Scission and Healing in a Spinning Elastomeric Cylinder at Elevated Temperature

When an elastomeric material is subject to sufficiently high temperature, macromolecular network junctions can undergo time-dependent scission and re-cross-linking (healing). The material system then consists of molecular networks with different reference states. A constitutive framework, based on the experimental work of Tobolsky, is used to determine the evolution of deformation of a solid rubber cylinder spinning at constant angular velocity at an elevated temperature. Responses based on underlying neo-Hookean, Mooney-Rivlin, and Arruda-Boyce models, were solved numerically and compared. Different amounts of healing were studied for each case. For neo-Hookean molecular networks, there may be a critical finite time when the radius grows infinitely fast and the cylinder "blows up." This time depends on the angular velocity and the rate of re-cross-linking. In addition, no solution was possible for angular velocities above a critical value, even without the effects of scission. Such anomalous behavior does not occur for Mooney-Rivlin or Arruda-Boyce network response. [DOI: 10.1115/1.1485757]

1 Introduction

The general form of the constitutive equation for nonlinear thermoelasticity used to represent the response of elastomeric material is expressed in terms of a temperature-dependent strain energy density function. Implicit in the formulation is the usual assumption that material response is due to a macromolecular mechanism that does not change during the thermomechanical process being considered. Tobolsky [1] presented experimental results, however, indicating that when the temperature becomes high enough a change can occur in the macromolecular network. This mechanism consists of scission and subsequent re-cross-linking of macromolecular network junctions. The process is time-dependent and can result in substantial changes in mechanical response and permanent set upon removal of applied loads.

Tobolsky’s results show that the nonlinear theory of thermoelasticity applies provided the temperature is maintained below a critical value. When this temperature is exceeded, scission and re-cross-linking of network junctions (referred to hereafter as ‘healing’) occur which requires the development of a new constitutive theory. In previous work, Wineman and Rajagopal [2] and Rajagopal and Wineman [3] developed a constitutive framework which applies when deformations are large enough to cause scission. By contrast, the present work uses this framework to express a constitutive theory that addresses temperature-induced scission and healing.

The problem of a rotating rubber cylinder has attracted the interest of a number of authors (see Horgan and Saccomandi [4] and Chadwick et al. [5]). A spinning rubber cylinder represents a very simple model of an automobile or aircraft tire, recognizing that the actual case likely involves nonuniform temperature fields which we will neglect here. Nevertheless, under certain operating conditions, these tires can experience a substantial increase in temperature. With recent events involving the failure of automobiles and aircraft tires, it is natural to study the problem of a spinning rubber cylinder using a constitutive theory which allows for scission and healing at increased temperatures.

Section 2 begins with a presentation of the constitutive theory for the response of rubber that undergoes temperature-induced scission and re-cross-linking. The problem of a rotating rubber cylinder is defined in Section 3, which reduces to an equation for the axial stretch ratio. The general constitutive framework of Section 2 allows the user to choose a specific underlying thermoelastic model. Responses based on neo-Hookean, Mooney-Rivlin, and Arruda-Boyce models, in turn, are studied for the spinning cylinder problem in Section 4. Results are illustrated with numerical examples, and comparisons are made for the different models.

2 Constitutive Framework

In the experiments conducted by Tobolsky [1], 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 range, the stress was observed to decrease with time. At the end of the time interval, the stress was removed and the specimen was returned to its original temperature. Tests were carried out for different 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 $\lambda$ is

$$\sigma(t) = 2n(t)kT\left(\lambda^2 - \frac{1}{\lambda}\right)$$

(1)

where $T$ is the absolute temperature, $k$ is the Boltzmann constant, and $n(t)$ is the current cross-link density. It was concluded that the decrease in $\sigma(t)$ was due to scission of molecular network cross links, resulting in a decrease in $n(t)$. The permanent stretch was due to a new network which formed in the stretched state (healing). The stress-stretch relation for the system back at the original low temperature consisting of the two networks was assumed to be

$$\sigma(t) = 2n_1kT\left(\frac{\lambda^2 - 1}{\lambda}\right) + 2n_2kT\left(\frac{\lambda}{\lambda} - \frac{1}{\lambda}\right)$$

(2)
where $\lambda$ 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. The second term in (2) expresses the assumption that the new network is formed stress free when the stretch ratio in the original network is $\lambda$. Tobolsky’s data also suggested that $n_1$ and $n_2$ are independent of the stretch ratio $\lambda$ up to a stretch ratio of about 4. It was also assumed (Tobolsky [1], and Tobolsky et al. [6]) that all broken molecular cross links reform to produce a new network in a stress free state. That is, there is conservation of cross links, $n_1 = n(0)$, which we hereafter refer to as complete healing. The validity of this assumption depends on the particular chemistry of the rubber being considered.

Neubert and Saunders [7] carried out tests similar to those of Tobolsky, but for a pure shear deformation. They measured permanent biaxial stretch after removal of stress and reduction of the temperature, and found that predictions based on a neo-Hookean model led to inaccurate predictions of permanent set. A Mooney-Rivlin material model led to better agreement with measured permanent biaxial stretch. Fong and Zapas [8] improved the agreement by using the Rivlin-Saunders model (9).

Using the uniaxial relations (1) and (2) as a guide, a three-dimensional constitutive framework is developed as follows. Consider a rubbery material in a stress free reference configuration at a low temperature $T_0$. It is assumed that there is a range of deformations and temperatures in which the material response is essentially 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 defined as $\mathbf{F} = \nabla \mathbf{x} / \nabla \mathbf{X}$. The left Cauchy-Green tensor is $\mathbf{B} = \mathbf{F} \mathbf{F}^T$. The Cauchy stress $\sigma$ is given by

$$\sigma = -p^0 \mathbf{I} + \sigma^0(\mathbf{B}, T) = -p^0 \mathbf{I} + 2W_0^0 \mathbf{B} - 2W_2^0 \mathbf{B}^{-1}$$

(3)

where $p^0$ arises from the constraint that deformations are isochoric, $I_1, I_2$ are invariants of $\mathbf{B}$ and $W_0^0 = \partial W_0 / \partial I_1$ and $W_2^0 = \partial W_2 / \partial I_2$ are partial derivatives of the strain energy density $W_0(I_1, I_2, T)$ associated with the original material.

For low temperatures, $T < T_{cr}$, no scission occurs. All of the material has its original reference state and the total stress is given by (3). At time $t=0$ the temperature is increased to a high temperature, $T \geq T_{cr}$, and scission of the original microstructural network is assumed to occur continuously in time. A scalar-valued function $a(t) \geq 0$ is introduced, which represents the rate at which volume fraction of new network is formed at time $t$. Thus, $a(t) dt$ is interpreted as the volume fraction of new material that has formed during the time interval from $t$ to $t + dt$. The volume fraction of original network remaining at time $t$ is denoted as $b(t)$. $b(t) \in [0,1]$ and is a monotonically decreasing function of $t$. For the sake of simplicity and consistent with Tobolsky’s observations, it is assumed that $a(t)$ and $b(t)$ do not depend on the deformation. He showed for experiments under uniaxial extension that this is reasonable provided the stretch remains less than 3 to 4. In addition, it is assumed that the rate of formation of new networks is given by

$$a(t) = -\eta \frac{db(t)}{dt},$$

(4)

where $\eta \in [0,1]$ is a scalar parameter that depends on the particular rubber system being considered. Tobolsky’s assumption of network conservation corresponds to complete healing, or $\eta = 1$. Complete scission, by contrast, occurs with no new network formation and can be modeled with $\eta = 0$. The work of Tobolsky does not address whether a time lag exists between scission and re-cross-linking. Accordingly, in the absence of experimental data on this point, Eq. (4) neglects any time lag between scission and healing.

Now consider an intermediate time $\hat{t} \in [0,t]$ and the corresponding deformed configuration of the original material. Due to the formation of new cross links, a network is formed in the interval from $t$ to $\hat{t} + d\hat{t}$ whose reference configuration is the current configuration at time $\hat{t}$. As suggested by Tobolsky [1] and Tobolsky et al. [6], this is assumed to be an unstrained configuration for the newly formed network. Under subsequent deformation, the motion of the newly formed material network coincides with the motion of the original material network. Stress arises in this newly formed material network due to its deformation relative to its unstrained configuration at time $\hat{t}$. At the later time $t$, the material formed at earlier time $\hat{t}$ has the relative deformation gradient $\mathbf{F} = \nabla \mathbf{x} / \nabla \mathbf{x}$, where $\mathbf{x}$ is the position of the particle in the configuration corresponding to time $\hat{t}$ and $s$ is its position at time $t$.

For simplicity, the new material network is also assumed to respond as an incompressible, isotropic, nonlinear elastic material. The left Cauchy-Green tensor $\mathbf{B} = \mathbf{F} \mathbf{F}^T$ is introduced for relative deformations of this network. The constitutive equation for the network formed at time $\hat{t}$ is then given by

$$\bar{\sigma} = -\rho \mathbf{I} + \dot{\sigma}(\mathbf{B}, T) = -\rho \mathbf{I} + 2 \bar{W}_0 \mathbf{B} - 2 \bar{W}_2 \mathbf{B}^{-1}$$

(5)

where $\rho$ arises from the constraint that deformations are isochoric, $I_1, I_2$ are invariants of $\mathbf{B}$, and $W_0 = \partial W_0 / \partial I_1$ and $W_2 = \partial W_2 / \partial I_2$ are partial derivatives of energy density of the new network, $\bar{W}(I_1, I_2, T)$. In general, the energy density associated with the newly formed material can differ from that associated with the original material.

The total current stress in the material is taken as the superposition of the stress in the remaining material of the original network and the stress in new networks. Thus,

$$\sigma = -p \mathbf{I} + b\sigma^0(\mathbf{B}, T) + \int_0^t a(\hat{t}) \dot{\sigma}(\mathbf{B}, T) d\hat{t}$$

(6)

where $p, b, \mathbf{B}, T, \sigma$ are evaluated at the current time $t$. The term $-p \mathbf{I}$ incorporates the corresponding terms in (3) and (5). The stress in the original network, $\sigma^0(\mathbf{B}, T)$, is expressed in terms of $W_0(I_1, I_2, T)$ by (3), and the stress developed in any new network, $\dot{\sigma}(\mathbf{B}, T)$, is expressed in terms of $\bar{W}(I_1, I_2, T)$ by (5).

Although Tobolsky assumed the response of the original and newly formed networks to be neo-Hookean, Neubert and Sanders [7] and Fong and Zapas [8] considered other possibilities. Thus, $W_0(I_1, I_2, T)$ and $\bar{W}(I_1, I_2, T)$ are left as yet, unspecified.

3 Boundary Value Problem Formulation

The boundary value problem consists of a solid cylinder of radius $R_0$, length $L_0$ in its undeformed configuration, and uniform mass density $\rho$, which is spinning about its central axis with a constant angular velocity $\omega$ (see Fig. 1). The temperature of the cylinder is changed at $t=0$ to a constant, uniform high temperature, $T > T_{cr}$, so that the material undergoes the scission-healing process. This chemically based relaxation process and the centrifugal loading cause the dimensions of the cylinder to change.

![Fig. 1 Reference and current configuration for spinning cylinder](Image)
with time. The cylindrical coordinates of a point in the reference and current configurations, are denoted by \((R, \Theta, Z)\) and \((r, \theta, z)\), respectively. It is assumed that plane sections remain plane and cylindrical surfaces deform into cylindrical surfaces, resulting in a deformation described by

\[
\begin{align*}
    r &= r(R,t), \quad R \in [0,R_0], \\
    \theta &= \Theta + \omega t, \quad \Theta \in [0,2\pi), \\
    z &= \lambda(t) Z, \quad Z \in [0,L_0].
\end{align*}
\]  

(7)

The relation between the coordinates \((r, \theta, z)\) of a particle in the configuration at time \(t\) and its coordinates \((R, \Theta, Z)\) in the current configuration is found by eliminating \((R, \Theta, Z)\) in (7), (8), (11), giving

\[
\begin{align*}
    \hat{r} &= r(R,\hat{t}) = \frac{R}{\sqrt[3]{\lambda(t)}}, \quad R \in [0,R_0] \\
    \hat{\theta} &= \Theta + \omega(\hat{t})t, \quad \Theta \in [0,2\pi) \\
    \hat{z} &= \lambda(\hat{t})Z, \quad Z \in [0,L_0].
\end{align*}
\]  

(11)

The physical components of the deformation gradient of the original network with respect to cylindrical coordinates are given by

\[
F(R,t) = \begin{bmatrix}
\frac{\partial r}{\partial R} & 0 & 0 \\
0 & \frac{r(R,t)}{R} & 0 \\
0 & 0 & \frac{1}{\sqrt[3]{\lambda(t)}} \\
\end{bmatrix}
= \begin{bmatrix}
1 & 0 & 0 \\
0 & \frac{1}{\sqrt[3]{\lambda(t)}} & 0 \\
0 & 0 & \lambda(t) \\
\end{bmatrix}.
\]  

(10)

The reference configuration of any new formed network at time \(\hat{t}\) is the configuration of the original network at time \(t\), and is defined by

\[
\hat{r} = r(R,\hat{t}) = \frac{R}{\sqrt[3]{\lambda(\hat{t})}}, \quad R \in [0,R_0] \\
\hat{\theta} = \Theta + \omega(\hat{t})t, \quad \Theta \in [0,2\pi) \\
\hat{z} = \lambda(\hat{t})Z, \quad Z \in [0,L_0].
\]  

(12)

The stress components are found by calculating \(\mathbf{B}(t)\) from (10) and \(\mathbf{B}(\hat{t})\) from (13) and substituting into the constitutive Eq. (6). Since \(\mathbf{B}(t)\) and \(\mathbf{B}(\hat{t})\) are diagonal matrices, no shear stresses exist and the normal stresses can be written in the form

\[
\begin{align*}
    \sigma_{rr} &= -p + F_{rr}, \\
    \sigma_{zz} &= -p + F_{zz}.
\end{align*}
\]  

(14)

In the subsequent analysis, only the expression for the difference \(F_{rr} - F_{zz}\) appears, which can be written

\[
F_{zz} - F_{rr} = b(T,t) \left(\frac{\lambda(t)}{\lambda(\hat{t})}\right)^2 \left(2W_1^0 + \frac{1}{\lambda(t)} - 2W_2^0\right) + \int_0^\hat{t} a(T,\hat{t}) \left(\frac{\lambda(t)}{\lambda(\hat{t})} - \frac{\lambda(\hat{t})}{\lambda(t)}\right) 2W_1^0 + \left(\frac{\lambda(t)}{\lambda(\hat{t})}\right)^2 2W_2^0 d\hat{t}.
\]  

(15)

The scission-healing process is assumed to occur sufficiently slowly that inertia terms involving \(\partial^2 r/\partial t^2\) and \(\partial^2 z/\partial t^2\) can be neglected. Hence, in the expressions for the acceleration, these terms are neglected and only the centripetal term is considered. The axial and circumferential components of the equations of motion reduce to

\[
\frac{\partial \dot{r}}{\partial \theta} = \frac{\partial \dot{r}}{\partial z} = 0,
\]  

(16)

and the radial component becomes

\[
\frac{\partial \sigma_{rr}}{\partial r} = -\rho \omega^2 r, \quad r \in [0,r_0(t)],
\]  

(17)

where use has been made of (14). Integrating (17) gives

\[
\sigma_{rr}(r_0(t),t) - \sigma_{rr}(r,t) = -\frac{\rho \omega^2}{2} [r_0(t)^2 - r^2].
\]  

(18)

The outer surface is traction-free at each time, so (17) reduces to

\[
\sigma_{rr}(r,t) = -\frac{\rho \omega^2}{2} [r_0(t)^2 - r^2].
\]  

(19)

Combining (19) and (14) gives an expression for the scalar field \(p\),

\[
-p = \frac{\rho \omega^2}{2} [r_0(t)^2 - r^2] - F_{rr}.
\]  

(20)

Substituting into (14) determines the axial normal stress,
\[
\sigma_{zz} = \frac{\rho \omega^2}{2} \left[r_0(t)^2 - r^2\right] + F_{zz} - F_{tr}.
\]  
(21)

Assuming that there is no resultant force on the ends of the cylinder leads to a boundary condition satisfied in the weak sense as

\[
2 \pi \int_0^{r_0(t)} \sigma_{zz} \, r \, dr = 0.
\]  
(22)

Integrating the axial stress (21), then leads to the equation

\[
F_{zz} - F_{tr} = -\frac{\rho \omega^2}{4} r_0(t)^2.
\]  
(23)

In view of (8), (23) reduces to

\[
\lambda(t)[F_{zz} - F_{tr}] = -\frac{\rho \omega^2}{4} R_0^2.
\]  
(24)

Substituting from (15) leads to

\[
b(T,t) \lambda(t) \left[ \lambda(t)^2 - \frac{1}{\lambda(t)} \lambda(t) \left[ 2W_1^0 + \frac{1}{\lambda(t)} \lambda(t) \right] d\tilde{t} - \frac{\rho \omega^2}{4} R_0^2, \right.
\]

where

\[
\lambda(t)[F_{zz} - F_{tr}] = -\frac{\rho \omega^2}{4} R_0^2,\]

(25)

a nonlinear Volterra integral equation for the axial stretch ratio, \( \lambda(t) \). Finally, dividing (25) by the shear modulus for infinitesimal deformations of the original network,

\[
\mu(T) = 2[W_1^0 + W_2^0],
\]

(26)

produces the nondimensional equation

\[
b(T,t) \lambda(t) \left[ \frac{1}{\lambda(t)} \lambda(t) \left[ 2W_1^0 + \frac{1}{\lambda(t)} \lambda(t) \right] d\tilde{t} - \frac{\rho \omega^2}{4} R_0^2, \right.
\]

where

\[
\lambda(t) = \frac{\mu(T)}{\lambda(t)},
\]

(27)

in which \( \lambda(T) = \omega/\omega_0(T) \), \( \omega_0(T) = 4 \mu(T)/\rho R_0^2 \), \( W_1^0 = 2W_0^0/\mu \) and \( \hat{W}_0 = 2 \tilde{W}_0/\mu \), \( \alpha = 1.2 \).

Furthermore, a nondimensional time and nondimensional time can be defined as follows. According to Tobolsky [1], the rate of scission for many rubbery materials is given by

\[
b(T,t) = \exp[-\alpha(T,t)],
\]

(28)

where

\[
\alpha(T) = \frac{k}{h} \exp\left[ -\frac{E_{act}}{RT} \right].
\]  
(29)

In (29), \( k \) 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, and \( E_{act} \) is an activation energy. For the particular material in Tobolsky’s experiments, \( E_{act} = 30.4 \text{ kcal/mol} \) (127.2 kJ/mol). In addition, Boltzmann’s constant can be written as \( k = N_A \theta \), where \( N_A = 6.023 \times 10^{23} \text{ mol} \) is Avogadro’s number. Defining \( \theta = RT/E_{act} \) as a nondimensional temperature, (29) is written as

\[
\alpha(\theta) = \frac{E_{act}}{h N_A} \theta \exp\left[ -\frac{1}{\theta} \right].
\]  
(30)

Introducing a characteristic time for scission, \( t_0 = 1/\alpha \), leads to the definition of a nondimensional time, \( \tau = \tilde{t}/t_0 = \alpha t \). According to (30), the characteristic time for scission is related to the nondimensional temperature as

\[
\lambda(\tau) \left[ e^{-\tau} + \eta \int_0^\tau e^{-\gamma} \lambda(\tau)^{-2} d\tilde{\tau} \right] - e^{-\tau} + \eta \int_0^\tau e^{-\gamma} \lambda(\tau) d\tilde{\tau} = -\Omega^2.
\]  
(34)

This characteristic time is plotted versus actual temperature for Tobolsky’s material in Fig. 2. Note the extreme temperature-dependence on this characteristic time. For example, the characteristic time is about 24 hrs for 100°C, but a 20°C increase gives a value of only 2.7 hrs, an order of magnitude reduction.

Finally, including the nondimensional time in (27) gives the governing equation

\[
e^{-\tau} \lambda(\tau)^{-1} \left[ w_0^0 + \frac{1}{\lambda(\tau)} w_0^0 \right] + \eta \lambda(\tau)
\]

(32)

4 Numerical Results

The response of the spinning cylinder to elevated temperature, for which scission-healing processes occur, is now investigated for three different material models, neo-Hookean, Mooney-Rivlin, and Arruda-Boyce. In the absence of experimental data to the contrary, we will assume that \( \omega_0 = \hat{\omega} \), i.e., the newly formed material has the same properties as the original material (this would be an interesting issue for further study). The nonlinear Volterra integral Eq. (32) for \( \lambda(\tau) \) was solved numerically by discretizing the integral term in time using the trapezoidal rule and solving the resulting nonlinear algebraic equation by Newton iteration. The time increment was chosen sufficiently small such that the time evolution of \( \lambda(\tau) \) had converged. A time increment of \( \Delta \tau = 1/100 \) produced converged results. For each material model, the response was evaluated for three cases: no healing (\( \eta = 0 \)), partial healing (\( \eta = 0.5 \)), and complete healing (\( \eta = 1 \)).

4.1 Neo-Hookean Response

Consider first the response when both the original network and the newly formed networks are neo-Hookean. In this case, the shear modulus is constant, defined by \( 2W_1^0 = \mu \), and \( W_2^0 = 0 \). Substituting the material parameters

\[
w_1^0 = \hat{w}_1 = 1, \quad w_2^0 = \hat{w}_2 = 0
\]  
(33)

into (32) gives the governing equation

\[
\lambda(\tau)^{-1} \left[ e^{-\tau} + \eta \int_0^\tau e^{-\gamma} \lambda(\tau)^{-2} d\tilde{\tau} \right] - e^{-\tau} + \eta \int_0^\tau e^{-\gamma} \lambda(\tau) d\tilde{\tau} = -\Omega^2.
\]  
(34)
Before considering any numerical results, several deductions can be made regarding (34). It is instructive to first consider the case when \( \eta = 0 \), that is, the original network undergoes scission but there is no subsequent cross linking. The governing Eq. (34) reduces to

\[
\lambda (\tau)^3 - 1 = e^{-\eta} \Omega^2.
\]  

(35)

At \( \tau = 0 \), the axial stretch ratio is given by

\[
\lambda (0)^3 - 1 = -\Omega^2.
\]  

(36)

It is, therefore, assumed that

\[
\Omega < 1, \quad \text{or} \quad \omega^2 < \frac{4\mu}{\rho R_0^2},
\]  

(37)
a necessary and sufficient condition to ensure a physically meaningful solution (\( \lambda(0) \in [0,1] \)) for a neo-Hookean material. This observation was made previously by Horgan and Saccomandi [4] and Chadwick et al. [5]. Furthermore, there is a subsequent time \( \tau_0^\eta \) given by

\[
\tau_0^\eta = -2 \ln \Omega,
\]  

(38)

when the length of the cylinder reduces to zero and the radius becomes infinite. It follows from (35) that \( d\lambda/d\tau \to -\infty \) as \( \tau \to \tau_0^\eta \). The radial increase becomes infinite according to (9), and time \( \tau_0^\eta \) can be interpreted as a critical runaway time.

Next, let \( 0 < \eta \leq 1 \), which allows for the formation of new networks. The right-hand equality represents the situation when the original network is completely transformed into new networks. It follows from (34) that

\[
\lambda (\tau)^3 = \frac{e^{-\tau + \eta} \int_0^\tau e^{-\xi} \lambda (\xi) d\xi - \Omega^2}{e^{-\tau + \eta} \int_0^\tau e^{-\xi} \lambda (\xi)^3 d\xi}.
\]  

(39)

and

\[
\frac{d\lambda (\tau)}{d\tau} = \frac{-e^{-\tau} [1 - \lambda (\tau)^3]}{3\lambda (\tau)^2 \int_0^\tau e^{-\xi} \lambda (\xi)^2 d\xi}.
\]  

(40)

At \( \tau = 0 \), (39) reduces to (36). Equation (37) is still needed to ensure a physically meaningful solution. Since \( \lambda (0) < 1 \) and (40) implies \( d\lambda /d\tau < 0 \), \( \lambda (\tau) < 1 \) and is monotonically decreasing. Next, consider the first two terms in the numerator of (39). Their time derivative is \( [1 - \eta \lambda (\tau)] e^{-\tau} \). The inequality \( 0 < \eta \leq 1 \), and the fact that \( \lambda (\tau) < 1 \), indicates that \( [1 + \eta \lambda (\tau)] e^{-\tau} \leq 0 \).

There are two cases to consider: \( \Omega \) near unity and \( \Omega \) near zero. First, if \( \Omega \approx 1 \), the first two terms in the numerator will monotonically decrease and there may be a time, denoted \( \tau_0^\eta \), when the stretch ratio reaches zero. Consequently, \( \tau_0^\eta \) satisfies

\[
e^{-\tau_0^\eta + \eta} \int_0^{\tau_0^\eta} e^{-\xi} \lambda (\xi) d\xi - \Omega^2 = 0.
\]  

(41)

Combining (38) and (41), gives

\[
e^{-\tau_0^\eta} = e^{-\tau_0^\eta} - \eta \int_0^{\tau_0^\eta} e^{-\xi} \lambda (\xi) d\xi.
\]  

(42)

The integral is positive, which implies

\[
\tau_0^\eta > \tau_0^\eta.
\]  

(43)

Rewriting the denominator of (40) as

\[
\lambda (\tau)^2 e^{-\tau + \eta} \int_0^\tau e^{-\xi} \lambda (\xi)^2 \lambda (\xi)^2 d\xi,
\]  

(44)

and taking the limit as \( \tau \to \tau_0^\eta \), \( \lambda (\tau) \to \lambda (\tau_0^\eta) = 0 \), the integral vanishes in the limit and the denominator approaches zero. It follows from (40) that \( d\lambda /d\tau \to -\infty \) as \( \tau \to \tau_0^\eta \). These results show that although new networks are formed, there may still be a critical runaway time \( \tau_0^\eta \). The consequence of the formation of new networks is to increase the critical runaway time \( \tau_0^\eta \). This implies that there is always a critical runaway time for any \( \eta \) for \( \Omega \) approaching unity.

The other case is where the angular velocity is small (\( \Omega \ll 1 \)). In this case the numerator of (39) may not vanish, leaving \( 0 < \lambda (\tau) < 1 \). Then, \( d\lambda /d\tau \to 0 \) according to (40), and a finite steady-state value is possible, \( \lambda (\tau) \to \lambda_\infty > 0 \).

Figure 3 shows the numerical results for the evolution of the axial stretch ratio \( \lambda (\tau) \) for a neo-Hookean material undergoing scission healing. The case of no healing (\( \eta = 0 \)), pure scission, is shown in Fig. 3(a) for different values of the nondimensional angular velocity \( \Omega \) between 0.5 and 0.9. The axial stretch starts at an initial value less than one and then decreases monotonically to zero as expected, consistent with the above analysis. As \( \Omega \) increases, \( \tau_0^\eta \) decreases. The case of partial healing (\( \eta = 0.5 \)), where one half of network junctions that undergo scission reform, is shown in Fig. 3(b). For large values of \( \Omega \) the axial stretch collapses to zero, but for small values (see \( \Omega = 0.5 \)) the axial stretch decreases but approaches a nonzero steady state value. The case of
complete healing ($\eta=1$), where all network junctions that undergo scission reform, is shown in Fig. 3(c). The axial stretch collapses to zero for large $\Omega$ and approaches a steady state value for small $\Omega$, but the limiting $\Omega$ between these two behaviors is larger (between 0.7 and 0.8) than for the partial healing case. For large angular velocity ($\Omega \sim 1$), the critical collapse time ($\tau^*_{\text{c}}$) gets smaller as $\Omega$ gets closer to unity.

It is interesting that a nonzero steady state value $\lambda_\infty$ can be achieved even for moderate values of $\Omega$. When $\lambda(\tau) \rightarrow \lambda_\infty$, (34) can be written as

$$
\lambda^2 \int_0^\infty e^{-\lambda(\hat{\tau})^2} d\hat{\tau} - \int_0^\infty e^{-\hat{\lambda}(\hat{\tau}) d\hat{\tau}} = -\Omega^2/\eta.
$$

(45)
a cubic equation for $\lambda_\infty$ akin to (36), once the integrals are known. Note that, since $0<\lambda(\hat{\tau})<1$, the first integral is larger than the second one $(\int_0^\infty e^{-\lambda(\hat{\tau})^2} d\hat{\tau} > \int_0^\infty e^{-\hat{\lambda}(\hat{\tau}) d\hat{\tau}}$, which allows (45) to be satisfied for $0<\lambda_\infty<1$. This is a result of the assumption that no time lag exists between scission of original networks and formation of new networks and the assumption that new networks are not allowed to undergo scission again. These act to stabilize the material against structural collapse.

4.2 Mooney-Rivlin Response. Consider now the response when both the original network and the newly formed networks are Mooney-Rivlin networks. In this case, the initial shear modulus is defined by $2W^0_1 + 2W^0_2 = \mu$. $W^0_1$ and $W^0_2$ are independent of $B$ and $W_1$ and $W_2$ are independent of $B$. The ratio of the two Mooney-Rivlin constants is defined as $B = W^0_2/W^0_1$. Noting that $W^0_1 = 1/(1 + \beta)$ and $W^0_2 = \beta/(1 + \beta)$ allows (32) to be written as

$$
e^{-\tau} \left[ (\lambda(\tau))^3 - 1 \right] \left[ 1 + \frac{1}{\lambda(\tau)} \right] + \eta \lambda(\tau)
$$

$$
\times \left[ e^{-\tau} \left[ \left( \frac{1}{\lambda(\tau)} \right)^2 - \frac{\lambda(\tau)}{\lambda(\tau)} \left( 1 + \frac{\lambda(\tau)}{\lambda(\tau)} \right) \right] d\tau
$$

$$
= -\Omega^2(1 + \beta).
$$

At $\tau = 0$, $\lambda(0)$ is the solution of

$$
[1 - \lambda(0)^3] \left[ 1 + \frac{\beta}{\lambda(0)} \right] = \Omega^2(1 + \beta).
$$

(46)

In contrast to (36), the left-hand side of (47) becomes unbounded as $\lambda(0) \rightarrow 0$ because of the nonzero constant $W^0_2$ in the Mooney-Rivlin response. Therefore, the solution $\lambda(0) = 0$ no longer exists. This can be seen in Fig. 4, which shows the initial axial stretch ratio for different angular velocities $\Omega$ and different values of $\beta$. Note that for $\beta = 0$, which is a neo-Hookean material, $\lambda(0) \rightarrow 0$ as $\Omega \rightarrow 1$. For nonzero $\beta$, however, $\lambda(0)$ never reaches zero for any $\Omega$. Therefore, no restriction on $\Omega$, such as (37), is needed to obtain physically meaningful results for a Mooney-Rivlin material.

At each time, the left-hand side of (46) becomes unbounded as $\lambda(\tau) \rightarrow 0$ because of the terms containing $B$ associated with Mooney-Rivlin response. A nonzero positive solution $\lambda(\tau)$ can be found without imposing restrictions of $\Omega^2$. Accordingly, for Mooney-Rivlin response, there does not exist a finite time when the axial stretch vanishes and the radius becomes infinitely large.

Horgan and Saccomandi [4] considered the equivalent of (47) for the case of nonlinear elasticity when $W^0_2$ and $W^0_1$ depend on the first invariant of $B$. They showed that for certain forms of $W^0_1$ (see Gent [10], determined from finite extensibility considerations, and Knowles [11], called the generalized neo-Hookean model) the axial stretch would always be nonzero. Thus, the nonphysical response found for neo-Hookean material does not occur for many other material models. This anomalous behavior seems to be a peculiarity of the neo-Hookean material model. It can be expected that there would not exist a finite time when the axial stretch vanishes if most any other model was used to represent the response of original and newly formed networks in a constitutive theory for scission healing.

Figure 5 shows the numerical results for the evolution of the axial stretch ratio $\lambda(\tau)$ for a Mooney-Rivlin material undergoing scission-healing. A typical value of $\beta = 0.2$ was used. The case of no healing ($\eta = 0$), or pure scission, is shown in Fig. 5(a) for different values of the nondimensional angular velocity $\Omega$, be-

![Fig. 4 Dependence of initial axial stretch for Mooney-Rivlin material with nondimensional angular velocity, $\Omega$, for different ratios of MR constants, $\beta = W^0_2/W^0_1$](image)

![Fig. 5 Evolution of axial stretch for Mooney-Rivlin material with $\beta = 0.2$: (a) no healing ($\eta = 0$), (b) partial healing ($\eta = 0.5$), (c) complete healing ($\eta = 1$)](image)
tween 0.5 and 1. The axial stretch starts at an initial value less than one and then decreases but only asymptotically approaches zero. The case of partial healing ($\eta=0.5$) is shown in Fig. 5(a). For large values of $\Omega$ the axial stretch approaches zero, but for small values the axial stretch approaches a nonzero steady-state value. The case of complete healing ($\eta=1$) is shown in Fig. 5(c). Again, the axial stretch approaches zero for large $\Omega$ and approaches a steady state nonzero value for small $\Omega$, but the transition value of $\Omega$ is larger.

4.3 Arruda-Boyce Response. As a final case, the response when both the original network and the newly formed networks behave as Arruda-Boyce materials (see [12]) is considered. Assuming incompressibility, the strain energy density of a three-term Arruda-Boyce material is given by

$$W = \mu \left( \frac{1}{2} (I_1 - 3) + \frac{1}{20\lambda_m^2} (I_1^2 - 3^2) + \frac{11}{1050\lambda_m^4} (I_1^3 - 3^3) \right)$$

(48)

where $\mu$ is the initial shear modulus and $\lambda_m$ is the locking stretch ratio, a material parameter, both of which could be temperature-dependent. In this case, $W_1^0$ is not constant, but $W_1^0=0$. Substituting the material parameter

$$w_1^0 = 1 + \frac{1}{5\lambda_m^2} I_1^1 + \frac{11}{175\lambda_m^4} I_1^3$$

(49)

with $I_1 = 2\lambda(\tau)/\lambda(\hat{\tau})^2$ and a similar expression for $\tilde{w}_1$ with $\tilde{I}_1 = 2\lambda(\tilde{\tau})/\lambda(\hat{\tau})^2 + [\lambda(\tau)/\lambda(\hat{\tau})]^2$ and then into (32), produces the governing equation.

The initial axial stretch solution $\lambda(0)$ is plotted in Fig. 6 as a function of angular velocities $\Omega$ for different values of $\lambda_m$. Similar to the Mooney-Rivlin case, $\lambda(0)$ is greater than zero for all values of $\Omega$, although one can see that as the material parameter $\lambda_m$ gets large $\lambda(0)$ approaches zero when $\Omega>1$.

Figure 7 shows the numerical results for the evolution of the axial stretch ratio $\lambda(\tau)$ for Arruda-Boyce material undergoing scission healing. A typical value of $\lambda_m=3$ was used. The case of no healing ($\eta=0$), or pure scission, is shown in Fig. 7(a) for different values of the nondimensional angular velocity $\Omega$ between 0.5 and 1. The axial stretch starts at an initial value less than one and then decreases, but only asymptotically approaches zero. Qualitatively, the response is similar to the Mooney-Rivlin case in Fig. 5(a). The cases of partial healing ($\eta=0.5$) and complete healing ($\eta=1$) are shown in Fig. 7(b) and Fig. 7(c). Again, the qualitative response is similar to that of the Mooney-Rivlin case, but the transition from a long time steady state behavior to a collapse behavior is more distinct in the Arruda-Boyce case. This case also confirms that the anomalous collapse behavior of the neo-Hookean case can be avoided by including a nonlinear polynomial dependence on $I_1$ in the energy density.

5 Summary and Conclusions

The boundary value problem of a spinning elastomeric cylinder undergoing temperature-induced scission and re-crosslinking was studied. The problem reduces to a nonlinear Volterra equation for the axial stretch ratio. The general constitutive framework allows the user to choose a specific underlying thermoelastic model for the original and healed microstructural material networks. Responses based on neo-Hookean, Mooney-Rivlin, and Arruda-Boyce models, were solved numerically and compared. Different amounts of re-crosslinking (healing) were studied for each case. Anomalous behavior was noted when using the neo-Hookean model, in that it was susceptible to premature and catastrophic collapse. In fact, no solution was possible for angular velocities above a critical value, even without the effects of scission. The Mooney-Rivlin and Arruda-Boyce cases, although quantitatively different, behaved qualitatively similar showing similar trends with angular velocity and healing rate. The study confirmed that the anomalous collapse behavior of the neo-Hookean case can be avoided by including a dependence on $I_1$ in the energy density, as in the Mooney-Rivlin case, or by including a nonlinear dependence on $I_1$, as in the Arruda-Boyce case.
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