{t}^2
\end{align*}
\]

The relation between shear stress \( \| \parallel \) and shear \( \| \| \) for simple shear is

\[
\| = 2b^{(1)} \left[ T(s) \right]_{0}^{t} \left[ \frac{\partial W^{(1)}}{\partial I_1} + \frac{\partial W^{(1)}}{\partial I_2} \right]
\]
\[ +2 \int_0^t a(\hat{t}) b^{(2)}(\hat{t}) \left[ W^{(2)} \right] \left| \begin{array}{c} \frac{\partial W^{(2)}}{\partial I_1} \end{array} \right|_{t=\hat{t}} + \left[ \frac{\partial W^{(2)}}{\partial I_2} \right] \left| \frac{\partial W^{(2)}}{\partial (\hat{t})} \right| \, d\hat{t} \, , \]  

in which

\[ I_1 = I_2 = 3 + \Box(t)^2 \, , \quad \hat{I}_1 = \hat{I}_2 = 3 + \Box(t)^2 \, . \]  

**Form for** \( b(t) \)

Now consider the form of \( b^{(l)} \). Let the temperature vary so that \( T(s) > T_{cr} \), \( 0 < s < t \), but let the deformation be fixed. For uniaxial extension with constant stretch ratio \( \Box \), (6) reduces to

\[ \Box(t) = 2b^{(l)} \left[ T(s) \right]_{0}^{t} \left[ 2 \left( \frac{1}{I_1} \right) \frac{\partial W^{(l)}}{\partial I_1} + \left( \frac{1}{I_2} \right) \frac{\partial W^{(l)}}{\partial I_2} \right] . \]  

Since \( b^{(l)} = 1 \) at \( t = 0 \) and is independent of the deformation, so is the ratio

\[ \frac{\Box(t)}{\Box(0)} = b^{(l)} \left[ T(s) \right]_{0}^{t} . \]  

When scission occurs at a constant temperature \( T \), i.e. \( T(s) = T > T_{cr} \), \( 0 < s < t \) let the right hand side of (13) be denoted by \( \Box(T,t) \). Then (13) is written as

\[ \frac{\Box(t)}{\Box(0)} = \Box(T,t) . \]  

\( \Box(T,t) \) is a material property that can be obtained experimentally, (see Tobolsky [2], Figure V.4, and Figure 2 of this paper).

\( b^{(l)} \left[ T(s) \right]_{0}^{t} \) can be determined from \( \Box(T,t) \) by the following construction:

Consider the time interval from \( t_i \) to \( t_i + \Box \) and let \( b^{(l)}(t_i) = b^{(l)} \left[ T(s) \right]_{0}^{t_i,t_i} \) denote the value of \( b^{(l)} \) at the beginning of the interval. Then
(a) Let the decrease of $b^{(1)}$ depend on the average temperature $\tilde{T}_i$ during this interval.

(b) If $\tilde{T}_i > T_{cr}$, let $b^{(1)}$ be given by $[\bar{T}_{i-1}, t_{i-1}^* + t_i^*]$, where $t_i^*$ is such that $\bar{T}_{i-1, t_i^*} = b^{(1)}(t_i)$.

(c) If $\tilde{T}_i < T_{cr}$, let $b^{(1)} = b^{(1)}(t_i)$, i.e. $b^{(1)}$ does not decrease.

Suppose $T(s) < T_{cr}$, $0 \leq s < t_1$ and $T(s) > T_{cr}$, $t_1 \leq s < t$. According to (c), $b^{(1)}$ is independent of the temperatures during $0 \leq s < t_1$ and depends only on the temperatures during $t_1 \leq s < t$. One can then write $b^{(1)}[T(s)_{t_1}^{t}, t]$. Figure 9a shows a multi-step temperature history and Figure 9b illustrates the construction using data from Figure 2.

Tobolsky ([2], p. 226) suggested for a number of rubbers that $\Box(T,t)$ can be represented in the form

$$\Box(T,t) = \Box(t/t_0(T)),$$  \hspace{1cm} (15)

For example, for a particular rubber vulcanizate, Tobolsky showed that

$$\Box(T,t) = \exp\left(\frac{t}{t_0(T)}\right),$$  \hspace{1cm} (16)

where

$$\frac{1}{t_0(T)} = \frac{k}{h} \exp\left(\frac{E_{act}}{RT}\right).$$  \hspace{1cm} (17)

In (17) $k$ is Boltzmann’s constant $(1.38066 \times 10^{-23} \text{ J/K})$, $h$ is Planck’s constant $(6.62608 \times 10^{-34} \text{ J s})$, $R$ is the gas constant $(8.314510 \text{ J/mol K})$ and $E_{act}$ is an activation energy whose value was found to be 30.4 kcal/mol. $t_0(T)$ represents a characteristic time for stress relaxation due to scission at temperature $T$. The
characteristic time is about 24 hrs at 100° C and decreases by an order of magnitude to 2.7 hrs at 120° C.

Wineman and Min [9] have used the procedure described above to show that when \( b(T,t) \) has the form in (15),

\[
 b^{(1)} \left[ T(s) \right]_0^t = \Box(t),
\]

(18)

where

\[
 \Box(t) = \int_0^t ds \frac{1}{\Delta_0(T(s))}.
\]

(19)

When the temperature is constant, Equations (14) and (15) reduce to (12).

**Example of Application**

The constitutive equation described above was used by Wineman and Min [9] to study a long hollow cylinder of an elastomeric material in which there is both circular shear and spatially varying scission and re-crosslinking. The cylinder is bonded to a fixed support at its inner radius \( R_i \) and a time dependent moment is applied to its outer surface of radius \( R_o \) about the centerline. This causes the cylinder to rotate about the fixed support. The outer surface is maintained at a constant temperature below the chemorheological temperature \( T_{cr} \) and the inner surface is heated to a temperature above \( T_{cr} \). Attention is restricted to the central portion of the cylinder so that end effects can be neglected.

The deformation and temperature distributions are axially symmetric. Each material element undergoes local simple shearing. The shear stress can be shown to vary inversely with the square of the radius. Each material element experiences a time varying temperature which also varies with radius. The shear stress and the scission and re-crosslinking process result in a shear that varies with radius and time.

The shear response of the material is described by Equation (10). The scission property \( b(T,t) \) is described in Equations (15)–(17) resulting in \( b^{(1)} \) being given by
Equations (18) and (19). \( b^{(2)}(t, \hat{t}) = 1 \). The thermal diffusivity \( \chi \) of the elastomer is assumed to be independent of the deformation, the temperature and scission and re-crosslinking. The original and newly formed networks are assumed to have neo-Hookean response so that in Equation (10),

\[
\frac{\partial W^{(1)}}{\partial I_1} + \frac{\partial W^{(1)}}{\partial I_2} = \frac{\partial W^{(2)}}{\partial \hat{I}_1} + \frac{\partial W^{(2)}}{\partial \hat{I}_2} = n_o kT, \tag{20}
\]

where \( n_o \) is the original crosslink density and \( k \) is Boltzmann’s constant.

Numerical results were obtained for the following data: (1) \( R_o/R_i = 2 \), (2) thermal diffusion time \( \sqrt{T} = R_i^2/\chi = 0.5 \) hours, (3) temperature at the outer radius is constant at \( T_o = 90^0C \), (4) temperature at the inner radius \( T_i \) increases at a constant rate from \( 90^0C \) to \( 110^0C \) over \( \sqrt{T}/4 \) hours, is held at \( 110^0C \) for \( \sqrt{T}/2 \) hours and is then returned at a constant rate to \( 90^0C \) over \( \sqrt{T}/4 \) hours, (5) a dimensionless moment \( M_o/(R_i^2 n_o kT_o) \) is applied at time \( t = 0 \), held constant at a value of 30 and then removed at \( 1.5 \sqrt{T} \).

Figure 10 shows the temperature histories at several radii. Note that the temperature at each radius has nearly returned to the initial value \( T_o = 90^0C \) by \( 1.5 \sqrt{T} \), when the moment is removed. Each material element experiences a different temperature above \( T_{cr} \) and hence a different scission history. This effect is seen in Figure 11, which shows the decrease in volume fraction \( b^{(l)} \) with time at different radii. The fastest decrease is at the inner boundary \( R_i/R_i = 1 \) where the temperature reaches the largest value. The decrease becomes very slow for \( \sqrt{T} \) when the inner boundary has returned to \( T_o = 90^0C \).

Figure 12 shows shear histories at various radii. Two histories are shown at each radius. The lower solid curve corresponds to a neo-Hookean material that is not undergoing scission. The upper curve corresponds to the scission model. Note that the curves for a given radius decrease as temperature increases. This is a consequence of the stiffening due to the increase of shear modulus with temperature in Equation (20). In the
scission model, this stiffening is offset by softening due to scission, and the shear is seen to again increase. These calculations were performed assuming no scission of the new network. If scission of the new networks were to occur, the softening would be enhanced and the shear would increase. For $1.5 \cdot t$, when the moment has been removed, the shear returns to zero in the neo-Hookean material since it has not undergone scission. On the other hand, the material that has undergone scission exhibits a residual shear distribution.

**Closing Comments**

The experimental results on a typical commercially available natural vulcanized rubber presented herein show substantial stress relaxation at elevated temperatures, material softening, permanent set, and creep due to microstructural changes. Each can occur in a rubber tire when the temperature becomes sufficiently high. The numerical example demonstrates that microstructural changes can localize within a region of an elastomeric structure, i.e. a tire. These effects contribute to a time dependent change in response characteristics that affect the performance and durability of the tire over time. Thus, it is important to develop a thermo-mechanical theory that accounts for these effects and can be used to simulate the operating conditions and thereby calculate a tire’s effective lifetime. The first steps in the development of such a model have been presented.

**Acknowledgements**

The financial support of the National Science Foundation (NSF grant CTS-9908925) is acknowledged with thanks. The interaction and materials supplied by Tenneco Automotive Corp. are also greatly appreciated.

**References**


Figure Captions

Figure 1. Temperature contours after 2.5 min in a bushing subjected to 10 Hz vertical displacement of the post.

Figure 2. F(t)/F(0) relaxation for various temperatures at $\ell = 2$.

Figure 3. F(t)/F(0) relaxation for various stretches at $T = 125^\circ C$.

Figure 4. Stress-stretch plots at room temperature for virgin material and for two samples subsequently held at $T = 125^\circ C$ and $\ell = 1.58$.

Figure 5. Increase of permanent stretch with scission at $T = 125^\circ C$.

Figure 6a. An experimental temperature history.

Figure 6b. Measured force relaxation and relaxation determined assuming that scission depends on the instantaneous temperature.

Figure 7a. Force response to a two step stretch history.

Figure 7b. Comparison of measured and predicted force relaxation during the second step.

Figure 8. Creep under constant engineering stress at $T = 125^\circ C$.

Figure 9a. A multi-step temperature history.

Figure 9b. Graphical construction of $b^{(1)}$ using the data in Figure 2.

Figure 10. Variation of temperature with time for several radii.

Figure 11. Variation of volume fraction $b^{(1)}$ with time for several radii.

Figure 12. Variation of local shear with time for several radii.
Figure 1. Temperature contours after 2.5 min in a bushing subjected to 10 Hz vertical displacement of the post.

Figure 2. $F(t)/F(0)$ relaxation for various temperatures at $\ell = 2$. 
Figure 3. $F(t)/F(0)$ relaxation for various stretches at $T = 125^\circ$C.

Figure 4. Stress-stretch plots at room temperature for virgin material and for two samples subsequently held at $T = 125^\circ$C and $\lambda = 1.58$. 
Figure 5. Increase of permanent stretch with scission at $T = 125^\circ C$
Figure 6a. An experimental temperature history.

Figure 6b. Measured force relaxation and relaxation determined assuming that scission depends on the instantaneous temperature.
Figure 7a. Force response to a two step stretch history

Figure 7b. Comparison of measured and predicted force relaxation during the second step.
Figure 8. Creep under constant engineering stress at $T = 125^\circ$ C.
Figure 9a. A multi-step temperature history

Figure 9b. Graphical construction of $b^{(1)}$ using the data in Figure 2
Figure 10. Variation of temperature with time for several radii.

Figure 11. Variation of volume fraction $b^{(i)}$ with time for several radii.
Figure 12. Variation of local shear with time for several radii.